INHIBITION OF COKE FORMATION IN ETHYLENE DI CHLORIDE CRACKING FURNACE TO IMPROVE SERVICE LIFE

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CERTIFICATE

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DEDICATION

This work is dedicated to our beloved parents and teachers.

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We are thankful to Allah Almighty for guiding and helping us throughout this project and thesis, for it was only him who gave us the strength to do it.

We would like to specially thank our supervisors Dr. Arshad Hussain and Dr. Syed Rafay Hussain Jafri for taking out time from their busy schedules to help us and give their valuable advices. We would also like to thank the IPO office for connecting us to the industry and giving us this project, which proved to be a great learning experience for us all.

In the end, we would thank our families for their constant support and motivation to achieve success in life.

ABSTRACT

The cracking of ethylene dichloride to vinyl chloride monomer is a very important process as it eventually produces polymers used in plastics. They have a very diverse function hence the polymer plant can be very beneficial if made cost effective. This can be achieved by an efficient cracking procedure in the furnace.

A thermal cracking furnace is used by Engro Polymer which cracks the feed at high temperature into VCM. As a result of this high temperature, coke deposition inside the furnace takes place which not only decreases the production but also damages the furnace tubes. We need to avoid the coke deposition. In order to do so, a number of different mechanisms can be used. Changing the type of cracking can be incorporated; it would not only reduce coke deposition but may also improve the quality of the process. A disadvantage of changing the cracking type is that it would increase the cost. A number of other mechanisms for inhibition of coke like introduction of phosphine groups in the feed, application of Sulphide groups on the tube walls and purification of the input stream can also be used.

The modification we suggest is changing the burner design of the furnace to remove the flame impingement points. Needle flame is changed to flower flame which improves the flux distribution inside the furnace and reduces coke. A burner and furnace design with its 3-D model is shown. This improves the production and increases the service life of the tubes.

NOMENCLATURE

EDC	Ethylene dichloride	ΔT_m	Log Mean Temperature Difference
VCM	Vinyl Chloride Monomer	T	Temperature
HCl	Hydrochloric Acid	P	Pressure
Pt	Platinum	s	Second
Pd	Palladium	K	Kelvin
Ni	Nickel	Kg	Kilogram
Co	Cobalt	kPa	Kilo Pascal
$CuCl_2$	Cupric Chloride	C_p	Specific Heat
Cl_2	Chlorine	$E_{a,j}$	Activation Energy
HIC Valve	Hot Idle Compensator Valve	ΔH°	Standard Enthalpy
Q	Total Heating Effect	ΔS°	Standard Entropy
A_{cp}	Cold Plane Area	R	Ideal Gas Constant
α_{cp}	Cold plane Factor	vol%	Percentage Volume
f	Furnace Heat Exchange Factor	wt%	Percentage Weight
T_G	Flue gases Temperature	hr	Hour
T_S	Maximum cold surface Temperature	Q_F	Furnace Duty
η	Efficiency	m_{fuel}	Mass of Fuel
^{o}F	Fahrenheit	$m_{air\ stoich}$	Stoichiometric Air Mass

R	Rankine	m_{air}	Actual Mass of Air Used
^{o}C	Celsius	A/F	Air to Fuel Ratio
d_o	Tube Diameter	T_{ref}	Reference Temperature
ctc	Center to Center Distance	G'	Air to Fuel Ratio
L	Exposed Tube Length	N_{tubes}	Number of Tubes
ft	Feet	Q_R	Heat of Recirculating Gases
kJ	Kilo Joules	Q_{wall}	Heat Absorbed by Wall
Btu	British Thermal Unit	$Q_{exhaust}$	Heat of Exhaust Gases
m	Meter	ε	Gas Emissivity

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Objective

The project is to examine the furnace at Engro Polymers and to suggest a modification that would inhibit the formation of coke inside the furnace tubes and increase the service life. Coke deposition is an essential process and cannot be avoided. Presently the plant has to do a shut down after every 45 days to remove the coke deposited by pigging. This shut down decreases the production. Our aim is to decrease the deposition of coke. This will increase the production time and mechanical cleaning would have to be done after 3 months. Tube damage due to coke deposition and flame impingement would be eliminated. Energy requirements will be reduced which would eventually result in cost effectiveness. The deposition of coke also reduces the tube internal diameter which provides less surface area for the reaction. Decreased coking would thus result in larger volumes of VCM in lesser time. The objective is to achieve all these goals with minimum changes in the present plant and greater economical effectiveness.

1.2 Cracking

Cracking is the process in which long chain heavier hydrocarbons are broken down into smaller chains. It occurs by breaking carbon-carbon bonds. This process is greatly affected by catalyst, pressure and temperature.

The process of cracking is most significant in petroleum industries where heavier alkenes and alkanes are broken down into petroleum, gasoline and naphtha etc. The lighter hydrocarbons are then used as fuel in vehicles and industries. The process of cracking can be broken down into four basic steps;

1. Initiation
2. Radical Decomposition
3. Radical Addition
4. Termination

1.3 Types of Cracking

There are three basic types of cracking used in industries. The selection of one particular type of cracking depends upon the process, cost and the efficiency we want to achieve. These types are;

1. Fluid Catalytic Cracking.
2. Hydro cracking
3. Steam Cracking
4. Thermal Cracking

1.3.1 Fluid Catalytic Cracking

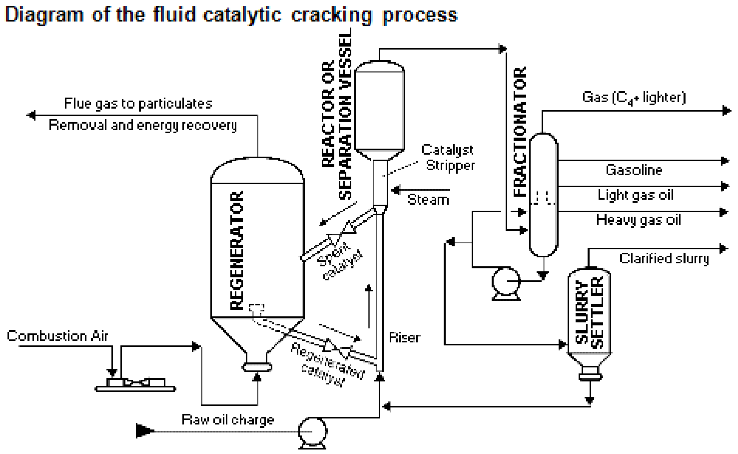
This type of cracking is most commonly used in the refineries and has completely replaced thermal cracking due to its efficiency to break down heavy carbons, reduced coke deposition, lesser energy requirements and better process conditions.

This process is most commonly used in the petroleum industry where the hydrocarbons are heated in the presence of a catalyst to break longer chain hydrocarbons into smaller chain hydrocarbons. As a result of this gasoline, olefinic gases and other valuable oils are produced. The advantage of using this type of cracking over thermal cracking is that the fuel produced as a result of fluid catalytic cracking has more octane rating. It also produces more olefinic gases which have more economical value in the market.

In the process of fluid catalytic cracking, a solid catalyst is first fluidized with the help of another supporting fluid. For example, water is added into sand to convert it to quicksand. This catalyst is then circulated through the reactor and the regenerator. With the application of heat and the use of catalyst, larger chains are converted into smaller chains. The products are then passed through fractionators where all the oils are separated from one another at their boiling points. A number of other steps are then further taken to get pure products.

After several cycles of the process, coke layer gets developed on the surface of the catalyst. The poisoned catalyst is then heated to burn off the carbon layer and obtain pure catalyst which is then re-circulated and reused for the process. This process produces less amount of coke as compared to thermal cracking. Decoking process is also easier but burning of coke releases harmful gases that need to be passed through environmental control unit and are then released in the atmosphere.

Figure 1: Fluid Catalytic Cracking



1.3.2 Hydrocracking

In the process of hydrocracking, the breakdown of heavier groups into lighter ones takes place by the process of hydrogenation. The catalyst used in the process consists of two parts. First part is the metal that promotes hydrogenation; second part is an acid that promotes cracking. The acidic part may be a crystalline zeolite plus binder (alumina) and amorphous oxide. The metal used can be a noble metal such as Pt and Pd or transitional metals of group 7A such as Ni or Co. The presence of metals does not only promote hydrogenation but also prevents the deposition of coke on the catalyst. The acid cracking function and the hydrogenation function of the catalyst can be balanced by changing the ratio of the two components in the catalyst. In this way by changing the ratio, we can optimize activity and selectivity.

This process is extremely exothermic and a constant temperature has to be maintained in the reactor. For this purpose, gaseous quenching is sometimes utilized. The conversion kinetics of Hydrocracking is usually explained by the change in the end products and is given by the following formula;

$$\% \, Conversion = \left(\frac{EP^{+}{}_{feed} - EP^{+}{}_{products}}{EP^{+}{}_{feed}}\right) * 100$$

Where EP^{+} is the fraction of material at temperature above the desired level. It is usually calculated in vol% and wt%.

Following are the main operating conditions which can be altered depending upon the objectives we want to achieve.

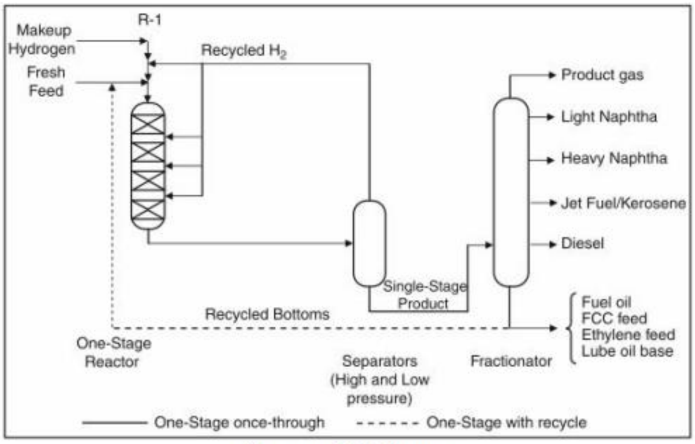
1. Concentration Level
2. Product Quality
3. Liquid space velocity per hour
4. Feed/ hydrogen ratio per cycle
5. Partial hydrogen pressure
6. Maximization of product

Two types of Hydrocracking methods are present. Choice of one particular type of Hydrocracking technique depends upon the efficiency of process that we want to achieve. These two types are;

1. One stage Hydrocracking
2. Two stage Hydrocracking

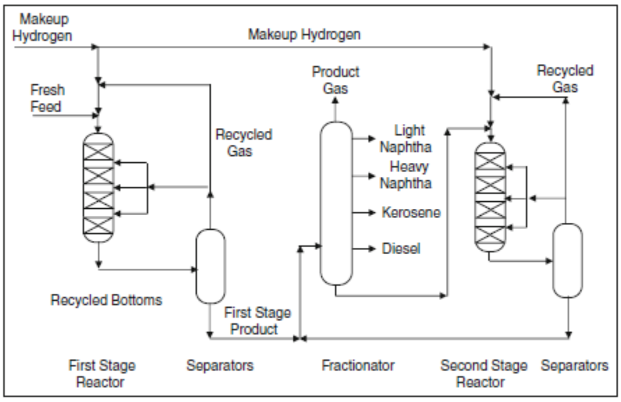
The diagrams below illustrate the two processes. Two stage Hydrocracking process is more efficient and costly than one stage process.

Figure 2: One Stage Hydrocracking



One stage HDC Process

Figure 3: Two Stage Hydrocracking



Two Stage HDC Process

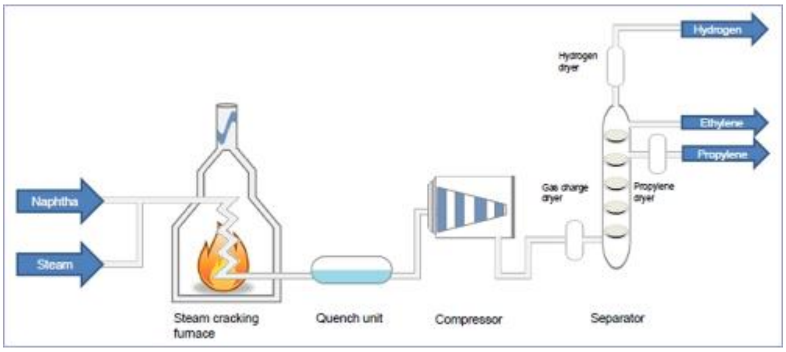
1.3.3 Steam Cracking

In the process of steam cracking, the fuel such as naphtha or other gases is mixed with steam to be used as fuel. The process occurs at a temperature of around 800 °C. The reaction time is in milliseconds. Since the process is exothermic, the gases produced are rapidly removed and are quenched to lower the temperature. This process is most commonly used to produce ethylene.

The end products obtained as a result of Steam cracking depend upon the operating conditions. Temperature is the major controlling factor. Other factors that influence the products formed are furnace residence time, hydrocarbon to steam ratio and composition of feed etc.

The most significant advantage of steam cracking is that in this process the deposition of coke in the furnace tubes is slow. The furnace can be operated several months without decoking. The decoking process requires the tubes of the furnace to be isolated after which steam or steam/air mixture is passed through the tubes that burns the solid carbon rich deposits and converts them into carbon dioxide and carbon monoxide which are then released into the atmosphere.

Figure 4: Steam Cracking



1.3.4 Thermal Cracking

Thermal cracking is the breakdown of larger chains into smaller chains at extreme conditions of temperature and pressure. The products obtained as a result of the process are high in Sulphur content. It is the cracking process that produces maximum amount of coke. An advantage of coke production is that it takes away the Sulphur content of the products.

The cracking occurs in the first step of the reaction called initiation while coke and heavy fractions are produced in the final step of the reaction. There are three types of thermal cracking process. These are;

1. Visbreaking
2. Delayed coking
3. Extreme thermal cracking

Visbreaking is the slightest of cracking procedures in which mild cracking process occurs to lower the viscosity of the oil and to produce carbons. In Delayed coking moderate cracking procedure takes place whereas in extreme thermal cracking sever cracking takes place that produces huge amounts of coke. This coke is then often burned to be used as fuel for cracking.

The cracking procedure under our study at Engro Polymers is thermal cracking. The process occurs inside a furnace. Details of the process are described in the coming chapters.

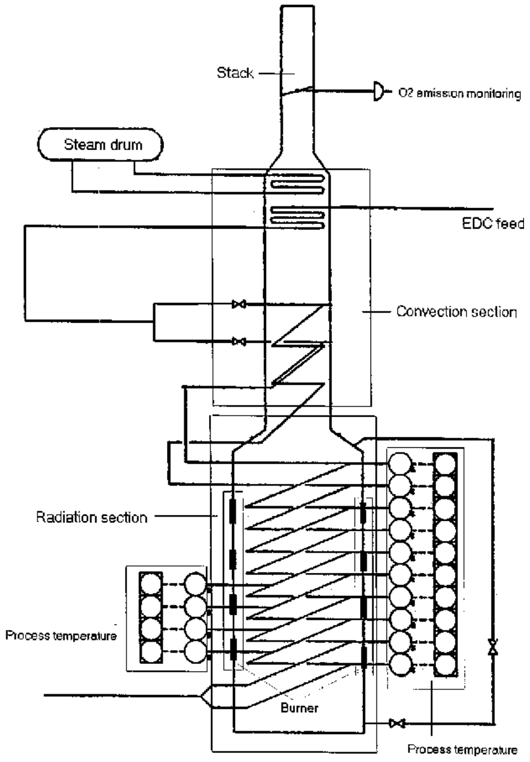
1.4 Thermal Cracking Furnace

Furnace is a closed vessel used most commonly in chemical plants and refineries in which combustion of fuel takes place and hot gases are released. Furnaces can be used as pre heater, a vessel for the cracking process and sometimes even as a reactor. The design thus depends upon the type of process, type of fuel, its heating duty and combustion air introduction method. However, there are some essentials that are mostly present in all furnaces.

Burners are rich with fuel from where the burning process takes place with the help of combustion air that is provided with the help of air blowers. The burners may be more than one in number and are usually arranged in cells that heat up the particular tube sets. The burner may be straight or inclined. They may be installed at the bottom of the furnace, top of the furnace or at the sides throughout the length. Heat is transferred from the burner in the first step to the tubes. These tubes in turn heat the first portion of the furnace called the radiation section or the firebox until the desired temperature is reached. Here heat is being transferred by radiation.

The hot gases then move from the radiation section to the convection section from where the heat is removed and is recycled through the plant to be used in the heat exchangers. The gases are then vented and then removed to the atmosphere through the flue gas stack.

Figure 5: Thermal Cracking Furnace



1.5 Furnace Burner

The vertical, cylindrical furnaces have burners facing upwards and are located at the bottom of the furnace. Some furnaces have side burners installed on both the sides of the furnace walls. The flame is present inside the burner tile which is made up of high temperature refractory. There are devices located at the bottom of the flame and the outlet of the air blowers called the Air registers. These are devices with open vanes and flaps that are used to control the shape of the flame, whether it swirls or spreads out. Too much spreading of flame causes impingements on the furnace tubes. A pre-mixer may be installed inside the burner to mix the fuel and air before lighting the flame to get better combustion. Some burners even use steam to preheat the air before mixing it with fuel for efficient combustion. Most burner flames are ignited by spark ignition transformers.

1.6 Draft

The force that causes the combustion air to enter the furnace is called draft. Heated air and the combustion gases rise in the furnace due to floatation, leaving a low-pressure region at the fire point. Due to this reduced pressure at the fire point, more air is pushed inside the furnace.

Draft is actually the negative pressure difference. In terms of the furnace, the difference between the pressure at the firebox and the atmospheric pressure is called draft. The pressure inside the fire box should be less than the atmospheric pressure. Draft does not describe air velocity or flow; it is a differential pressure.

In order to maintain a proper air to fuel ratio inside the fire box a correct draft has to be maintained. When enough oxygen is not supplied to the fire box, carbon monoxide is produced instead of carbon dioxide. Carbon monoxide produces one third of the total heat that is formed with carbon dioxide. Further starvation of oxygen causes the un-burnt fuel to be accumulated inside the firebox. The presence of both, carbon monoxide and the un-burnt fuel is hazardous because it can cause the furnace to explode. Firebox explosions are a potential hazard in a working furnace. Thus, sufficient amount of air should always be present inside the fire box to maintain safety. For this a particular draft should always be maintained.

1.7 Draft Control

Both excess and reduced draft conditions can be hazardous to the furnace function. Therefore, an optimum draft control becomes necessary. When the draft is less, the firebox is at negative pressure thus more air can enter the flame.

However, in such conditions; the upper convection section goes to positive furnace pressure. A positive pressure on the convection section forces the combustion products out of the leaks inside the furnace which attack the furnace walls and cause corrosion. Furnace repair becomes very expensive and millions may be spent to repair the furnace damage caused by low draft.

Excess draft may also be dangerous. Even when the air shutters are controlling the flow of air entering into the firebox, leaks in the furnace can cause the outside air to enter with more force. This leakage reduces the temperature of the combustion gases and it becomes harder to maintain the temperature of the furnace. Consequently, more heat has to be provided to maintain the temperature which eventually means more fuel consumption.

1.8 Stack

The flue gas stack is present at the top of the furnace in form of a cylindrical structure. It stores the gaseous discharge from the furnace and brings it up high in the atmosphere where it will no longer harm the personnel.

A stack damper is present inside the furnace that works like a butterfly valve and regulates the pressure draft inside the furnace, which is what actually pulls the flu gas through the convection section. Heat lost through the stack is also regulated by the furnace damper. As the damper closes, the heat flow out of the stack decreases but the pressure inside the furnace increases to a very large value. This can be hazardous if air leakages are present inside the furnace. The flames can escape out of the firebox furnace which may cause an explosion due to the increased pressure.

1.9 Stack Effect

The movement of air into and out of chimneys, flue gas stacks and other containers due to buoyancy is called Stack effect. This is due to the difference in air density of the outside and inside air resulting from the temperature and moisture difference in the two regions. Greater the height of the structure and the thermal difference between in air inside and outside, greater is the buoyancy and eventually greater is the stack effect. Stack effect is also called chimney effect and is used to regulate natural ventilation, infiltration and fires. The stack effect that is present in the stacks of industrial furnaces are somewhat similar to that present in the normal buildings but the temperature difference here is greater, as the temperature inside the stack is higher as compared to the ambient air. The industrial stack is designed such that it provides very less obstruction to the flue gases and enhances the stack effect so that the energy requirements of the fans are reduced.

1.10 Flue

A flue is an opening or a pipe from a chimney that exhausts gaseous waste from a furnace, burner, fire place or generator to the outside air. They are usually operated by the stack effect. Sometimes a blower may be installed to push the combustion products out. As these gases consist of carbon monoxide and other harmful compounds, proper draft and replacement with fresh air is necessary.

1.11 Insulation

Insulation is a vital part of a furnace because it makes sure that heat is confined within the furnace. Firebrick, castable refractory, ceramic fiber and other refractory materials are used for insulation. The floor of the furnace is usually made with castable type refractory whereas insulation is glued or nailed with the walls. Most commonly ceramic fiber is used for the floor because of its high density and maximum temperature rating.

1.12 Types of Furnaces

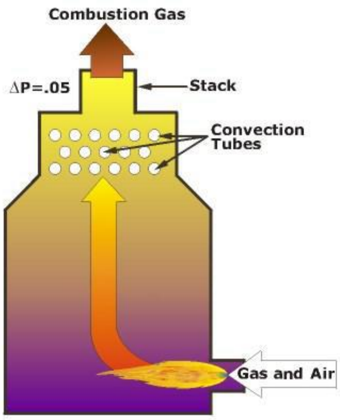
There are four basic types of furnaces;

1. Natural draft furnace
2. Induced draft furnace
3. Forced draft furnace
4. Balanced draft furnace

1.12.1 Natural Draft Furnace

Natural draft furnace does not use a blower or fan but uses the natural tendency of the hot gases to rise due to their low weight as compared to the outside air. As warm air is lighter than the cold air thus rising of these gases becomes easier. The rising gas creates a low-pressure area at the firebox as a result of which new cooler air enters. Cooler air makes its way to the furnace fuel where burning takes place. The draft of the natural draft furnace depends upon the temperature difference between the hot combustion air and the outside air, position of air shutters, position of dampers and height of the furnace.

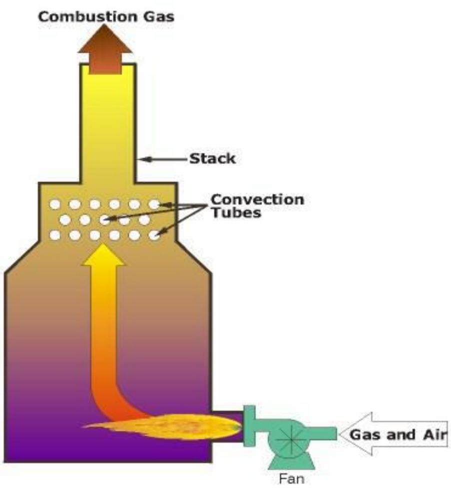
Figure 6: Natural Draft Furnace



1.12.2 Forced Draft Furnace

In forced draft furnaces, a fan or a blower is used to regulate the way of air to the burning area of the furnace. It is sometimes necessary when restriction to the passage of air flow to the burner is observed. This increased air restriction may be due to restricted burner shrouds or may be due to the installation of a pre heating system for combustion air.

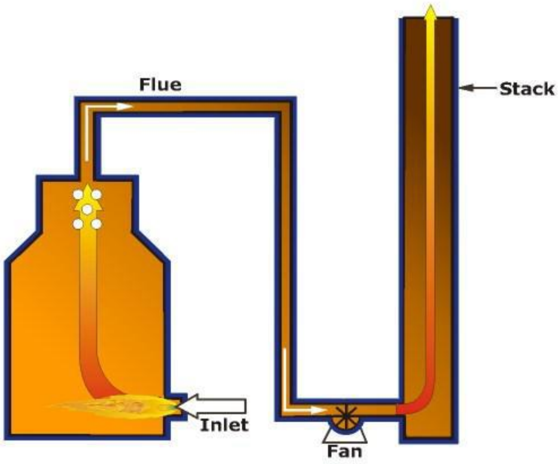
Figure 7: Forced Draft Furnace



1.12.3 Induced Draft Furnace

In induced draft furnaces, the passage of air from the burner to the stack is assisted with the help of a fan. It is mostly used when the stack is not sufficiently high or when there is a restriction in the furnace ductwork to the stack. The presence of a heat recovery unit at the outlet of the furnace also sometimes restricts the flow of combustion gases.

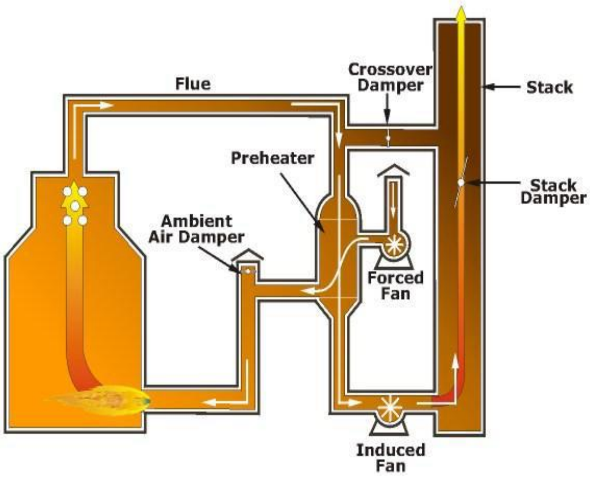
Figure 8: Induced Draft Furnace



1.12.4 Balanced Draft Furnace

In Balanced Draft furnace, fans are present both at the intake and flue side of the firebox. This is installed in case of restriction in the pre-heater heat recovery system. Flow restrictions are caused as both the combustion air and the flue gases must pass through the heat recovery unit. Forced and induced draft fans are installed in the proper duct to overcome these restrictions.

Figure 9: Balanced Draft Furnace



1.13 Fuel Selection in Furnace

The selection of fuel depends upon the following factors;

1. Cost of the fuels available.
2. Tolerance to impurities (e.g. ash, water, metals etc.).
3. Design of the furnace.
4. Environmental sensitivity of the area (e.g. Sulphur, particulates etc.).

Fuels may include;

1. Natural Gas
2. Coal
3. Gasoline
4. Hydrogen
5. Wood

A compromise between cost and calorific value is made to obtain most effective fuel. If only natural gas is used it is very costly. Currently at Engro a mixture of natural gas and hydrogen is used in the ratio 70:30 to get a cost effective and efficient fuel.

1.14 Thermal Efficiency of a Furnace

Thermal efficiency of a furnace is given by;

$$\eta = \frac{\text{Heat absorbed by the coils}}{\text{Heat released by the fuel consumption}}$$

1.15 Heat Transfer Within the Furnace

1.15.1 Introduction to Heat Transfer

The process of flow of thermal energy due to the difference in temperatures of two surfaces is called heat transfer. This transfer of thermal energy takes place due to the vibration, collision or movement of molecules. On the basis of these different methods of heat transfer, the process is classified into three basic modes that are;

1. Conduction.
2. Convection.

3. Radiation.

1.15.1.1 Conduction

In this mode of heat transfer, thermal energy is transferred due to the vibrations of the molecules placed closer to one another. Denser materials transfer most easily through conduction therefore usually solids transfer heat through this process. Conduction is governed through Fourier's law that explains that the rate of conduction through a slab is directly proportional to cross sectional area and the temperature gradient. This can mathematically be written as;

$$Q=kA\left(\frac{dT}{dx}\right)$$

Where k is the conductivity constant, A is the cross-sectional area, T is the temperature and x is the thickness of the slab.

Mechanism

The process of conduction is initiated by a source which increases the vibrations in a molecule of the slab, as a result of this kinetic energy of the molecule increases. This increase in the kinetic energy causes the next molecule to start its vibrations. Due to the successive increase in kinetic energy of molecules and vibrations, heat is transferred from one place to another.

1.15.1.2 Convection

In this mode of heat transfer, thermal energy is transferred from one surface to another by the actual movement of molecules from one place to another. This type of heat transfer is mostly present in fluids. Convection is governed by Newton's law of cooling according to which the rate of heat transfer is directly proportional to area and temperature difference.

$$Q=h_cAdT$$

There are two types of Convective heat transfer;

1. Natural Convection
2. Forced Convection

1.15.1.2.1 Natural Convection

The process of transfer of heat by molecules under the presence of natural buoyancy forces such as density and temperature difference is called natural convection. Hot air rising from the surface of a radiator can be taken as an example of natural convection. The hot air from the surface moves from an area of higher temperature to an area of lesser temperature. The process also occurs when a liquid or a gas expands or contracts due to the change in temperature of the surrounding. Acceleration fields such as gravity and centrifuge play an important role in Natural Convection.

1.15.1.2.2 Forced Convection

When molecules are rushed from one place to another by means of a mechanical device such as a fan or a blower, this is called forced convection.

1.15.1.2.3 Energy Transfer by Convection

A heat source present causes the molecules to expand as a result of which they move upward. During the motion of the molecules, they transfer their heat to the colder molecules. Thus, a thermal current move through the medium. Heating of a room with warm air through a blower can be taken as an example of Convection.

1.15.1.3 Radiation

Some substances radiate thermal energy from their surfaces in form of electromagnetic waves. This is called radiation. The electromagnetic waves generated do not require medium for their propagation. Although gases can also transfer heat through radiation but most commonly this mode of heat transfer occurs between solid surfaces.

The process of radiation is governed by Stephan Boltzmann law which states that the total thermal radiation power that is emitted from a radiating source is directly proportional to the fourth power of the absolute temperature. This can mathematically be written as;

$$E= \sigma T^4$$

1.16 Furnace Design and Heat Transfer Process

There are two basic sections of the furnace, divided on the basis of modes of heat transfer. These are;

1. Radiation Section
2. Convection Section

The radiation section is where the tubes receive direct heat from the flame. It is the hottest region of the furnace. Heat transfers in form of radiation from the flames to the interior of the tubes. Studs are used to hold the insulation in place on the walls of the furnace.

There is an area between the first two rows of tubes of the convection section and the top of radiation section called shield section. This is so called because this region is still exposed to thermal radiations and it shields the convection region from getting any radiations. The area at the top of radiation section where the flu gas exits the radiation section and just enters the shield section is called bridge zone. A tube is used as a connection between the convection and the radiation section. The outlet of this tube is outside the furnace so that temperature inside the convection section and its efficiency can be found. In the convection section, the temperature is lower than the radiation section and heat is recovered which can then be used throughout the plant for heat transfer.

1.17 Coke

During the process of EDC pyrolysis, coke is formed on the inside of tubes of the furnace. The coke formation is inevitable and is increased due to the presence of impurities in the feed. Due to the formation of coke, heat transfer surface inside the furnace is decreased and the pressure drop increases. It decreases the thermal efficiency of the furnace and increases the fuel requirements in the firebox to maintain the EDC conversion. Furthermore, due to the deposition of coke, skin temperature of the reactor increases that eventually damages the metal of the tube. The area available to for EDC conversion is also decreased when coke gets deposited. The tubes get narrowed and require cleaning afterwards. As a result of this the utility and maintenance cost is increased. This may increase the chances of plugging in the downstream units.

The formation of coke takes place throughout the furnace from the firebox to the top where the gases are quenched. However, the highest amount of coke deposition occurs in the radiation section because the burner flame directly hits the tubes here.

It is believed that coke is not directly formed from active hydrocarbons directly. Instead, hydrocarbons at very high temperature form tar droplets. These tar droplets deposit inside the tube walls and convert into coke at high temperature by hydrogenation.

EDC is a major cause of coke formation but the presence of impurities inside the feed promotes coking. Chloroprene is one of the compounds that takes part actively in the coke formation and is called coke initiator. About 50-60% of carbon present in chloroprene is converted into coke. Other major coking agents are benzene and ethylene. 1,2 dichloropropene is a common impurity present in the EDC feed which is a stronger coking agent as compared to EDC. 1,1,2 trichloroethane, acetylene and butadiene are also contributors to the coke formation.

1.18 Decoking

Decoking is the process of removing the coke residue from the inside of the furnace tubes. This process is done after every 45 days and the furnace is shut down. Presently, the coke removal is done by three common methods as follows;

1. Steam Air Decoking
2. Mechanical Pigging
3. On-Line Spalling
4. Chemical cleaning

1.18.1 Steam Air Decoking

In this process, a mixture of steam and air is passed through the inside of furnace tubes while heating from the outside. This shrinks the coke deposited inside the tubes. As a result of this coke is converted chemically into carbon monoxide, carbon dioxide and water which are then vented to the atmosphere. Due to the release of these gases, this procedure is not environment friendly. It is most efficient for the radiation section but it does not guarantee the complete removal of coke. In cases like these, the tubes need to be dismantled and removed which becomes very expensive. Also only trained personnel can perform this procedure as a number of complications are attached with the process like overheating of tubes and damaging of the heater etc.

1.18.2 Mechanical Pigging

In this process, the cleaning of the tubes is done by inserting a mechanical pig with water inside the tubes. The pig is inserted by means of a pig launcher and can also be used for viewing the inside of the tubes. The pig moves freely through the tubes driven by a motive fluid. The surface of the pig is such that it scraps off all the coke from the tubes. There are different sizes of pigs available. They are smaller than the inside diameter of the tubes.

The pigs are usually pumped through the tubes several times until the required initial pressure difference is obtained inside the tubes. This mechanical process of decoking is mostly used in industries because of its high efficiency, low cost and environment friendly nature.

1.18.3 On-Line Spalling

This process of decoking is most advantageous because it does not require the furnace to be turned off. The operation can be carried out with the furnace in service. It ensures that there is no loss in the throughput and there are minimum reliability problems. However, the problem with this kind of decoking technique is that it cannot be used for all furnace designs and configurations.

In this process, alternatively heated and cooled steam is passed through the tubes to create expanding and contracting effects. This spalls the coke from tube walls. This process has comparatively less environmental effects. A disadvantage of this process is that it is not 100% effective. Another decoking technique has to be employed with it for complete decoking, especially in the convection section. Due to the sudden contraction in expansion processes, the tubes of the furnace may also damage.

1.18.4 Chemical Cleaning

In this process, an acid is passed through the tubes of the furnace. The acid softens the coke build up which can then be flushed. Water is then pumped through the tubes to take out the acid and coke mixture. Special care must be taken with the chloride content inside the water as higher chloride content may lead to corrosion inside the tubes.

This process is not environmentally friendly. The chemical used have to be disposed safely which increases the cost for the procedure.

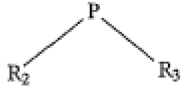
1.19 Methods to Prevent the Formation of Coke

Several techniques have been tested and used now to decrease the amounts of coke deposited inside the ethylene dichloride furnaces. Such design changes would be beneficial as they would result in significant cost reductions. Some of those methods are;

1. Addition of Phosphorous groups
2. Addition of Sulphide groups
3. Changing the burner design
4. Purifying the feed

1.19.1 Addition of Phosphorous Groups

It is several times researched upon and proven that exposing the heat transfer surface of the furnace to phosphine groups reduces the deposition of coke. The general formula of phosphine groups are as follows;



Where R1, R2 and R3 can be same or different. They can be alkyl, aryl, alkylaryl, hydrogen or chlorine etc. Examples of phosphides that can be used are phosphorous trichloride, tri-n-butyl phosphine, tri dodecyl phosphine, tribenzyl phosphine, tris(p-tolyl)phosphine, tris(anthracenyly)phosphine , tris(2-methoxyphenyl)phosphene, tri-phenyl phosphine, tri-n-octyl phosphine etc.

Coke is actually formed due to the increased temperature inside the furnace tubes. Coke formation is increased in the presence of metals like copper and nickel. Usually the tubes of the furnace are made up of these metals because they are thermally stable and resistant to heat. If the tubes are not constructed with a copper or nickel alloy, they may deteriorate and damage due to the high temperature. Thus, usage of these metals is necessary. To overcome this challenge, phosphine groups are used. The presence of phosphine groups inside the furnace forms a protective layer on the walls of the tubes which does not let the EDC and VCl to interact with coke catalysts and thus coke formation is decreased.

The inhibition of coke can be done in different methods. Either phosphine groups are added to the raw feed of EDC or a pretreatment of furnace coils with the phosphine groups is done. The heat transfer surface can also be exposed to the phosphine groups by spraying, painting or chemical vapor deposition. Sometimes phosphine groups are blended into a conversion booster or a solvent and are then added.

All these processes decrease the amount of coke deposited inside the furnace tubes and hence make the process cost efficient by decreasing the down. But at the same time, they also increase the chances of impurities present in the EDC feed as phosphine is present in it. It would have to be removed eventually by adding a distillation tower which would add to the cost. Spraying of tubes with phosphine groups is also not very effective as it would wear off after some times and tubes would need to be replaced hence adding to the cost.

1.19.2 Addition of Sulphide Groups

Coke formation can be inhibited by the continuous addition of Sulphide groups such as dimethyl Sulphide and dimiethyl disulphide. These groups also form a protective coating over the tubes of the furnace which decreases the interaction with the coking catalysts. As a result, the formation of coke and other undesired substances is decreased. These substances are however rarely used because of their very bad smell. To decrease this effect, odorants are then added to the mixture.

1.19.3 Changing the Burner Design

The coke deposited inside the tubes of the furnace is majorly due to the high temperatures inside. The designs of the burner of the furnace are such that they point directly to the tubes of the radiation section as a result of which at those specific points, very high flame exposure is present and coke gets deposited in that region. If we change the burner design such that these flux impingement points are removed, the amount of coke deposited can be decreased to a significant amount.

1.19.4 Purifying the Feed

The feed that is introduced to the furnace consists of heavier carbons, lighter carbons and most prominently EDC. For the production of VCM, EDC cracking is required but the presence of heavier carbons produces byproducts and increases the deposition of coke. If we purify the feed to remove the heavier compounds, the coke deposition can be limited. This can be done by installing a distillation column before the furnace to remove the heavier compounds from the feed. An increased cost will be added because of the additional distillation column.

CHAPTER 2

VCM PLANT

2.1 Introduction

The project is for Engro polymers that produce Vinyl chloride monomer that is eventually used in the market for the production of PVC. The raw materials used for the process are ethylene and chlorine. The plant produces 610 MT/day of VCM. The process is divided into four basic units as follows;

1. Low temperature Chlorination Unit
2. Oxy-chlorination Unit
3. Purification Unit
4. Cracking Unit

2.1.1 Low Temperature Chlorination

Ethylene combines with chlorine directly in the presence of a heterogeneous catalyst to form EDC. The catalyst used is most commonly ferric chloride. The temperature and pressure conditions of the process are 49°C and 150KPa respectively. Cooling water is used to remove the excess heat produced by the exothermic reaction. The products of the reaction are 99% liquid EDC and 1% chlorinated hydrocarbons.

$$C2H4 + Cl2 \longrightarrow C2H4Cl2 \qquad \triangle H= -79{,}100 \text{ Btu/lbmol of EDC}$$

Ethylene dichloride is fed in excess as compared to the stoichiometric requirements so the Cl2 is the limiting reactant and is utilized completely in the process. Gases are sent to the incinerator before being discharged to the atmosphere, whereas the liquid crude is set for storage after water and caustic wash. To the gas below the explosive limit and to dilute the chlorine bound oxygen, natural gas is added to the gaseous mixture.

2.1.2 Oxy-Chlorination

In this unit, HCl recycled from the cracking unit is reacted with ethylene to produce more EDC. Air is injected as a source of oxygen to start the reaction. The reaction takes place at the temperature and pressure of 230°C and 350KPa respectively in the presence of CuCl2 as catalyst. It takes place in the gaseous phase in a fluidized bed reactor, charged with the catalyst. A low-pressure saturated steam is generated at 1034kPa that removes the heat of reaction from the reactor.

$$C2H4 + 2HCl + \frac{1}{2}\, O2 \longrightarrow C2H4Cl2 + H2O \qquad \triangle H = -104{,}000 \text{ Btu/lbmol of EDC}$$

EDC and water separated from one another through stripping. Water is sent to the waste water treatment and EDC is sent for storage. Gaseous streams are sent to the incinerator before they are discharged into the atmosphere.

2.1.3 Purification Unit

The EDC separated in the previous step is sent to a distillation column where it is purified. Water, light and heavy compounds are all separated.

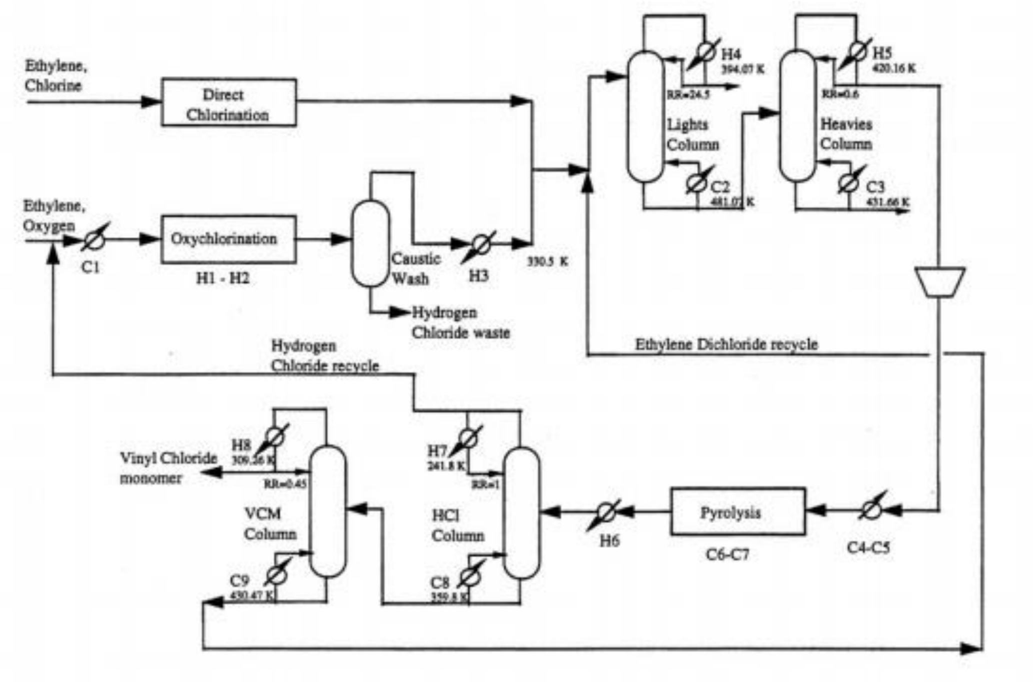
2.1.4 Cracking Unit

EDC produced is dried and is sent to the cracking unit where under high temperature it decomposes into VCM and hydrochloric acid.

$$C2H4Cl2 \longrightarrow C2H3Cl + HCl \qquad \triangle H = -30{,}500 \text{ Btu/lbmol}$$

The temperature of the cracking furnace is 490°C and the overall conversion into products is 96%. The products and the un-reacted EDC are cooled immediately in the quenching tower. This is done to minimize the coke formation which would eventually cause the reaction to start in the reverse direction. The products are separated into Hydrochloric acid, un-reacted EDC and VCM. HCl is recycled back for the oxy-chlorination. EDC is purified and recycled back to the raw materials. VCM is sent to storage.

Figure 10: Cracking Unit



2.2 Area of Focus

The prime area of our focus is where thermal decomposition of ethylene dichloride to vinyl chloride and hydrochloric acid takes place. The pyrolysis reaction takes place inside the tubes of a thermally fired furnace at high temperature and pressure. The products obtained in gaseous form are than quenched in the quenching column by multiple recirculation.

The cooled products of the quenching tower are then fed to a purifying section in which EDC, VCl and HCl are separated through fractional distillation. The un-reacted EDC is purified by fractional distillation and is recycled back to the inlet of the pyrolysis furnace.

The HCl purified is used in the oxy hydro-chlorination of EDC. The conversion per pass of EDC is 50% (32% VCM, 18% HCl, 50%EDC), with overall efficiency of 96% of VCM and HCl after distillation. VCM produced as a result of this process is 99% pure and HCl is 99.5% pure.

2.2.1 Furnace Process Conditions

The pyrolytic cracking of ethylene dichloride takes place in radiation section of the furnace as a result of which Vinyl chloride monomer is produced. The burner of the furnace heats the walls of tubes up to a high temperature of 871-982°C. As a result, the walls provide the necessary heat to the reaction coils in which cracking takes place. EDC is stored as a clean, dry raw material in a drum which enters the furnace at a high pressure of 3447-4136kPa. This pressure is attained by means of steady flow pumps. Flow controllers are installed to control the flow of feed into the furnace. The EDC feed enters the top of the convection section and flows downwards through the coils. The feed is heated up to 248°C in the convection section. As it moves downwards to the radiation section, its temperature increases to 493-507°C. The temperature corresponds to the feed of almost 40,000kg/hr of EDC.

The conversion of EDC obtained can be adjusted with the temperature and pressure conditions. However, at a very high temperature and pressure, coking starts to occur which eventually affect the heat transfer inside the furnace. Due to the reason, the coil exit pressure is limited to 1861kPa to retard by product formation and coke deposition.

Before entering the burner of the furnace, flue gas passes through a flow recorder, a field solenoid valve, HIC valve and a flow trim valve actuated by the furnace exit temperature. The HIC and the flow trim valve operate in the same direction as the flow of the fuel. Major flow adjustments are made by the HIC while only minor operations are done by the flow trim valve. The exit gas from the furnace consists of EDC, VCl and HCl. The gases pass from here directly into the quench column.

2.3 Furnace Reactions

2.3.1 Main Reaction

The cracking of Ethylene Dichloride (EDC) is a first order reaction. It carries on with the free radical association and disassociation. It is also a homogenous reaction. Initially what happens is the furnace is that EDC is added at the inlet and as it passes through the reaction tubes it gets disassociated into Vinyl Chloride (VCl) and Hydrochloric Acid (HCl). So, at the end of the reaction tubes the three components obtained are namely EDC, VCl and HCl.

As soon as soon as the reaction ends and the product in obtained at the outlet of the furnace, the product is at around 900K. Therefore, in order to stop the reaction and the cracking of Vinyl chloride from occurring any further, the products are quenched in the quench column. Where the products are cooled down by their own recirculation inside the quench column. It is done to stop the cracking of Vinyl Chloride which is essentially our obtainable product ultimately. If Vinyl Chloride gets cracked any further, it forms Coke which is a carbon rich deposit that deposits on the inner walls of the furnace tubes and hence lowers down the thermal conductivity of the furnace walls by adding a layer of insulation. It also increases the power and energy requirement to provide a greater heat flux to overcome the heat losses.

The main reaction is shown as follows:

$$C_2H_4Cl_2 + E \quad \text{->} \quad C_2H_3Cl + HCl$$

The reaction mentioned above essentially shows that Ethylene Dichloride required Energy for it to dissipate into the ultimate product Vinyl Chloride (VCl) and a side product Hydrochloric acid (HCl).

Since the reaction requires energy to be carried forward, it is an endothermic reaction. The energy required for this reaction to be carried forward is H = 70 kJ/mol. The conversion for the above-mentioned reaction is usually limited to about Fifty percent (50%) per pass. This is done to minimize the formation of impurities in the reaction which can further contribute to the formation of Carbon rich deposits inside the tube that lower the heat transfer across the furnace walls. This reaction is carried on by free radical and hence is a chain reaction.

The chain reaction mechanism is shown as follows:

- **Initiation:**

  $C_2H_4Cl_2 \quad \text{->} \quad \cdot C_2H_4Cl + Cl\cdot$
- **Propagation:**

  $C_2H_4Cl_2 + Cl\cdot \quad \text{->} \quad \cdot C_2H_3Cl_2 + HCl$

- **Propagation:**

  $\cdot C_2H_3Cl_2 \quad \text{->} \quad C_2H_3Cl + Cl\cdot$

- **Termination:**

  $\cdot C_2H_4Cl + Cl\cdot \;\; \rightarrow \;\; C_2H_3Cl + HCl$

- **Termination:**

  $\cdot C_2H_3Cl_2 + \cdot C \;\; \rightarrow \;\; C_2H_3Cl_3$

The two most important radicals that carry this chain reaction out are namely chloride radical ($Cl\cdot$) and 1,2-dichloroethyl radical ($\cdot C2H3Cl2$). These two radicals are responsible for carrying the whole chain reaction shown above. The formation of a free radical promotes the reaction and the compound producing these radicals is termed as a promoter while the inhibition of the reaction takes place when these radicals are consumed up in the reaction and the specie taking up or consuming this radical will be known as an inhibitor.

2.3.2 Side Reactions

The major source for these side reactions to occur is the impurities present in these reaction tubes. These impurities are either a part of the Ethylene Dichloride (EDC) feed or are formed in the reaction as result of the variation of the cracking temperature inside the furnace.

When the temperature inside the cracking furnace is low, not many impurities are formed and the major by product in the furnace remains EDC itself with little small quantities of chloromethane and methane. This variation in the temperature is majorly responsible for the conversion of Ethylene Dichloride to Vinyl Chloride. The lower the temperature lesser the conversion and higher the temperature, higher the conversion. So, as the reaction temperature is increased to eventually increase the conversion of the reaction many other by products, which are mostly the impurities, are formed.

2.3.3 Byproducts

The byproducts most commonly include acetylene, vinylidene chloride and chloroprene being the most important, as well as small amounts of methane, ethylene, butadiene, vinyl acetylene, methylene chloride (dichloromethane), cis and trans-dichloroethylene. As EDC is converted even further, mono- and dichloroethylene appear, as well as chloroethane, chloro-vinyl acetylene, methyl acetylene and trace amounts of propylene, trichloroethylene, benzene and 1,1,2-trichloroethane.

Of all the impurities that have been mentioned above, some of these promote the chemical chain reaction while others tend to inhibit the chain reaction. An initiator would always promote the cracking reaction and would always move the reaction in such a way that chlorine radicals are formed and the reaction progresses in such a way that Ethylene Dichloride (EDC) gets dehydrochlorinated and forms Vinyl chloride (VCl).

Whereas, a cracking inhibitor would always tend to interfere between the chain reaction and would tend to cease the reaction from further continuing by altering the chain reaction mechanism and making it stop some way or the other way. Therefore, the cracking inhibitors tend to stop the formation of the chlorine and the 1,2-dichloroethyl radical and hence stop the dehydrochlorination of Ethylene Dichloride (EDC) required to form the Vinyl Chloride monomer (VCM).

The radical chain mechanism shown above is also initiated if the carbon to chlorine bond activation energy of the hydrocarbon compounds thus formed is higher than that of the carbon to chlorine bond activation energy of Ethylene Dichloride (EDC). This ensures that as the reaction goes on proceeding, the dehydrochlorinated compound does not dissipate or disassociate, rather the Ethylene Dichloride fed in the feed only disassociates and gives rise to the required compound. If the activation energy of the compounds thus formed was lesser it would result in the dissipation of the formed compounds themselves and proceeding the reaction to the formation of VCM would be very difficult. So, these initiators and inhibitors of the chemical reaction tend to determine the extent of the reaction and also the percentage of the conversion achievable through this reaction and also the selectivity of the reaction. Further will be discussed the role of these initiators and inhibitors of the cracking reaction chain mechanism separately and their effect on the reaction would be determined.

2.3.4 Cracking Initiators

There are Carbon Tetrachloride molecules present inside the EDC feed stream. They are mostly the promoters of the cracking reaction. But since these promote the reaction, they also promote the EDC cracking down to VCM which means greater by product formation and hence more coking.

The chlorine radical inside the CCl_4 molecule separates out and lay the foundation of chlorine free radical chain reaction mechanism and hence formation of 1, 1-dichloroethylene, 1, 1 dichloroethane, chloroprene, chlorobenzene and penta-chloroethylene increases.

$$CCl_4 \quad -> \quad \cdot CCl_3 + Cl\cdot$$

2.3.5 Effect of Chloroform

Unlike the CCl_4 molecules the chloroform molecules contain lesser atoms of chlorine atoms hence their chain reaction effect of causing the byproduct formation. But till even if it is lesser the byproducts still form which include chlorobenzene, trichloroethylene and 1,1-dichloroethylene.

$$CH_3Cl \quad -> \quad \cdot CH_3 + Cl\cdot$$

2.3.6 Effect of Oxygen

It is mostly seen that at an oxygen concentration of less than 2% the dehydrochlorination of the EDC feed starts to happen. This dehydrochlorination also promotes the burning of the EDC feed which means that the pyrolysis gas will now contain carbon monoxide and carbon dioxide gases. This also deposits a carbonaceous deposit inside the furnace.

So, it is seen that mostly these oxides are responsible of the initiating effect of the radical chain mechanism. But is it also seen that when this oxygen concentration is increased more than 2% then this initiation effect is also reduced. Hence, to minimize the chain mechanism we should keep the oxygen concentration above the 2% value.

2.4 Mathematical Model

The reaction occurring inside the cracking furnace is a reversible reaction as some of VCM produced is also converted back to EDC. Thus, the overall reaction that is occurring is the difference between the forward reaction and the reverse reaction. The equation is given as;

$$r_j = k_{f,j} \prod_{k=1}^{NC} C^{n_f, k_j} - k_{r,j} \prod_{k=1}^{NC} C^{n_r, k_j}$$

In the above equation r_j represents the overall reaction rate. k_f, k_r represent the rate constants of forward and reverse reactions respectively. C represents the concentrations whereas n represents the order of the reaction. The kinetics of the forward reaction is calculated as follows;

$$k_{f,j} = A_j T^b \exp(\frac{-E_{a,j}}{RT})$$

The above rate is calculated with the help of Arrhenius equation. A is the pre exponential factor. $E_{a,j}$ is the activation energy for the reaction, T is the absolute temperature and R is the ideal gas constant. b and j are the constants used to calculate the deviations from the Arrhenius equation.

The equation for the reverse reaction and its kinetics are calculated with the help of equilibrium constant. At a constant temperature and pressure, equilibrium constant can be calculated from standard enthalpy (ΔH°) and standard entropy (ΔS°). Thus, the equation can be constructed as follows;

$$K_J = \frac{k_{f,j}}{k_{r,j}}$$

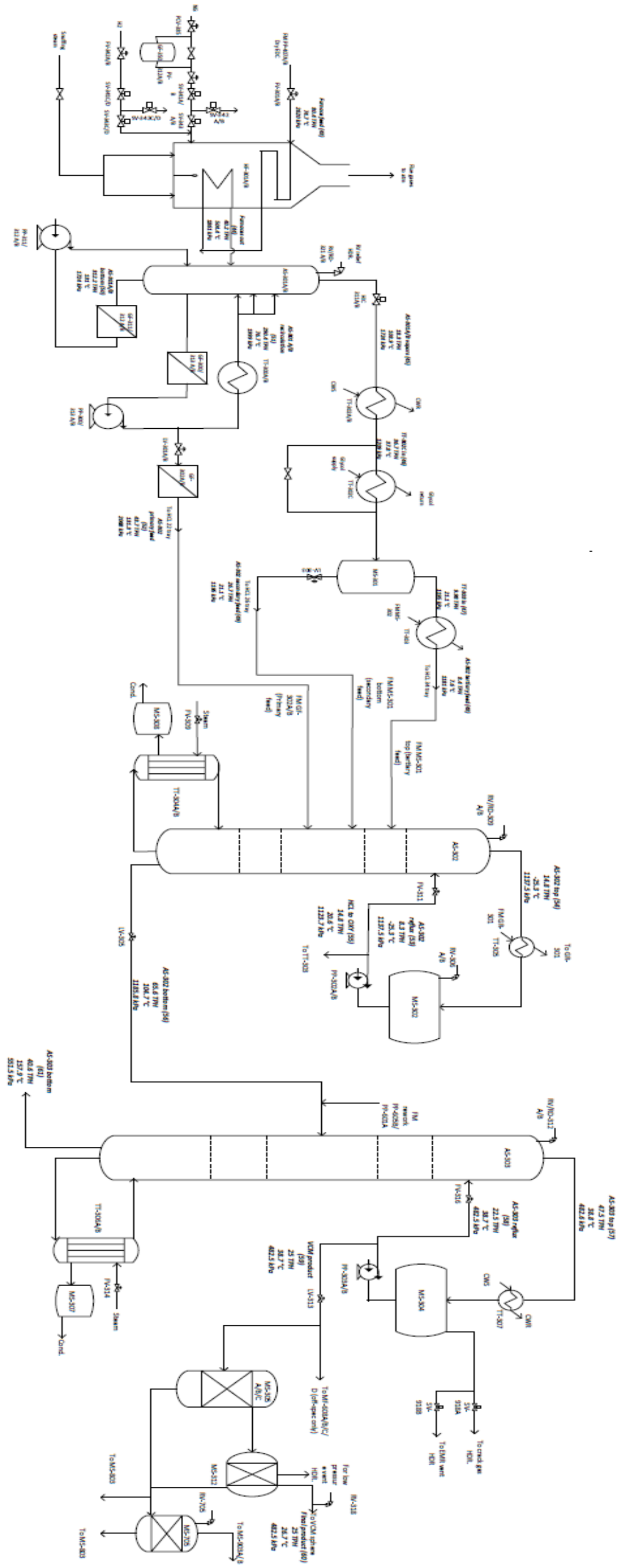
Where

$$K_j = \exp(\frac{\Delta S^\circ{}_j}{R} - \frac{\Delta H^\circ{}_j}{RT})(\frac{P}{RT})^{\Sigma_{i=1}^{NC} nr,ij-nf,ij}$$

2.5 Piping and Instrumentation Diagram (PID)

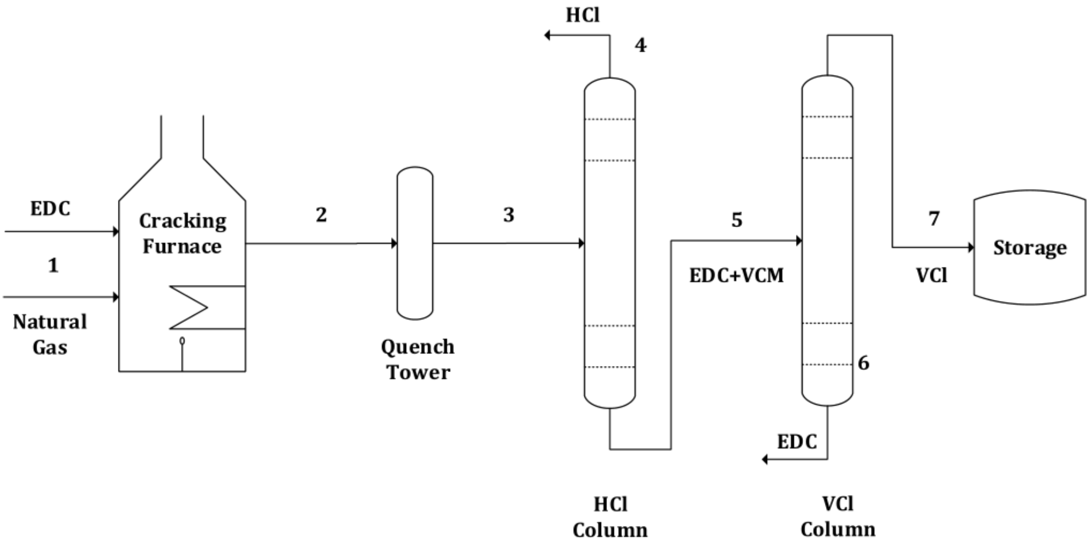
The figure below shows the PID of the area on which the project is based;

Figure 11: PID of Plant



2.6 Process Flow Diagram

Figure 12: Process Flow Diagram



CHAPTER 3

MATERIAL BALANCE

In order to find out the flow rates and compositions of the various streams coming and going of the stream, material balance was done. It was applied across the furnace, quench column and the two distillation towers used afterwards for purification. All the calculations were done manually and were then verified by creating a model in Aspen HYSIS.

The following assumptions were taken during the mass balance:

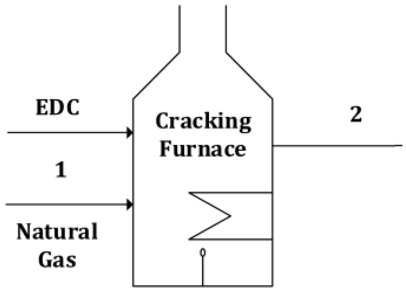
- Basis = 1 hour
- Unsteady State Process (Coke Accumulation)
- Chemical Process, Reactions occurring
- Material Balance in Kilograms (kg)

Accumulation = Flow In – Flow Out + Generation – Consumption

The portion of the plant on which material balance is applied is as follows. Each stream is given a number, whose composition is given in detail in the tables below;

3.1 Furnace

Figure 13: Furnace



Stream 1 is the input stream of EDC feed. The maximum composition comprises of pure EDC but it also has impurities present. These are shown in the table below;

3.1.1 Stream 1

Table 1: Material Balance on Stream 1

Sr. no.	Component	Mass (kg)	Mass Fraction (wt %)
1	EDC	40,000	99
2	VCl	0	0
3	HCl	0	0
4	Ethyl Chloride	2.00E-05	5.00E-10
5	dichloroethylene	3.00E-04	7.50E-09
6	butadiene	5.00E-03	1.25E-07
7	1,1-dichloroethane	1.00E-04	2.50E-09
8	Chloroprene	5.00E-05	1.25E-09
9	Chloroform	4.00E-04	1.00E-08
10	CCl4	5.00E-05	1.25E-09
11	Benzene	2.00E-03	5.00E-08
12	Trichloroethylene	3.50E-03	8.75E-08
13	Bromochloroethane	1.00E-04	2.50E-09
14	Beta trichloroethane	1.50E-04	3.75E-09
15	Perchloroethylene	5.00E-05	1.25E-09
16	Tetrachloroethane	5.00E-05	1.25E-09
17	Lighter hydrocarbons	241	0.59
	Total	**40241**	

Stream 1 enters the furnace. It is heated with the help of fuel and oxidizer. Inside the furnace, EDC is converted to VCM. The overall conversion is 99%. On the basis of this conversion, the composition of stream 2 is calculated and is given in the following table;

3.1.2 Stream 2

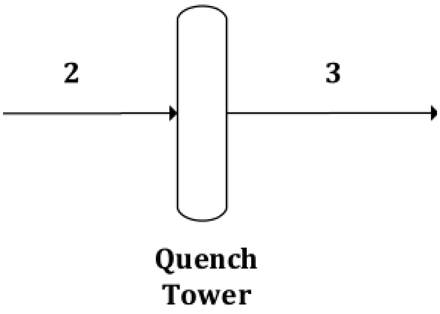
Table 2: Material Balance on Stream 2

Sr. no.	Component	Mass (kg)	Mass Fraction (wt %)
1	EDC	1599.84	39.7
2	VCl	24198	60.2
3	HCl	14156	35.2
4	Light Hydrocarbons	199.79	0.49
	Total	**40153.6**	

Inside the quench tower, no reaction is taking place. Only heat is removed from the stream 2 to decrease its temperature. Therefore, there is no difference in the composition of stream 2 and 3.

3.2 Quench Tower

Figure 14: Quench Tower



Stream 2 is sent to the quench tower where it recirculates a few times. As a result of this, the temperature of stream is reduced. Since neither a chemical reaction is taking place nor is a stream entering. Thus, the material balance remains undisturbed. Stream 2 and 3 are shown in the table below;

3.2.1 Stream 3

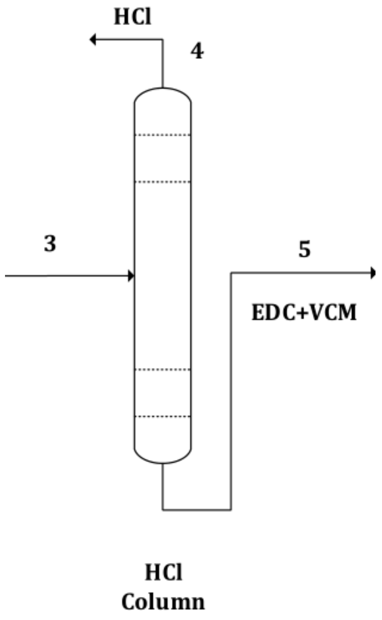
Table 3: Material Balance on Stream 3

Sr. no.	Component	Mass (kg)	Mass Fraction (wt %)
1	EDC	1599.8	39.8
2	VCl	24240	60.3
3	HCl	14156	35.2
4	Lighter Hydrocarbons	199.7	0.49
	Total	**40195.6**	

3.3 HCl Purification Section

Two purification sections are present after the quench tower. In the distillation column, a mixture of EDC and VCM is obtained from the bottoms while pure HCl is obtained from the top. The HCl obtained by this process is 99% pure. On the basis of this all the material balance of this section is done, to obtain the composition of the streams 4 and 5.

Figure 15: HCl Column



3.3.1 Stream 4

Table 4: Material Balance on Stream 4

Sr. no.	Component	Mass (kg)	Mass Fraction (wt %)
1	EDC	417.4	1.73
2	VCl	23699.9	98.0
3	HCl	56.6	0.23
4	Lower Hydrocarbons	6.6	0.03
	Total	**24180.5**	

3.3.2 Stream 5

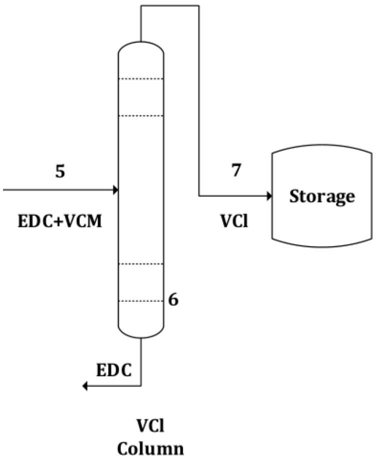
Table 5: Material Balance on Stream 5

Sr. no.	Component	Mass (kg)	Mass Fraction (wt %)
1	EDC	1599.8	6.18
2	VCl	24183.6	93.5
3	HCl	56.6	0.22
4	Lower Hydrocarbons	6.6	0.02
	Total	**25846.6**	

3.4 VCl Purification Section

In the second distillation tower, purification of VCl is taking place, now the top product obtained is VCl with a purification of 99%. This was taken as the basis of calculation for the mass balance in this section. EDC is obtained at the bottoms which is recycled to the feed inlet where it is reused.

Figure 16: VCl Purification Section



3.4.1 Stream 6

Table 6:Material Balance on Stream 6

Sr. no.	Component	Mass (kg)	Mass Fraction (wt %)
1	EDC	417.4	1.73
2	VCl	23699.9	98.0
3	HCl	56.6	0.23
4	Lower Hydrocarbons	6.6	0.03
	Total	**24180.5**	

3.4.2 Stream 7

Table 7: Material Balance on Stream 7

Sr. no.	Component	Mass (kg)	Mass Fraction (wt %)
1	EDC	417.4	1.73
2	VCl	23699.9	98.0
3	HCl	56.6	0.23
4	Lower Hydrocarbons	6.6	0.03
	Total	**24180.5**	

3.5 Summary

A summarized table for the mass balance of the concerned area of plant is shown in the table below which shows the mass of feed, product and the coke deposited inside the furnace per hour.

Table 8: Material Balance Summary

Component	1 (kg)	Furnace (kg)	2 (kg)	3 (kg)	4 (kg)	5 (kg)	6 (kg)	7 (kg)
EDC	40,000	-	1599.8	1599.8	Traces	1599.8	1182.4	417.4
VCl	-	-	24198	24240	56.39	24183.6	483.6	23699.9
HCl	0	-	14156	14156	14099.3	56.6	0	56.6
Coke	0	41.660	-	-	-	-	-	-
Lighter compounds	241	-	199.79	199.7	6.6	6.6	180	6.6
Total	**40,241**	**41.660**	**40153.6**	**40195.6**	**14162.4**	**25846.6**	**1846.2**	**24180.5**

3.6 Coke Deposition

In order to show the effect of coke deposition on the feed flow rate through the tubes of the furnace, we begin our calculations from the first hour of production. At this time, there is no coke deposition therefore its value is taken as zero. After the reaction starts, coke deposition starts to occur with it. We have already calculated the coke deposited per hour in the previous calculations. From that we calculate the coke deposited after a day. The calculations indicate that 999kg of coke would be deposited after 24 hours. This coke deposition will reduce the feed flow rate by a certain value which is shown in the table below.

If we assume that the coke deposition remains constant every day, we see that after 23 days the feed flow rate is reduced to half. Consequently, the production of VCM is also reduced to half. Presently, Engro Polymers conducts the pigging process after 23 days to remove the coke deposited. Thus, there are almost 12 shutdowns per year to remove the coke deposited.

Table 9: Coke Deposition

Days	Feed (kg/hr)	Coke Deposited Per Day (kg)	Total (kg/hr)	Total (kg/day)
1	40,241	0	40,241	965784
2	40241	999.84	41,241	989780.16
3	39241.16	999.84	40,241	965784
4	38241.32	999.84	39,241	941787.84
5	37241.48	999.84	38,241	917791.68
6	36241.64	999.84	37,241	893795.52
7	35241.8	999.84	36,242	869799.36
8	34241.96	999.84	35,242	845803.2
9	33242.12	999.84	34,242	821807.04
10	32242.28	999.84	33,242	797810.88
11	31242.44	999.84	32,242	773814.72
12	30242.6	999.84	31,242	749818.56
13	29242.76	999.84	30,243	725822.4
14	28242.92	999.84	29,243	701826.24
15	27243.08	999.84	28,243	677830.08
16	26243.24	999.84	27,243	653833.92
17	25243.4	999.84	26,243	629837.76
18	24243.56	999.84	25,243	605841.6
19	23243.72	999.84	24,244	581845.44
20	22243.88	999.84	23,244	557849.28
21	21244.04	999.84	22,244	533853.12
22	20244.2	999.84	21,244	509856.96
23	19244.36	999.84	20,244	485860.8
TOTAL	694,580	21,996	716,576	17,197,835

3.7 After Modification

If we change the burner design from forward burners to inclined burners, coking is reduced by 70%. This is because 70-80% of coking is due to the impingement points while 30% is due to impurities. Once we eliminate the impingement points, we can reduce coking by a significant amount. As a result of this modification an increase in production by 33tons per month can be obtained.

(Cont'd)

Table 10: EDC After Modification

State	**EDC In (ton)/month**	**EDC Out (ton)/month**
With Coking	694.6	399.4
Without Coking	796.5	432.5

CHAPTER 4

ENERGY BALANCE

The basic equation used for the energy balance is as follows;

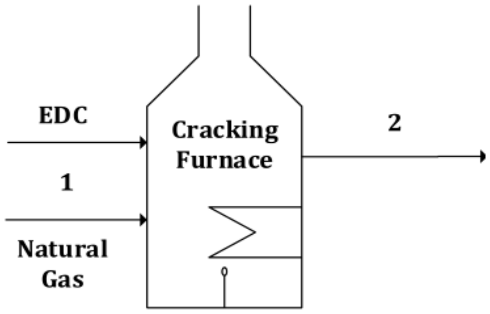
$$\Delta[\boldsymbol{m}\ (\boldsymbol{H}+\mathbf{12}\boldsymbol{u}\mathbf{2}+\boldsymbol{zg})]=\boldsymbol{Q}+\boldsymbol{Ws}$$

Since there is no velocity and height change in the system, Velocity and potential head turn to zero. Also, no work is being done the system, so the final equation ends up as follows;

$$\Delta\boldsymbol{H}=\boldsymbol{Q}$$

4.1 Furnace

Figure 17: Furnace



C_p values for all the components were found from literature. Multiplying each C_p with their respective mole mass fraction, we found C_p of the mixture which is shown as follows;

Table 11: Energy Balance in Furnace

C_p Stream	Mass (kg)	Temp In (^oC)	Temp Out (^oC)
1.262	40154	74.7	504.4

By using the formula,

$$\Delta H = mC_p\Delta T$$

We calculated enthalpy of stream 1 and 2 as follows;

$$H_1 = 2.6 \times 10^6$$

$$H_2 = 2.2 \times 10^7$$

$$\mathbf{\Delta H = 1.9 \times 10^7}$$

Since chemical reaction is also taking place inside the furnace, heat of formation of VCM will also be incorporated. The cracking reaction is as follows;

$$\underset{\textbf{EDC}}{C_2H_4Cl_2} \longrightarrow \underset{\textbf{VCM}}{C_2H_3Cl} + HCl \qquad H_{formation} = +218 kJ/mol$$

In the mass balance table 2, it was calculated that VCM produced was 24198 kg. Converting it to moles, we get;

$$\text{No of moles} = \frac{\text{mass}}{\text{moleculor mass}}$$

$$\text{No of moles} = \frac{24198}{62.498} = 387.18 \text{ moles}$$

Therefore $H_{formation}$= +218kJ/mol * 387.18 = 84,405.32 kJ

$$\mathbf{H_{formation} = 8.4 \times 10^4 \text{ kJ}}$$

Now total heat is,

$$Q = \Delta H + H_{formation}$$

$$Q = 1.9 \times 10^7 + 8.4 \times 10^4 \text{ kJ}$$

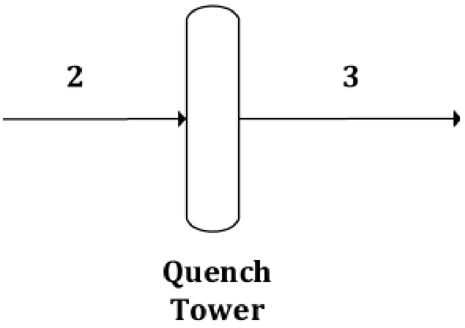
$$\mathbf{Q = 1.91 \times 10^7 \text{ kJ}}$$

4.2 Quench Tower

Inside the quench column, heat transfer is taking place so the total enthalpy can be calculated from the following formula;

$\Delta H = mC_p\Delta T$

Figure 18: Quench Tower



Again, we calculated the mass fractions of each component and multiplied them to their respective heat capacity. Adding all the heat capacities gave the heat capacity of the feed as follows. The temperatures of each stream are also given in the table.

Table 12: Energy Balance in Quench Tower

Cp Stream	Mass (kg)	Temp in (°C)	Temp out (°C)
1.044	40154	504.4	131

Calculating the enthalpy,

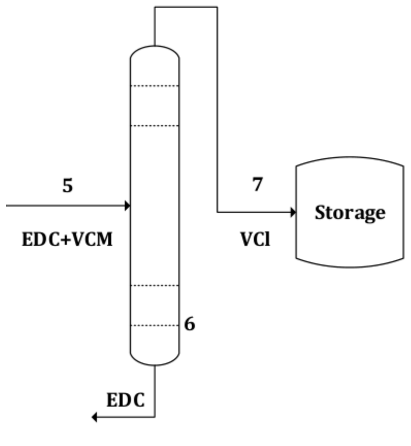
$$H_2 = 2.2 \times 10^7$$

$$H_3 = -1.56 \times 10^7$$

$$\mathbf{\Delta H = -3.7 \times 10^7}$$

4.3 Purification Column

Figure 19: Purification Column



4.3.1 Stream 6

Table 13: Energy Balance in Purification Column (a)

Cp Stream	Mass (kg)	Temp in °C	Temp out °C
0.944	24138.9	104.7	38.8

$H_5 = -7.4 \times 10^5$

$H_6 = -1.5 \times 10^6$

$\mathbf{\Delta H = -7.6 \times 10^5}$

4.3.2 Stream 7

Table 14: Energy Balance in Purification Column (b)

C_p Stream	Mass (kg)	Temp in (°C)	Temp out (°C)
1.04	1846.12	104.7	157.9

$H_5 = -7.4 \times 10^5$

$H_7 = 1 \times 10^5$

$\mathbf{\Delta H = 8.5 \times 10^5}$

CHAPTER 5

MODIFICATION

5.1 Current Practice and Modification

At present, the furnace used by Engro Polymers has burners installed at the two side walls. On each side 36 burners are installed, arranged in 9 rows. Hence in total 72 burners are used to fire the furnace. The design of these burners is such they fire horizontally towards the furnace, forming a needle flame. A needle flame is a pointed flame that produces the highest amount heat at the point at which it hits the surface. This generates points of impingements on the tubes which creates rings that act as active sited for the formation of coke. Also, the formation of impingements gives rise to localized cracking. In this type of cracking, heat is not distributed evenly throughout the furnace, as a result of which the required furnace temperature is not achieved everywhere. EDC conversion is hindered and coke formation is larger at areas with higher temperature.

Figure 20: Needle Flame (Left) and Flame Impingement (Right)

A lot of problems arise as a result of this type of design. The capacity of EDC flow decreases as coke deposition narrows the tubes. Less surface area is provided for the reaction to occur which eventually decreases the production of VCM from the optimized volume that we want to achieve.

Another major problem that arises due to the needle flame is that the deposition of coke causes an increase in the differential pressure inside the furnace. This changes the process conditions for the production of VCM. Once coke starts to deposit, the heat transfer is also decreased as a result of which more heat is needed to provide the temperature conditions feasible for the production. Thus, fuel consumption and energy requirements increase. This makes the process expensive. To overcome both these problems, decoking has to be done every 23 days. Hence after every 23 days, plant shut down has to occur which corresponds to loss of time for production.

Some post combustion issues are also associated with this design. When fuel is released from the burner, some of it remains un-combusted between the burner and the furnace tubes. Excess air is present in the environment. When this excess air contacts with the un-combusted fuel, cracking starts to occur on the outer side of the furnace tubes which results in deposition of matter on the outer surface. These deposits hinder the heat transfer process and more energy is then required to obtain the desired temperature inside the furnace.

In order to overcome all these problems, we propose to change the burner design from one having needle flame to one having a flower flame. This can be obtained if we install multiple nozzles at the end of each burner. Now, instead of a single point flame, a flower type flame would be obtained like the ones inside the kitchen stoves of houses.

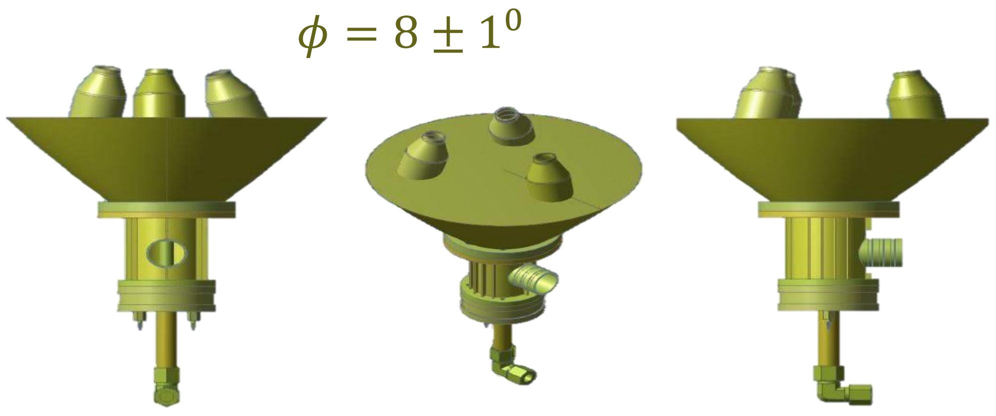
Figure 21: Flower Flame

This design would be very effective because it would decrease the amount of coke formed to a significant value. Since now, single point firing is not taking place, localized cracking will not take place and flux would be distributed evenly through the furnace tubes. This type of cracking is called balanced cracking. This will eliminate the impingement points that were present before. 36 burners are present on each side of the furnace. Thus, this design modification would eliminate 72 impingement points and 72 coking sites. When these coking points are removed the problems described above will all be eliminated.

Another major advantage of using this type of flame is that the furnace could be changed from higher pressure furnace to a lower pressure furnace. This would bring significant changes in the product purification and energy requirements. The feed introduced to the furnace consists of heavier carbon compounds, lighter carbon compounds and EDC. At higher pressure, the heavier compounds are cracked which affect the purity of the VCM product. Also, the cracking of heavier ends produces larger amounts of coke deposits which eventually create all the problems. If we shift the furnace conditions to a lower pressure, only EDC is cracked, pure VCM is produced and the process becomes more energy and cost efficient.

The furnace design with multiple nozzles with an angle of inclination of 8 degrees was modeled on AutoCAD. Details of the model are described in the coming sections. An overview of the design is shown as follows;

Figure 22: 3D Model of Tri-Nozzle Burner



5.2 Calculations of the Equipment Design

5.2.1 Furnace Design

The major parts of a furnace include a Radiant section, Convection section, stack, tubes, piping and instrumentation, burners and insulations. The furnace design relates the required heater duty to the required number of the burners, coils, dimensions and insulation, etc.

The heat transferred to the cold surface in a furnace s given by the following equation:

$$\frac{\sum Q}{\alpha_{cp} A_{cp} f} = 0 \cdot 173 \left[\left(\frac{T_G}{100} \right)^4 - \left(\frac{T_s}{100} \right)^4 \right] + 7\,(T_G - T_s)$$

Where,

Q is the heat transferred to the cold surface,

T_G is the temperature of the flue gases in Rankine,

T_s is the temperature of the surface of the tubes in Rankine,

A_{cp} is the surface area of the cold surface,

α_{cp} is the factor by which the cold surface area must be reduced to get the effective area.

In order to achieve a feasible furnace design, we ought to know the following information:

1. The heater duty which is required by the reaction taking place [Btu/hr]:
   This is found out to be **56 x 10^6 Btu/hr**.
2. The efficiency of the Burner:
   This is found out to be **90%.**
3. The Fuel value:
   This can be given as **50 x 10^6 Btu/hr** or **76.3 kBtu/kg.**

4. The air to fuel ratio will be given as:

   As, m_{air} = (Air/Fuel) x m_{fuel}

$$\left(\frac{A}{F}\right)_{ST} = 4.76\left(x+\frac{y}{4}\right)\frac{MWair}{MWfuel}$$

$$C_nH_m + \left(n+\frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow nCO_2 + (m/2)\ H_2O$$

   For 0.7 moles of CH_4 and 0.3 moles of H_2 the above equation can be written as follows:

$$0.7\ CH_4 + 1.4\ (O_2 + 3.76\ N_2) \rightarrow 0.7\ CO_2 + 1.4\ H_2O$$

$$0.3\ H_2 + 0.15\ (O_2 + 3.76\ N_2) \rightarrow 0.3\ H_2O$$

   Fuel moles = 1 mol

   Air moles = 0.15 + 1.4 = 1.55

$$x+\frac{y}{4} = 1.55$$

$$\left(\frac{A}{F}\right)_{ST} = 4.76\ (1.55)\frac{29}{11.8}$$

   The ratio comes is **18.13**.

5. Temperature of inlet air which is 31°C. In Fahrenheit will be T = 88°F.
6. Amount of steam will be **0 lb**.
7. Tube diameter will be **d_o = 6.25** inches or **0.52 ft**.

   The center to center distance will be **7 inches**.

8. The length of the tubes exposed will be **55 ft**.
9. Average flux q [Btu/hr ft^2] will be calculated as:

$$q = \frac{56\times10^6}{hr}\frac{1}{(55)^2}$$

$$\mathbf{q = 18{,}512\ Btu/hr\ ft^2}$$

10. Now the heat transfer will be given by the equation as follows:

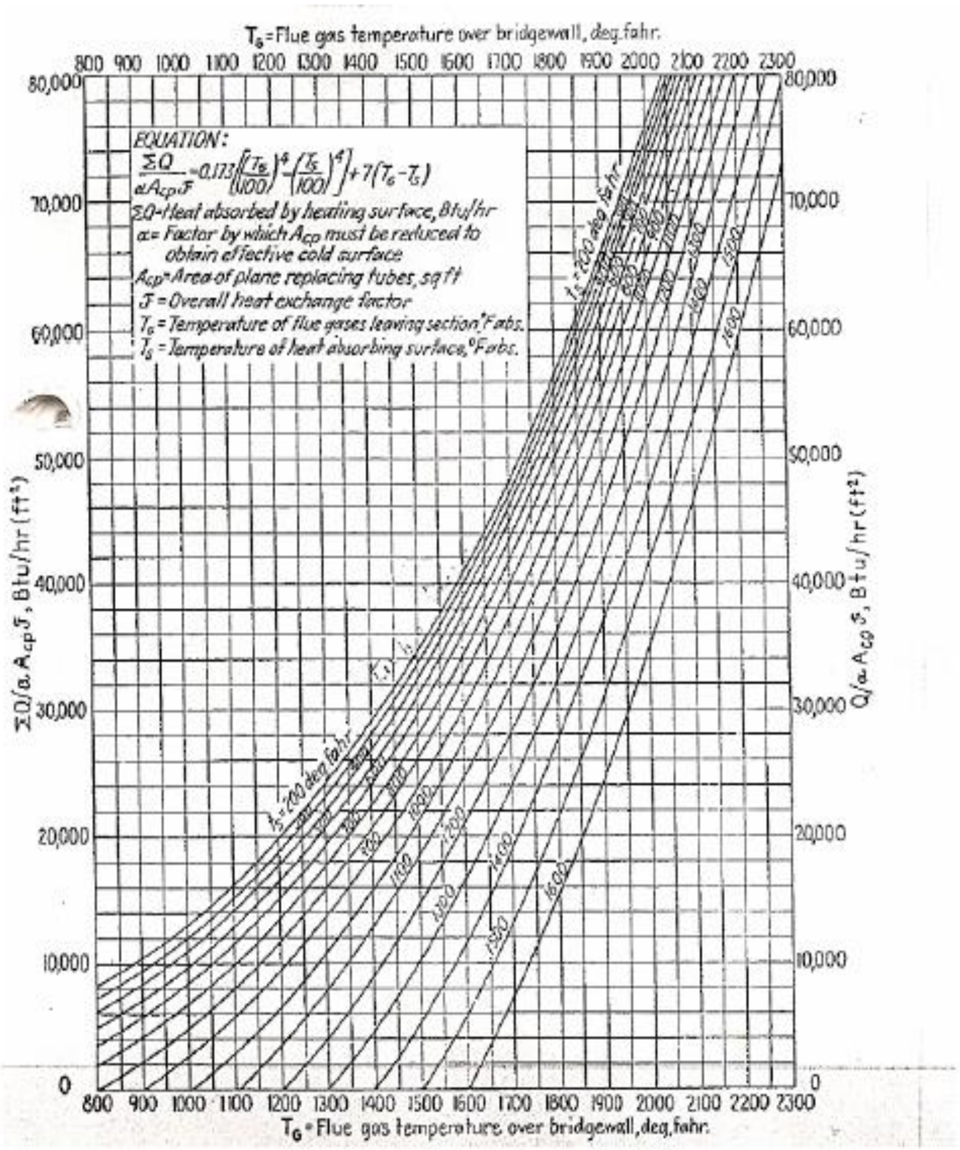
$$\frac{\Sigma Q}{\alpha_{cp}A_{cp}f} = 2\ \times \text{Average flux (q)}$$

   This will be calculated as **= 18512 x 2 = 37,024.8.**

11. Now a surface temperature will be assumed which will be T_S use the chart below to find out the outlet temperature which will be T_G.

From the graph down below, now find out the relevant T_G, and later on in the future calculations we will find out whether this T_G is close to what we have approximated in point 10 or not.

Figure 23: Graph to Determine T_G



12. The value of T_G from it will be calculated as:

T_G = 1850°F.

As now we have found out this value, we will carry out the further calculations which will include the whole design of the furnace to check whether the T_G calculated this way is accurate or not. If it comes out to be accurate then all the values mentioned above will be taken as correct.

Now a detailed design will be done for finding out whether our above assumptions are true or not.

1. The heat released by the burners in total would be calculated by dividing heater duty by the efficiency:

$$Q_F = \frac{\text{heater duty}}{\eta}$$

$$Q_F = \frac{56 \times 10^6}{0.9}$$

The value of Q_F will be **62 x 10^6 Btu/hr**.

2. Now from the already known values we will find out the mass of the fuel required:

$$m_{fuel} = \frac{Q_F}{\text{Fuel value}}$$

This value is already known through literature and experiments this will be 76.3 x 10^3 Btu/kg. So,

$$m_{fuel} = \frac{62 \times 10^6}{76.3 \times 10^3}$$

This value comes out to be $\mathbf{812 \frac{kg}{hr}}$ **or** $\mathbf{1790 \frac{lb}{hr}}$.

3. For the above found out mass we will now the corresponding value of mass of air required for the reaction.

$$m_{air\ stoich} = \left(\frac{A}{F}\right)_{st} \times m_{fuel}$$

The stoichiometric A/F ratio has already been found out to be 18.13 and the mass of fuel is also known already. So, by putting these values in the above equation we get:

$$m_{air\ stoich} = 18.13 \times 812 \text{ kg}$$

the answer obtained would be **14,723 kg/hr**.

4. Now the air used is mostly in excess of the stoichiometric amount of air. This excess amount is usually 25% of the stoichiometric amount. The calculations will be:

$$m_{air} = 1.25 \times m_{air\ stoich}$$

$$m_{air} = 1.25 \times 14{,}723$$

This will be calculated as **18,404 kg/hr** or **40,573 lb/hr**.

5. The heat liberated by the inlet air will be now calculated. This will be calculated by the following equation:

$$Q_{air} = m_{air} \times c_{p_{air}} \times (T_{air} - T_{ref})$$

T_{ref} is taken as 60^oF,

Cp_{air} is taken to be 0.24 Btu/lb ^0F,

$$Q_{air} = 0.24 \times 40573 \times (88 - 60)$$

This value will be calculated as **272650 Btu/hr**.

6. Now atomizing steam will be calculated which will give the rise in the temperature. The furnace that we are designing does not use steam to heat the streams so we will mot incorporate this factor.

7. Now the heat which is taken up by the walls of the furnace will be calculated by the following equation:

$$Q_{wall} = 2\% Q_F$$
$$Q_{wall} = 0.02 \times Q_F$$
$$Q_{wall} = 0.02 \times 62 \times 10^6$$

This value is calculated to be **124 x 10^4 Btu/hr**.

8. The heat released through the exhaust gases will now be calculated by the following equation:

$$Q_{exhaust} = m_{fuel} \times (1 + G') \times Cp_{avg} \times (T_G - 520)$$

The T_G used here will used in Rankine (°R) and G' will be the air to fuel ratio. T_G will be estimated close to that which was previously found out by the graph.

Now taking T_G = 1909.7 °F,

$$Cp_{avg} = \sum_i x_i Cp_i$$

Here x usually refers to moles of CO_2 and H_2O. From the previous calculations the moles will be calculated as:

$$x = 0.7 + 1.4 + 0.3$$

Through this, the total moles come out to be 2.4 and the mole fractions will be:

$$x_{CO2} = 0.29$$
$$x_{H2O} = 0.71$$

The Cp of CO_2 is 37.35 Btu/lb°F or 0.081 Btu/lb°R,

The Cp of H_2O is 0.4767 Btu/lb°F or 1.03 x 10^{-3} Btu/lb°R.

$$Cp_{avg} = [(0.29 \times 1.03 \times 10^{-3}) + (0.71 \times 0.081)]$$

The calculated value will now be **0.06 Btu/lb°F**.

By putting these values in the major equation, we get,

$$Q_{exhaust} = 1790\,(1 + 18.13) \times 0.06 \times (1909 - 520)$$

The final value of $Q_{exhaust}$ will be **2853786 Btu/hr**.

9. Now the total heat effect will be calculated by the following equation:

$$Q = Q_{fuel} + Q_{air} + Q_{steam} + Q_R - Q_{wall} - Q_{exhaust}$$

In this equation the term of Q_R may be neglected if there is no recirculation involved. Q_{steam} will also not be included as there is no atomizing steam involved.

$$Q = (62 \text{ x } 10^2) + (272650) - (2853786) - (1240000)$$

The final answer is calculated as **58 x 10^6 Btu/hr**.

10. Now we will calculate the number of tubes required inside the furnace to carry the desired reaction. The formula for it would be:

$$N_{tubes} = \frac{Q}{2\pi rLq}$$

From the assumptions and provided data shown above we will put the values in the above equation. Here the length would be taken as the total length of the radiation and the convection section. This length would be **94 ft**.

$$N_{tubes} = \frac{58 \times 10^6}{2\pi\left(\frac{0.52}{2}\right) \times 5696 \times 94}$$

The final value of the number of tubes will be **66 tubes**.

11. Now the cold surface area available for heat exchange will be calculated. The following formula would be used:

$$A_{Cp} = ctc \ \times L \times N$$

$$A_{Cp} = 0.58 \ \times 55 \times 66$$

The final answer from the above equation will be **2105 ft^2**.

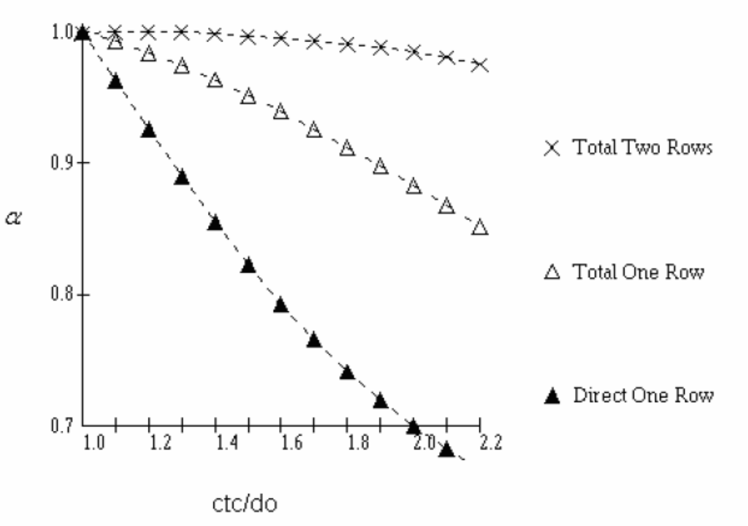
12. The ctc/diameter ratio will be calculated to find the value of α from the graph down below:

$$\frac{ctc}{d_0} = \frac{7}{6.625}$$

ctc/d_o will be 1.12.

From the following graph the intersection between the ctc/d_o and the single row of reaction tubes will be checked.

Figure 24: Graph to Determine α



The value of α from the graph above is found out to be **0.98**.

13. Now the total exposed area of the furnace will be calculated which taken in heat from the burners. The following ratio is present for us:

Length : Width : Height

55 : 11.625 : 23.91

The area will be calculated by the following formula:

$$A_T = (2 \text{ x Area of right/ left side}) + (\text{Area bottom}) + (2 \text{ x Area of back/front})$$

$$A_T = (2 \text{ x } 23.91 \text{ x } 11.62) + (11.62 \text{ x } 55) + (2 \text{ x } 23.91 \text{ x } 55)$$

$$A_T = 555 + 639 + 2630$$

The total area found out would be **3825.1 ft²**.

14. The total refracting surface will be given by the following formula that gives the effective refracting surface:

$$A_R = A_T - \alpha A_{cp}$$

$$A_R = 3825 - (0.98 \text{ x } 2105)$$

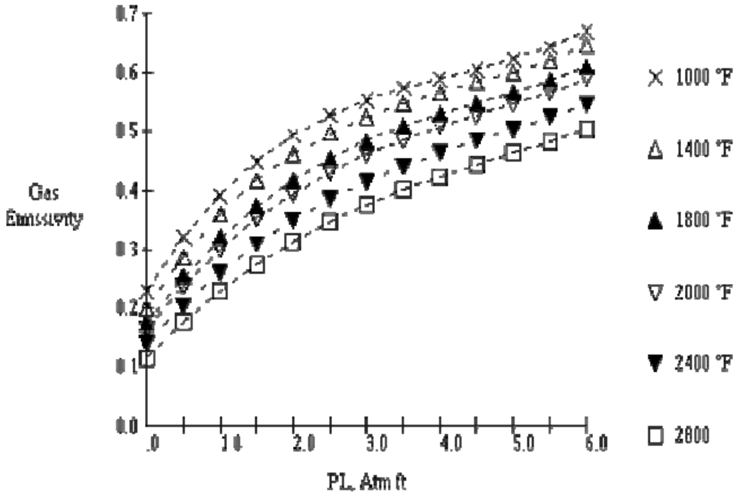
$$A_R = 3825 - 2063$$

The calculated value for it will be **1221 ft²**.

15. The gas emissivity ε of the flue gases will be calculated from the graph down below. This graph is against the emissivity and pL, which is the product of partial pressure of carbon dioxide and water and the length of the furnace. The units will be atm-ft. Knowing the pL product and the

temperature of the hot flue gases we can find the emissivity through their intersection from the graph down below:

Figure 25: Graph to Determine Gas Emissivity (ε)



The product pL will be calculated by:

pL = (P_{CO2} + P_{H2O}) x Length

at 1450^{o}F,

P_{CO2} = 0.099 atm

P_{H2O} = 0.15 atm

$$pL = (0.099 + 0.15) \times 11.62$$

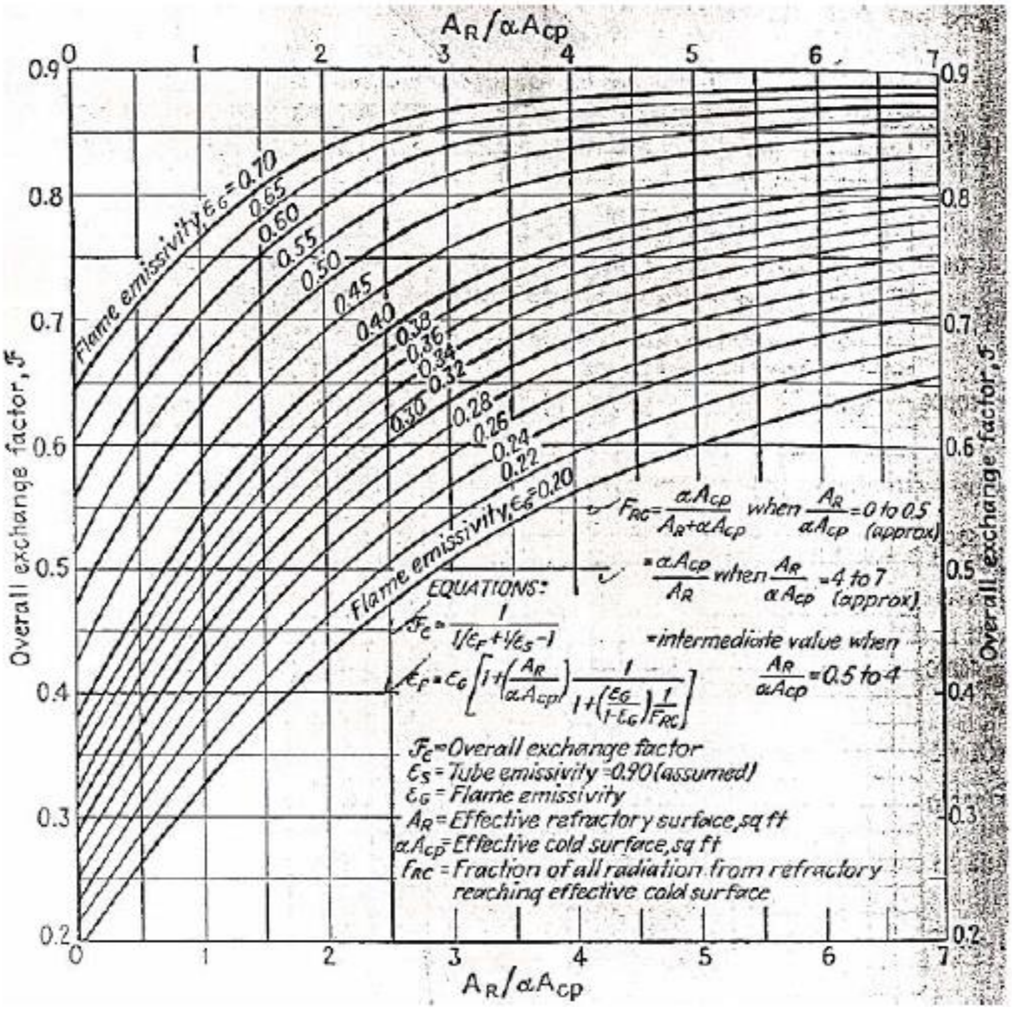
This value will be calculated as **5.73 atm-ft**.

$$\varepsilon = 0.65.$$

16. Now by incorporating this emissivity value and the factor of $\frac{A_R}{\alpha A_{cp}}$ we will obtain a factor **"f"** from the graph down below. It will be the overall heat exchange factor.

The factor $\frac{A_R}{\alpha Acp} = \frac{3825.1}{1221 \times 0.98}$ = 3.197

Figure 26: Graph to Determine Overall Heat Factor (f)



The value of f obtained from the graph will be **0.86**.

17. The value of the following factor will now be calculated:

$$\frac{\sum Q}{\alpha_{Cp} Acpf}$$

This factor will be calculated as:

$$\frac{\sum Q}{\alpha_{Cp} Acpf} = \frac{58 \times 10^6}{0.86 \times 0 \cdot 98 \times 1221}$$

This value will be calculated as **56,326.**

18. Now we go back to the first graph to find the value of T_G. if this value comes close to the values that we assumed beforehand then our furnace has a feasible design otherwise the calculations will have to be repeated.

So, from the graph above the value of T_G = 1950°F and 1065°C.

Since the first T_G value is 1010°C and the second value is 1065°C, these values are quite close hence we say that our furnace has a feasible design.

5.2.2 Burner Design

For the burner design we will take the whole burner duty and divide it by the number of burners to get the duty required of a single burner. With this we will find the mass of the fuel being injected and its release speed which will lead us to the diameter of the burner nozzle. The following steps will be followed:

1. The duty of the furnace will first be noted down which is 56 x 10^6 Btu/hr. This will be 1.64 x 10^7 J/s.
2. The duty of a single burner would be calculated as follows:

$$\text{Duty of one burner} = \frac{\text{Furnace duty}}{\text{no. f burners}}$$

The number of burners is 24 in our new proposed design.

$$\text{Duty of one burner} = \frac{1.64\ \times 10^7}{24}$$

Thus, the duty of a single burner would be 6.8 x 10^5 J/s.

3. The fuel heating value has already been identified above which will give us the mass flow rate of the fuel through the following equation:

$$\text{mass flow rate} = \frac{\text{Burner duty}}{\text{Fuel Heating value}}$$

$$\text{mass flow rate} = \frac{6.8\ \times 10^5}{80.5 \times 10^6}$$

These calculations give us the value of mass flow rate to be **8.45 x 10^{-3} kg/s**.

4. Now the volumetric flow rate will be obtained from the mass flow rate and the density of the fuel as follows:

$$\text{Fuel density} = (0.7\ \times \text{density of methane}) + (0.3 \times \text{density of hydrogen})$$

$$\text{Fuel density} = (0.7\ \times 0.668) + (0.3 \times 0.8988)$$

The calculated density will be **0.49 kg/m³**.

Now,

$$\text{Volume} = \frac{\text{Mass flow rate}}{\text{Density}}$$

$$\text{Volume} = \frac{8.54 \times 10^{-3}}{0.49}$$

The volumetric flow rate will now be 0.017 m^3.

5. Now we will assume the speed of the flame release and fuel injection to be 5 m/s. Now the area will be calculated as follows:

$$\text{Area} = \frac{\text{Volumetric flow rate}}{\text{Speed of fuel release}}$$

$$\text{Area} = \frac{0.017}{5.3}$$

This way the area calculated will be 3.21 x 10^{-3} m^2.

6. The diameter will be calculated as follows:

$$\text{Diameter} = 2 \times \sqrt{\frac{3 \cdot 21 \times 10^{-3}}{\pi}}$$

The diameter is calculated to be 0.06 cm or **6 cm**.

The diameter of our multi nozzle burners will be 6 cm. There will be three nozzles on one burner and each will have a diameter of 6 cm. These nozzles will be inclined towards each other to have a radial and uniform flame envelope.

CHAPTER 6

AUTOCAD MODELLING

Modelling was done using AutoCAD software which helped us visualize our project and then analyze it.

6.1 AutoCAD

AutoCAD is a commercial computer-aided design and drafting software application. Developed and marketed by Autodesk, AutoCAD was first released in December 1982 as a desktop app running on microcomputers with internal graphics controllers. AutoCAD can create any 2D drawing and 3D model or construction that can be drawn by hand. The program also allows the user to group or layer objects, keep objects in a database for future use, and manipulate properties of objects, such as size, shape, and location.

To model our project, some of the following commands were used.

- **Subtract:** With SUBTRACT, you can create a 2D region object by subtracting one set of existing region objects from another, overlapping set.
- **Union:** Combines two or more 3D solids, surfaces, or 2D regions into a single, composite 3D solid, surface, or region
- **Extrude:** Creates a 3D solid from an object that encloses an area, or a 3D surface from an object with open ends.
- **Revolve:** Revolves 2D objects around an axis making 3D solids.
- **3DRotate:** easily rotate an object from the plane x,y to x,z or to y,z or vice versa.
- **Sweep:** Creates a 3D solid or 3D surface by sweeping a 2D object or sub-object along an open or closed path.
- **Scale:** Enlarges or reduces selected objects, keeping the proportions of the object the same after scaling.
- **Array:** Creates copies of objects arranged in a pattern.
- **Move:** Moves objects a specified distance in a specified direction.
- **Align:** Aligns objects with other objects in 2D and 3D.

- **Blend:** Creates a spline in the gap between two selected lines or curves. Select each object near an endpoint. The shape of the resulting spline depends on the specified continuity.

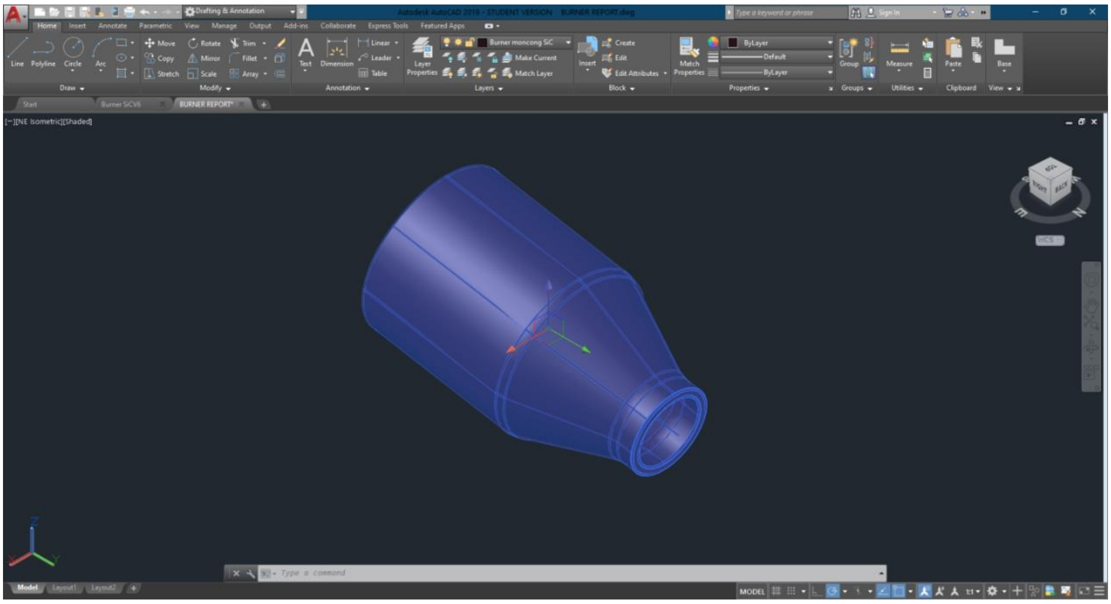
The User Co-Ordinate System (UCS) was also altered at times to align and rotate parts.

6.2 Modeling

Following Steps were performed during the making of the model:

1. First the sketch for half of the valve was made and then revolve command was used to rotate it through 360 °

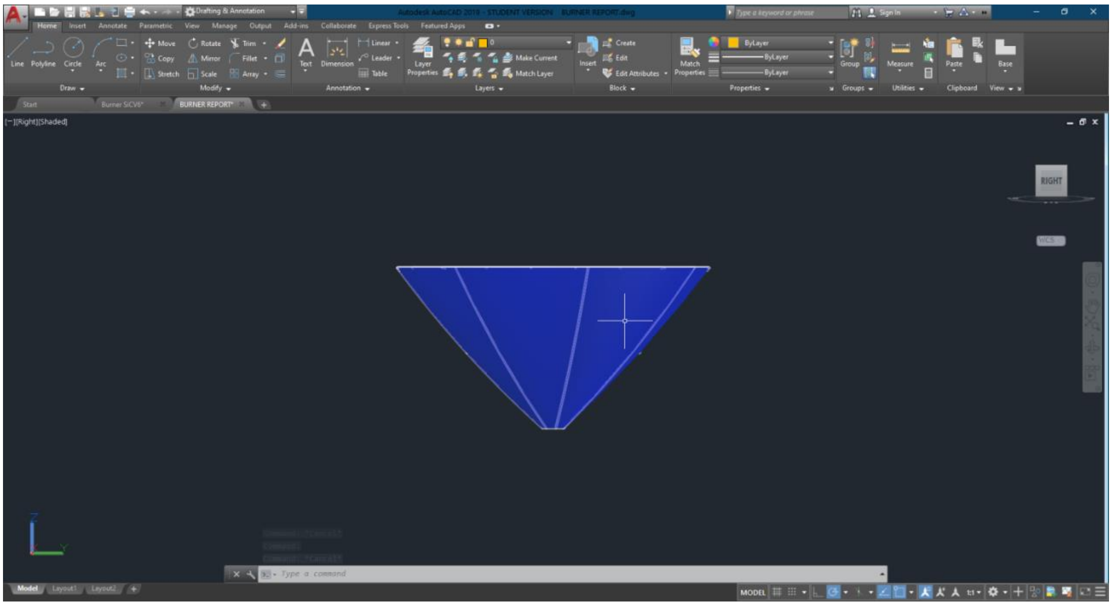
Figure 27: AutoCAD Modelling (a)



(Cont’d)

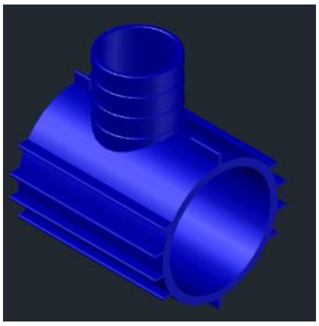
2. Then the barrel was modelled similarly by making a half sketch and then using revolve command.

Figure 28: AutoCAD Modelling (b)



3. The blue part of the air inlet pipe was modelled by making a whole sketch and extruding it to the required length. The upper hole was first made using extrusion and subtraction and inserted in the main pipe using the subtract command. Moreover, the outer extrusions were made using array command.

Figure 29: AutoCAD Modelling (c)



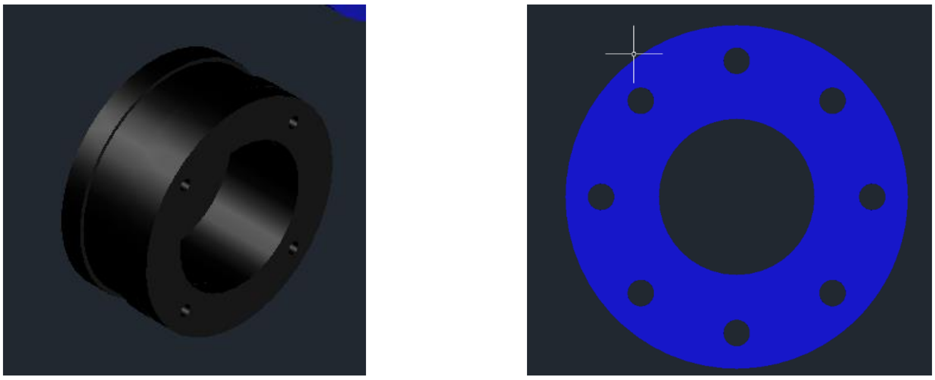
4. The Fuel Atomizer was made by firstly making a half sketch of its shape inner shape and revolving it around its axis. After the Blend command was used to between the edges to make it smooth and filled. Then an angled

sketch for making the spaces was made and using array was copied to all around the object. Then using the subtract command we got our atomizer.

Figure 30: AutoCAD Modelling (d)

5. The black part of the air inlet pipe and the blue part connecting the barrel and the air inlet pipe both were modelled on the same principle. First, the sketch of a circle was made. For holes we used the array command and modified our sketch with respect to the number of holes required and then used extrusion command to fabricate it. Both parts were scaled according to requirement.

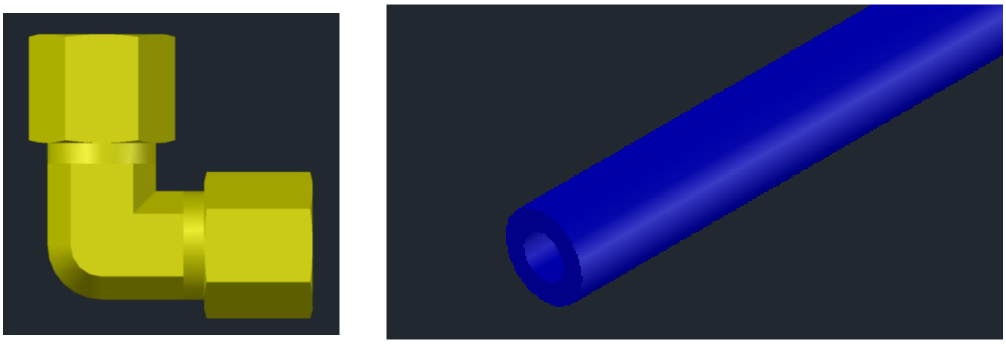
Figure 31: AutoCAD Modelling (e)



6. Now the fuel intake pipes consist of the combination of the long blue thin pipe and the yellow pipe. The blue pipe has two segments. Both had the same principle as a circular sketch was extruded but on a different scale and finally the two segments were combined. However, for the yellow pipe first the outermost part was made using sketch, blend, and extrusion. Then a little circular sketch was extruded as a connection between the middle and the upper parts. The middle part was sketched in in parts. First the inner extrusion was done. Then one by one the others and then finally

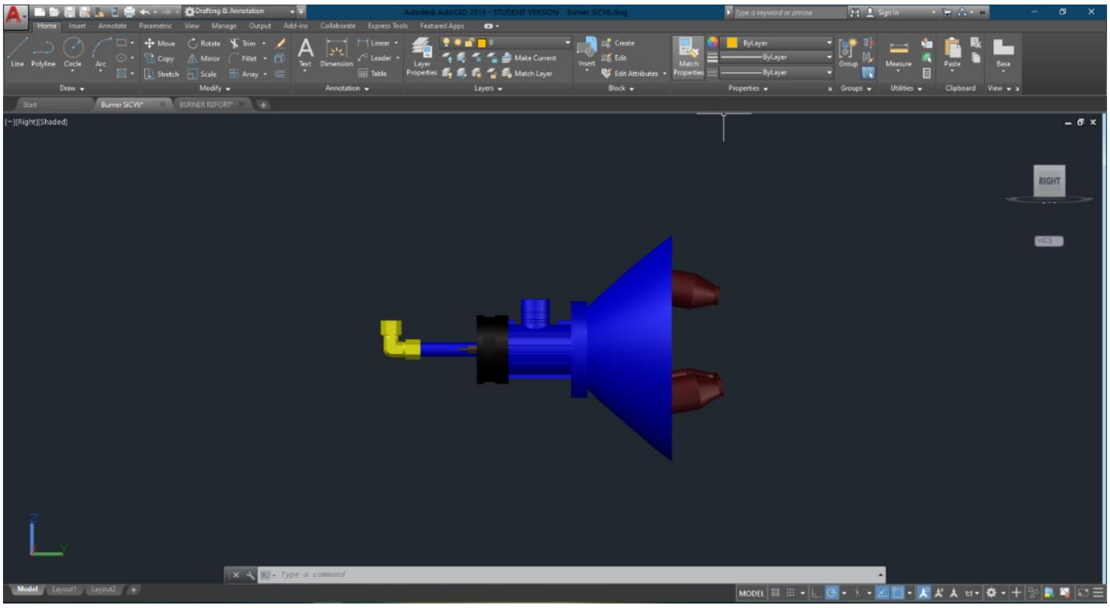
mirrored and using union made into one. The upper part of the yellow pipe was simple copied and rotated 90° to it and all these were combined as one.

Figure 32: AutoCAD Modelling (f)



7. After modeling all these parts separately, they were then aligned using the move, and align commands.
8. The valve was used to make three copies of itself and then placed on the barrel. Then each of them was rotated separately 10° in the directions required giving us our final model.

Figure 33: AutoCAD Modelling (g)



CHAPTER 7

SIMULATION

Simulation is the part of our project which helps us demonstrate our designed plant with the working conditions that are assigned to optimize our process. For this purpose, we use the software 'ASPEN HYSYS'. It also gives an idea about the workability of our process.

7.1 Aspen HYSYS

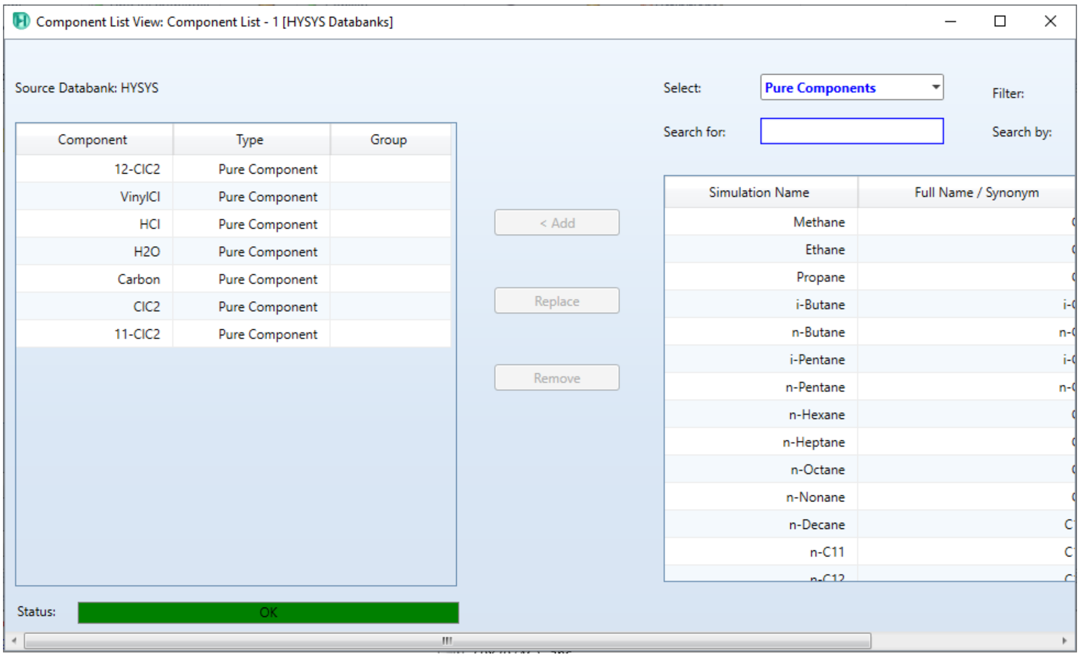
ASPEN HYSYS is a chemical process simulator which uses different mathematical models. HYSYS also solves many chemical engineering core problems like mass balance, energy balance, chemical kinetics, vapor-liquid equilibrium, pressure drop etc. HYSYS is used in industry and academia for steady-state and dynamic simulation, process design, performance modelling, and optimization.

For simulating a process using HYSYS several steps are to be followed.

1. A thermodynamic model is to be selected. A thermodynamic model is used to represent the phase equilibrium behavior and energy level of liquids, solids or vapors. There are total 30+ models already installed in the simulation software which are used for different working conditions. The thermodynamic model used for our project is "Peng-Robinson". Reason for this selection is the high-pressure process involving hydrocarbons. Peng Robinson is the most enhanced model and is used for high temperatures and pressures. It specially treats the components and has one of the largest binary interaction databases.
2. Next step comprises of the selection of components that are required for our process.

(Cont'd)

Figure 34: List of Components



Component List View: Component List - 1 [HYSYS Databanks]

Source Databank: HYSYS

Select: Pure Components

Filter:

Search for:

Search by:

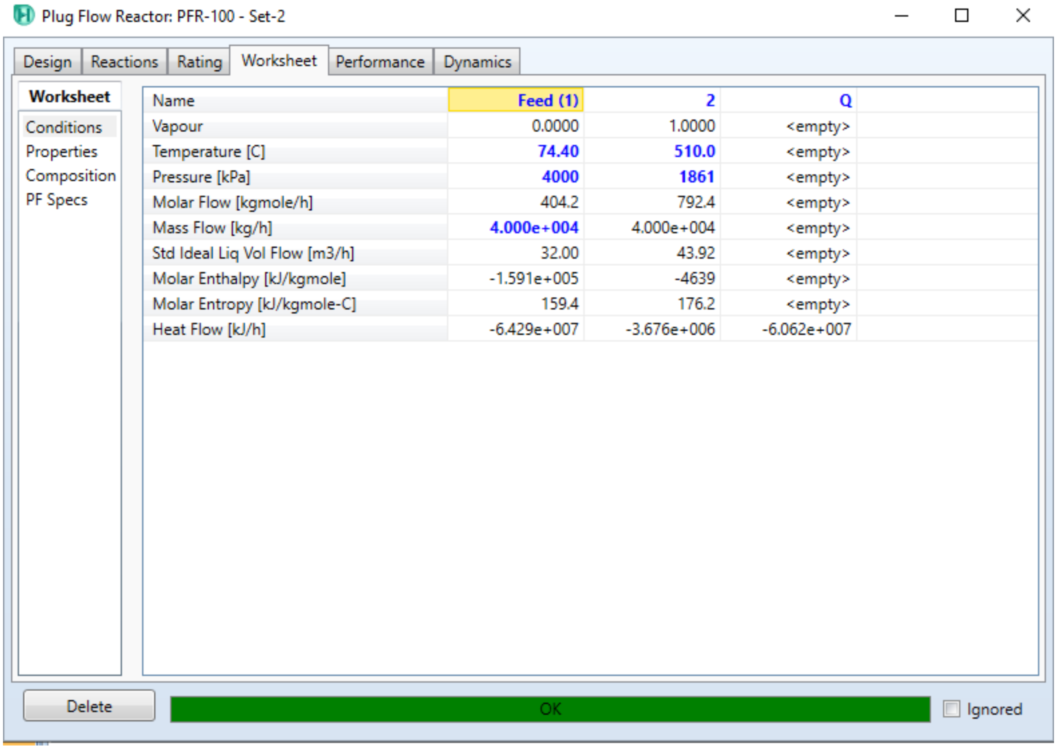
Component	Type	Group
12-ClC2	Pure Component	
VinylCl	Pure Component	
HCl	Pure Component	
H2O	Pure Component	
Carbon	Pure Component	
ClC2	Pure Component	
11-ClC2	Pure Component	

Simulation Name	Full Name / Synonym
Methane	
Ethane	
Propane	
i-Butane	
n-Butane	
i-Pentane	
n-Pentane	
n-Hexane	
n-Heptane	
n-Octane	
n-Nonane	
n-Decane	
n-C11	
n-C12	

Status: OK

3. After the selection of components, a reaction set is added and attached to the thermodynamic model.
4. Then moving on to the simulation environment. First, a plug flow reactor was added and all the required data along with the reaction set was fed.

Figure 35: PFR Worksheet

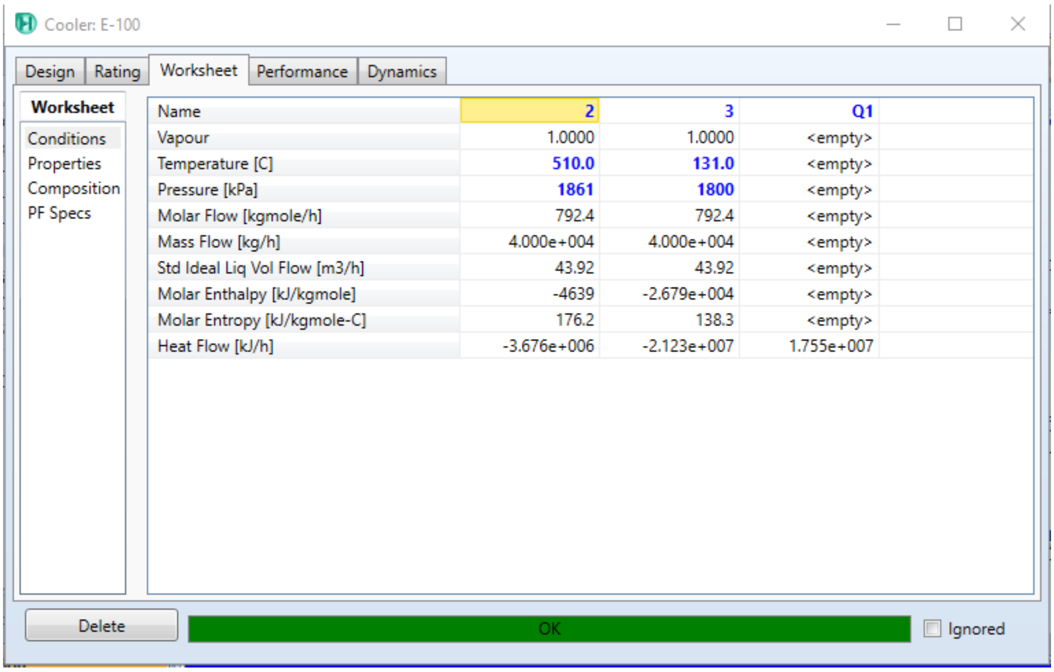


Plug Flow Reactor: PFR-100 - Set-2

Name	Feed (1)	2	Q
Vapour	0.0000	1.0000	<empty>
Temperature [C]	74.40	510.0	<empty>
Pressure [kPa]	4000	1861	<empty>
Molar Flow [kgmole/h]	404.2	792.4	<empty>
Mass Flow [kg/h]	4.000e+004	4.000e+004	<empty>
Std Ideal Liq Vol Flow [m3/h]	32.00	43.92	<empty>
Molar Enthalpy [kJ/kgmole]	-1.591e+005	-4639	<empty>
Molar Entropy [kJ/kgmole-C]	159.4	176.2	<empty>
Heat Flow [kJ/h]	-6.429e+007	-3.676e+006	-6.062e+007

5. The product from the reactor is to cooled using a quenching tower but due to the unavailability of this specific equipment, cooler was used instead.

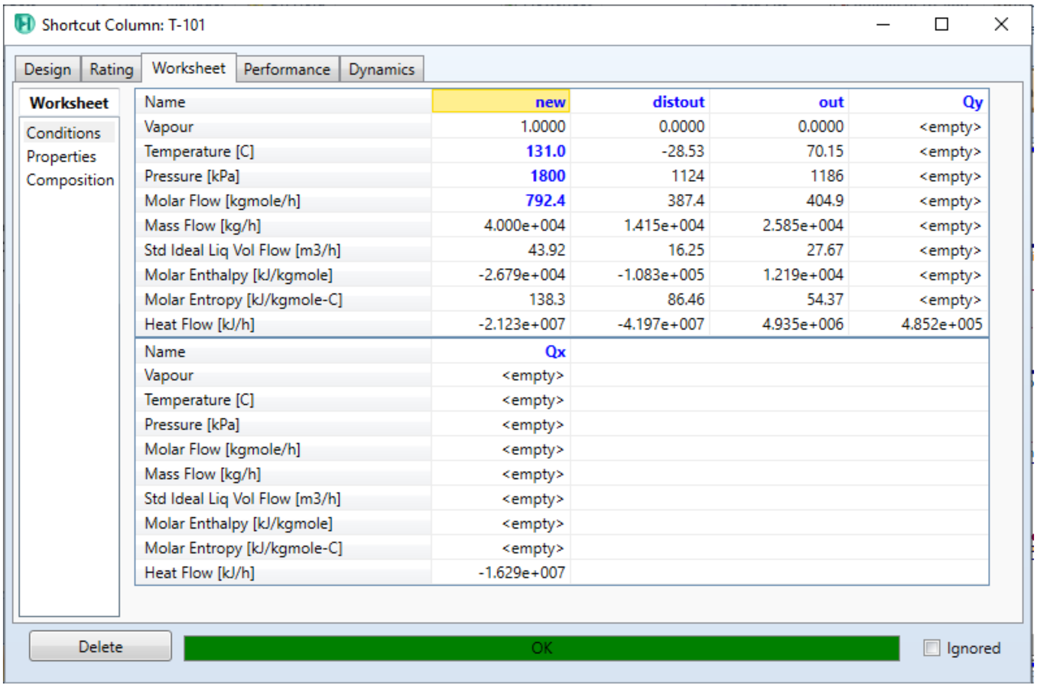
Figure 36: Cooler Worksheet



Name	2	3	Q1
Vapour	1.0000	1.0000	<empty>
Temperature [C]	510.0	131.0	<empty>
Pressure [kPa]	1861	1800	<empty>
Molar Flow [kgmole/h]	792.4	792.4	<empty>
Mass Flow [kg/h]	4.000e+004	4.000e+004	<empty>
Std Ideal Liq Vol Flow [m3/h]	43.92	43.92	<empty>
Molar Enthalpy [kJ/kgmole]	-4639	-2.679e+004	<empty>
Molar Entropy [kJ/kgmole-C]	176.2	138.3	<empty>
Heat Flow [kJ/h]	-3.676e+006	-2.123e+007	1.755e+007

6. A shortcut distillation column was used to find out the values of number of trays, reflux ratio, reboiler and condenser pressure and feed inlet plate.

Figure 37: Shortcut Column Worksheet (a)

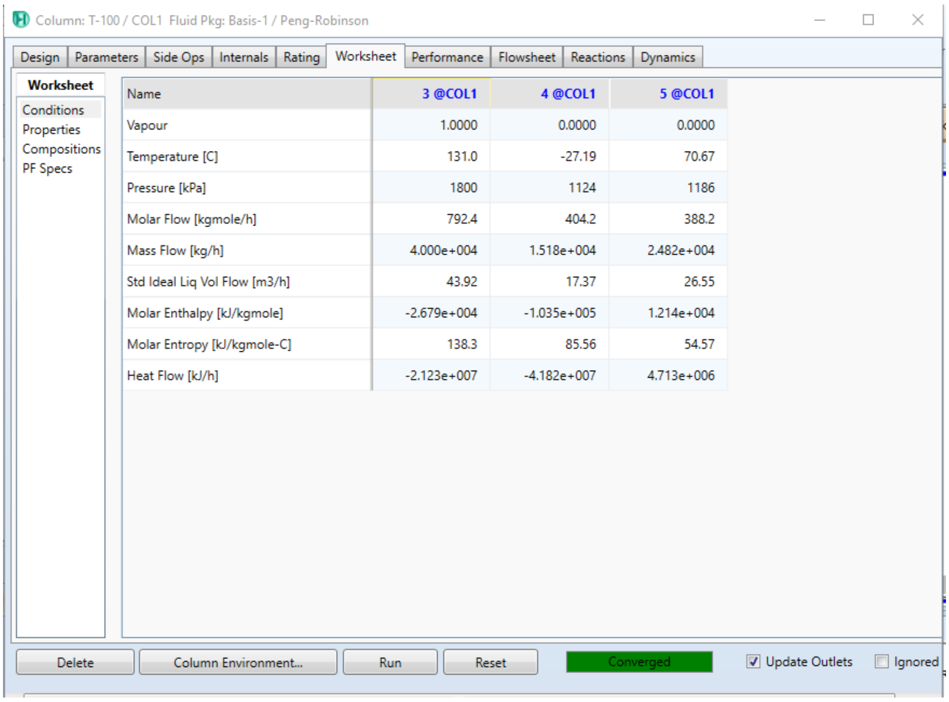


Name	new	distout	out	Qy
Vapour	1.0000	0.0000	0.0000	<empty>
Temperature [C]	131.0	-28.53	70.15	<empty>
Pressure [kPa]	1800	1124	1186	<empty>
Molar Flow [kgmole/h]	792.4	387.4	404.9	<empty>
Mass Flow [kg/h]	4.000e+004	1.415e+004	2.585e+004	<empty>
Std Ideal Liq Vol Flow [m3/h]	43.92	16.25	27.67	<empty>
Molar Enthalpy [kJ/kgmole]	-2.679e+004	-1.083e+005	1.219e+004	<empty>
Molar Entropy [kJ/kgmole-C]	138.3	86.46	54.37	<empty>
Heat Flow [kJ/h]	-2.123e+007	-4.197e+007	4.935e+006	4.852e+005

Name	Qx
Vapour	<empty>
Temperature [C]	<empty>
Pressure [kPa]	<empty>
Molar Flow [kgmole/h]	<empty>
Mass Flow [kg/h]	<empty>
Std Ideal Liq Vol Flow [m3/h]	<empty>
Molar Enthalpy [kJ/kgmole]	<empty>
Molar Entropy [kJ/kgmole-C]	<empty>
Heat Flow [kJ/h]	-1.629e+007

7. Now the values obtained from the shortcut distillation column, are used as the input data of distillation column.

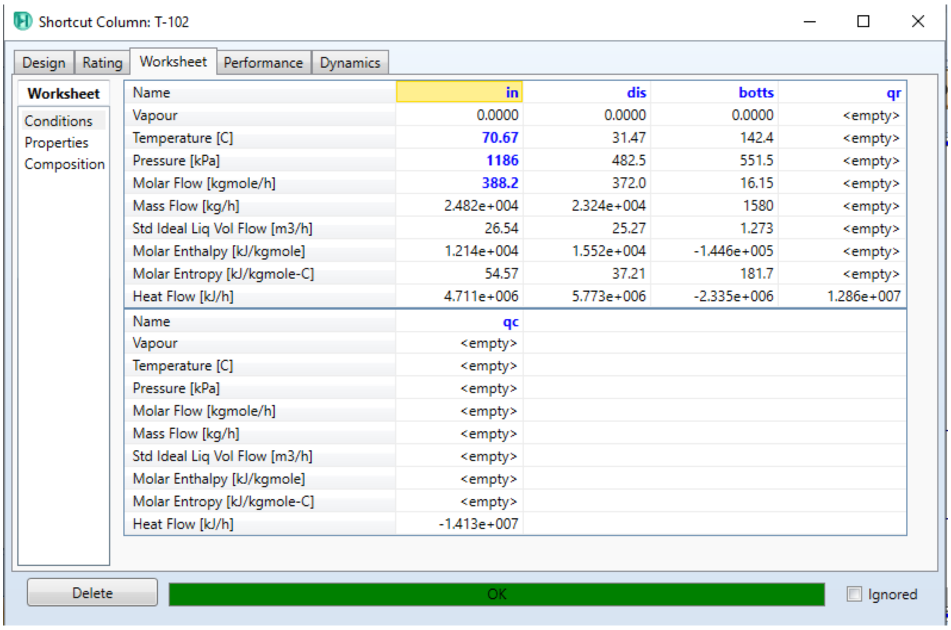
Figure 38: Distillation Column Worksheet (a)



Name	3 @COL1	4 @COL1	5 @COL1
Vapour	1.0000	0.0000	0.0000
Temperature [C]	131.0	-27.19	70.67
Pressure [kPa]	1800	1124	1186
Molar Flow [kgmole/h]	792.4	404.2	388.2
Mass Flow [kg/h]	4.000e+004	1.518e+004	2.482e+004
Std Ideal Liq Vol Flow [m3/h]	43.92	17.37	26.55
Molar Enthalpy [kJ/kgmole]	-2.679e+004	-1.035e+005	1.214e+004
Molar Entropy [kJ/kgmole-C]	138.3	85.56	54.57
Heat Flow [kJ/h]	-2.123e+007	-4.182e+007	4.713e+006

8. Again, a shortcut distillation column was used to calculate the values of reflux ratio, number of column trays, reboiler and condenser pressure and feed inlet tray.

Figure 39: Shortcut Column Worksheet (b)

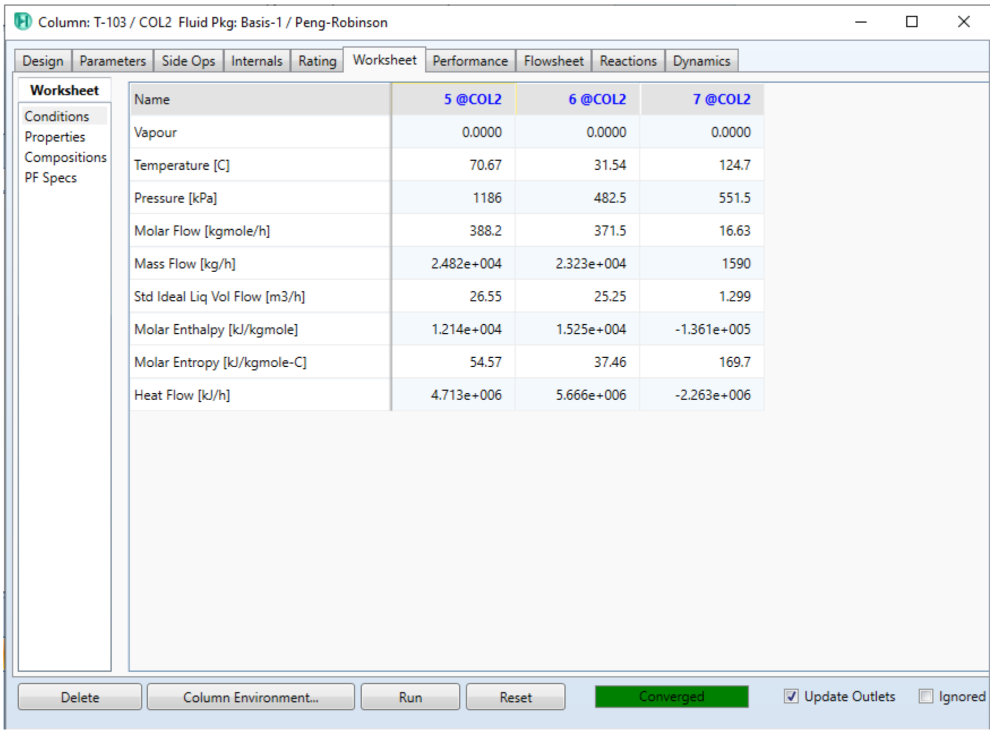


Name	in	dis	botts	qr
Vapour	0.0000	0.0000	0.0000	<empty>
Temperature [C]	70.67	31.47	142.4	<empty>
Pressure [kPa]	1186	482.5	551.5	<empty>
Molar Flow [kgmole/h]	388.2	372.0	16.15	<empty>
Mass Flow [kg/h]	2.482e+004	2.324e+004	1580	<empty>
Std Ideal Liq Vol Flow [m3/h]	26.54	25.27	1.273	<empty>
Molar Enthalpy [kJ/kgmole]	1.214e+004	1.552e+004	-1.446e+005	<empty>
Molar Entropy [kJ/kgmole-C]	54.57	37.21	181.7	<empty>
Heat Flow [kJ/h]	4.711e+006	5.773e+006	-2.335e+006	1.286e+007

Name	qc
Vapour	<empty>
Temperature [C]	<empty>
Pressure [kPa]	<empty>
Molar Flow [kgmole/h]	<empty>
Mass Flow [kg/h]	<empty>
Std Ideal Liq Vol Flow [m3/h]	<empty>
Molar Enthalpy [kJ/kgmole]	<empty>
Molar Entropy [kJ/kgmole-C]	<empty>
Heat Flow [kJ/h]	-1.413e+007

9. The data obtained is used as input for the distillation column.

Figure 40: Distillation Column Worksheet (b)

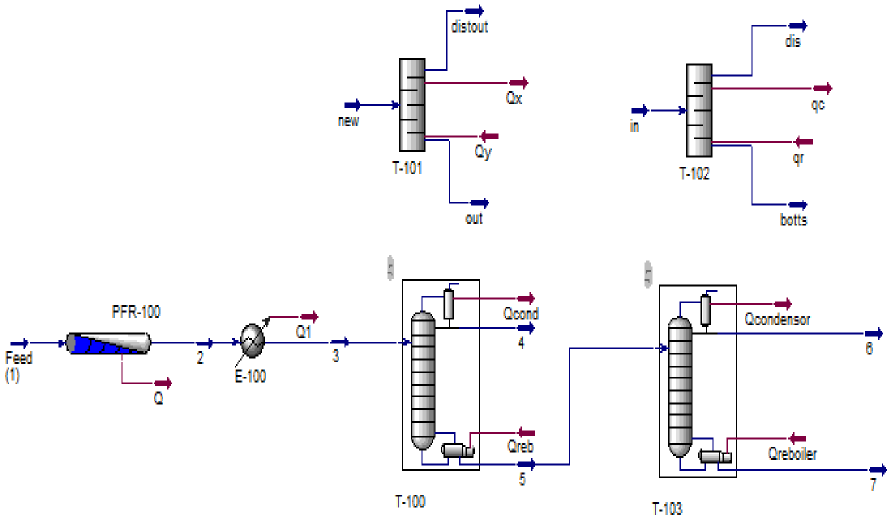


Name	5 @COL2	6 @COL2	7 @COL2
Vapour	0.0000	0.0000	0.0000
Temperature [C]	70.67	31.54	124.7
Pressure [kPa]	1186	482.5	551.5
Molar Flow [kgmole/h]	388.2	371.5	16.63
Mass Flow [kg/h]	2.482e+004	2.323e+004	1590
Std Ideal Liq Vol Flow [m3/h]	26.55	25.25	1.299
Molar Enthalpy [kJ/kgmole]	1.214e+004	1.525e+004	-1.361e+005
Molar Entropy [kJ/kgmole-C]	54.57	37.46	169.7
Heat Flow [kJ/h]	4.713e+006	5.666e+006	-2.263e+006

☑ Update Outlets ☐ Ignored

10. After simulating all the equipment that are a part of our process, the overall process is shown as below.

Figure 41: Hysys PFR



CHAPTER 8

INSTRUMENTATION AND PROCESS CONTROL

Instrumentation is the basic and technologically efficient way of controlling industrial processes. It uses microprocessors and sensors to control the process conditions. Some parameters than can be studied with sensors are level, flow temperature and pressure.

Instrumentation is very important for a safe process. Explosive events may be caused due to flow of excessive fuel or excess air. Thus, this flow has to be continuously monitored and controlled. This can be done by instrumentation. It establishes conditions that are essential for process optimization. In this way production can be maximized by reducing the losses.

8.1 Types of Control Systems

There are two basic types of control systems in industry;

1. Open Loop Control System
2. Closed Loop Control System

8.1.1 Open Loop Control System

An open loop controller is a very simple system. It sends the input signal to the control element as a result of which output is produced. Such a system does not depend upon the output in any way rather it depends upon the input signal only.

Figure 42: Open Loop Control

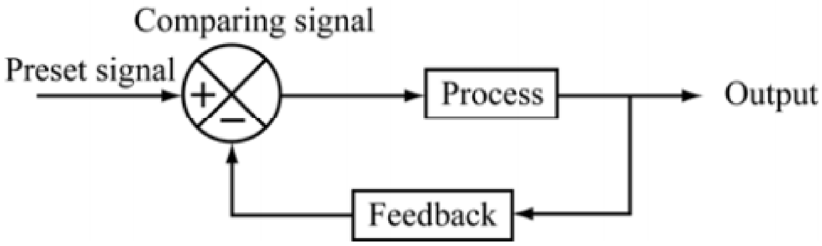
Example of such system can be taken as an electric fan. When we turn on the button of the fan, we are providing an input signal. This signal is sent to the control element as a result of which output is produced that is the spinning of the fan. The speed with which the fan is rotating does not alter the input signal in the future. Hence it is an example of an open loop system.

The open loop system is very basic and cannot make decisions on its own on the basis of the output. As a result, this system cannot be incorporated into an automatic system. Sometimes it may even require continuous monitoring. Due to these reasons, it is not desirable to be used in industry.

8.1.2 Closed Loop System

The closed loop system uses the output signal to attain a certain set point in the input value. This type of system is called Feedback mechanisms. Closed loop system is always equipped with a signal that continuously monitors the output signal to compare it with the input signal. It modifies the input signal and brings it to the desired set point.

Figure 43: Closed Loop Control



Closed loop systems are more automatic in nature. Modern system and appliances are now equipped with them in place of open loop systems due to their advancement and easy operations. There are three types of feedback mechanisms used that are;

1. Proportional Controller
2. Proportional Integral Controller
3. Proportional Integral Derivative Controller

8.1.2.1 Proportional Controller

A proportional controller studies the output signal and modifies the input signal proportional to the difference between the actual value and the desired value. These controllers can be used when the difference between deviation and set point is not very large and when the deviation is not sudden. These controllers help reduce the steady state error and make the system stable. However, the disadvantages of these systems are that offset is obtained in proportional controller systems.

8.1.2.2 Proportional Integral Controller

Proportional Integral controller is the combination of Proportional and Integral controller. Integral controller takes the integral of the error signal and adds it into the input signal. This type of controller decreases the stability of the input. It also reduces the steady state error in the input signal drastically. Due to this characteristic they are commonly used in industry.

8.1.2.3 Proportional Integral Derivative Control

The combination of proportional, integral and derivative control is used in most applications due to their fast reaction to error, accurate set point control and quick warm up time. They are mostly used to control as temperature controllers. They are very easy to implement and feasible to use. In a system with constant perimeters and limited knowledge of the process, PID controllers are often not recommended.

8.2 Instrumentation and Process Control Inside the Furnace

The furnace is operated at a very high temperature. Any change in temperature from the set point can cause serious damage to the plant and the people working around. To avoid that two major controllers are incorporated that are;

1. Temperature Controller
2. Flow Controllers

8.2.1 Temperature Controller

The temperature inside the furnace is a very sensitive perimeter. Decreasing the temperature below the requirements decreases the reaction rate and production is reduced. Increasing the temperature increases the formation of coke. Very high temperatures are also dangerous to operate and can even be life threatening. The most important temperature that has to be stable inside the furnace is the temperature of the radiation section. This is because this temperature decides the heat that would be transferred to the convection section. Also, major conversion into VCM takes place in the radiation section. In order to control the temperature at a certain set point, a sensor and controller has to be installed inside the radiation section. This is not feasible because the temperature inside the radiation section is very high for sensors to bear. Thus, in order to cater this problem, a control system is installed above the radiation section, just at the beginning of the convection section. A PID controller is used to decrease the error to the minimum and bring the temperature at the set point in case of an offset. PIDs are most effective when controlling the temperature. Here the control variable is the temperature above the radiation section while the manipulated variable is the flow valve of the inlet fuel which heats the system if temperature decreases.

8.2.2 Combustion Control

The process of combustion is controlled inside the furnace burner. An optimum flow of fuel and air is interacted so that they produce less carbon monoxide and more carbon dioxide. The fuel flow is managed at a particular point with the help of the flow valve which uses a proportional integral controller. The outcome of the flow generates an error signal which is modified to a given set point and then used as a reference for the input signal.

The combustion control and sensor is installed above the radiation section. There are two reasons of installing the sensor there. Firstly, the high temperature of the radiation section can damage the sensor; hence it has to be installed above it. Secondly, this particular location for the installation of sensor is important because up till this point, a lot of combustion has taken place. The amounts of CO in this section are the indication of how much fuel to air ratio need to be altered for an ideal combustion. Here the control variable is the concentration of carbon monoxide and carbon dioxide above the radiation section while the manipulated variable is the opening valve of the fuel and air. A Summarized table showing all the controls inside the furnace is shown as follows;

(Cont'd)

Table 15: Specifications of Controllers

Equipment	**Name of Controller**	**Type of Controller**	**Manipulated Variable**	**Control Variable**
Furnace	TC	PID	Fuel Flow Rate	Temperature
	FC	PI	Fuel Input Valve Opening	CO_2 Concentration
	FC	PI	Air Input Valve	CO Concentration

CHAPTER 9

ECONOMIC ANALYSIS

9.1 Introduction

Costing is of utmost importance in engineering projects. It gives an initial very rough estimate that helps choose between the various possible designs proposed in engineering projects. The costing thus helps to decide which design or alternative to go for based on economic analysis or economic projections.

The field of chemical engineering is based majorly on production cost effectively. It aims to reduce the productions costs by optimizing the processes such that lesser capital is spent as the running cost and more revenue is generated out of it and the yield and conversion of the processes also increases. This can properly be evaluated my looking at cost estimates and the projection of certain projects.

9.2 Capital Cost of Engineering Projects

This capital cost of engineering projects depends on accuracy of the available designs for the project, the time utilized on making the cost projects and estimates and the accuracy of the data regarding the cost of objects available.

It further has these 3 types based on the above-mentioned cases:

9.2.1 Preliminary Estimates

These estimates are usually the approximate estimates. The details of costs and the time allocated for it is usually lesser. Its purpose is mostly to make the cost estimates for the initial selection of an alternative between several project options. Its accuracy is usually having a tolerance of 30%.

9.2.2 Authorization Estimates

These estimates are also known as budgeting estimates. These estimates include greater time allocation and a more accurate costing is done. This is done with the intent of getting a budget approval. It incorporates largely the contingency costs and some order cancellation costs as well just in case an order gets delayed so that the firm may be able to cancel its order and order from elsewhere to stop from any delays in project. The accuracy of these budgeting estimates usually allows a tolerance of 5% in its estimates.

9.2.3 Detailed Estimates

These estimates are usually based on final quotations obtained from the vendors. These estimates are mostly based on almost completed designs of the project and finalized vendor quotations. It contains a detailed breakdown of the raw material, contingency, construction and commissioning cost. These estimates usually have a tolerance of 5-10% in their values.

9.2.4 Project Cost Estimates

From here on our project cost estimates will be discussed. As our project contains the design changes of the burners used inside the furnace, hence we will be estimating all the capital investments and savings related to it.

Firstly, the production increase due to our project will be considered. This production increase is shown in the table below:

Table 16: Production Increase

Production Increase	
Production per month with coke (kg)	13,994,000
Production per month w/o 70% coke (kg)	14,325,000
Increase in production per month (kg)	33,084
Increase in production per month (Ton)	33

This table shows that due to the coking the production per month of VCM was lesser but as the coking has been reduced to about 70% the production capacity will also increase. Through this increase we will get a production increase of about 33,084 kgs which translate to 33 tons.

This production increase will translate into 397 tons of production increase per year as well. Hence greater the production increase greater will be the revenue increased for the said operations.

This revenue increase is shown in the table below:

Table 17: Revenue Increase

Revenue Increase	
Price of VCM per ton in 2011 ($)	900
Price of VCM per ton in 2020 with 14% inflation ($)	1026
Increase in VCM production (ton)	33
Increase in Revenue ($)	33858

In the above table it is shown that first of all the market price of VCM in the year 2011 is taken after which the inflation rate till the year 2020 was checked. His came out to be 14% and we incorporated the inflation factor the VCM price per ton came out to be $ 1026.

When considering the increase in the production of VCM, which is 33 tons, we find the total revenue increase by multiplying the tons increased with the price of VCM per ton. This came out to be $ 33,858.

Moreover, we also have another cost saving of the reduction in fuel consumption:

Table 18: Fuel Cost Reduction

Fuel Cost Reduction	
Cost of fuel with coke ($/Month)	104017.8
Cost of fuel w/o coke ($/Month)	102648.6
Difference in fuel costs ($)	1369.2

The fuel consumption was greater in the routine process as there was greater coke accumulation. This layer of coke formed inside the furnace coils formed an insulation layer hence it consumed more fuel to transfer heat across it and maintain the same process temperature of 504.4°C inside the furnace.

Since with the modification we claim to reduce the coking up to 70%, we also assume that the throughput of the plant will also increase. But even after increasing the throughput our fuel costs are still lesser than before and in total the new modification gives us a cost saving of about $ 1369.

9.3 Equipment Costing

The equipment that we have designed is a new design proposed. This design is not present already in the market so the limitation for us would be that there is not a proper source that can provide us with a quote regarding out equipment.

A detailed literature review was done which involved studying different design parameters that helped us make a reasonable estimate of the burners. These were:

- The same duty burners available on the internet were checked to get an idea of their pricing.
- The burners having the material of construction of stainless steel were majorly kept under consideration.
- The duties of the burner having the same duty of one of the nozzles of the tri nozzle burners were also considered.

Given all of these factors following is the costing for these burners:

Table 19: Burner Costing

Burner Costing	
Burner cost ($)	3200
Needed burners	24
Total burner cost ($)	76800

This table shown above gives us the purchase cost of burners but we will be needing the cost of the purchasing, equipment installation and its commissioning and labor fee. This is shown in the following table:

Table 20: Major Equipments Used and Total Purchase Cost

Sr.	**Item**	**Fluid Processing**
1	**Major Equipment, Total Purchase Cost**	**PCE**
	f1 Equipment erection	0.4
	f2 Piping	-
	f3 Instrumentation	0.2
	f4 Electrical	0.1
	f5 Buildings, process	-
	f6 Utilities	-
	f7 Storages	-
	f8 Site development	-
	f9 Ancillary buildings	-
2	**Total physical plant cost (PPC)** **PPC = PCE (1 + f1 + f2 + …….f9)**	**115200**
	f10 Design and Engineering	0.3
	f11 Contractor's fee	0.05
	f12 Contingency	0.1
3	**Fixed Capital = PPC (1 + f10 +…..f12)**	167040

Furthermore, the return on investment is an important aspect of the costing which is shown in detail in the following table:

(Cont'd)

Table 21: Return on Investment

Return on Investment	
Fixed Capital Cost ($)	167040
Revenue increase per month ($)	33858
Revenue increase per year ($)	406296
Revenue growth in 5 months ($)	167258.52

This table very clearly shows that with the additional revenue made through the production increase we will pay our capital investment back in a period of 5 months only.

CHAPTER 10

HAZOP ANALYSIS

HAZOP stands for Hazard and operability study. HAZOP Analysis finds out the possible deviations that can occur from the original process design and cause risks to the environment around. Once these possible deviations are pointed out, we can also study what their consequences would be and how to overcome in the emergency situation.

10.1 Procedure

1. Study the P&ID and divide the plant into sections (e.g. Furnace, distillation column etc.)
2. Opt for a study node
3. Figure out the intent of the study
4. Select a process parameter
5. Apply a guide-word
6. Find out the cause
7. Evaluate problems
8. Actions
9. Write down the information.
10. Repeat the procedure from step 2 on the next section.

To proceed with the HAZOP and risk assessment we need to first study the normal plant operation which has to be studied by the following procedures;

1. Normal mode of operation.
2. Reduced throughput operation.
3. Startup procedure.
4. Shut down procedure.
5. Shut down during emergency.

6. Commissioning.
7. Operating modes during special conditions.

Once all these procedures have been studied, only then can we apply the risk assessments in case of deviations.

10.2 Guide Words

Small guide words are used in industry to create the imagination of what would occur if the process deviates from its original conditions. Most commonly used words are no, less, more, as well, other than etc. These short words give information about the effects of deviations at a single glance thus make it easier to do the HAZOP Analysis. Some of these words and their meaning are as follows;

Table 22: Guide Words

Guide Word	Meaning
No	Negation of the proposed intent
Low	Quantifiable decrease
High	Quantifiable increase
Part of	Qualitative decrease
As well as	Qualitative decrease
Other than	Complete substitution

10.3 HAZOP on Different Processes

10.3.1 HAZOP on Furnace

Intention: Converts EDC to VCM and HCl at 510^{o}C and 1861kPa

Line: 1

Intention: Transfers Process feed to the reaction tubes inside the furnace

Table 23: HAZOP on Furnace (Line 1)

Guide Word	Deviation	Cause	Consequence	Action
Low	Feed Flow	• Low discharge flow towards furnace • Trip on high amps • Furnace tube coking • High quench pressure	• Disturb cracking/ conversion rate • Damage to tubes • Furnace trip on Low flow security • Decreases furnace efficiency	• Check pumps discharge pressure, for its efficiency. • Check recycle valve control valve opening and bypass line for any passing issue. • Immediately start stand by pump for hot startup of furnace • Check conversion rate, reduce cracking rate if possible
High	Feed Flow	• Pressure drop across the tube is low • Overload of purification system	• Disturb cracking/ conversion rate • Damage to tubes • Furnace trip on High flow security • Decreases furnace efficiency	• Adjust the load and outlet temperatures keeping the cracking rate • Take the feed valve on manual • Check and verify DCS and field valve opening • Prepare the furnace for shutdown and decoking

Part Of	Feed Pressure	- Discharge pressure deviates - Low/ high flow from inlet valve - Incorrect set point pressure	- Outlet temperature controlling issue - Furnace flow control issue - Conversion rate disturbs	- Check the amps of the pump from the field - Check the set point pressure on PIC controller - Verify the DCS reading from the local field PG

Line: 2

Intention: Transfer furnace products to the quench column for cooling

Table 24: HAZOP on Furnace (Line 2)

Guide Word	Deviation	Cause	Consequence	Action
Part Of	Exit temperature	- Natural gas high or low pressure - Burner extinguished - High or low EDC flow to furnace	- Disturbed crack rate - Formation of by products - Coke formation in the tubes - Unconverted EDC	- Verify the DCS pressure from field - Try to balance the hydrogen fuel flow - Adjust the load as per the outlet temperature - Check burners' condition and light up if in case extinguished. - Keeping the outlet temperature as per the

				crack rate requirements adjust the NG flow

Line: 3

Intention: Air take up and proper fuel combustion for furnace heating.

Table 25: HAZOP on Furnace (Line 3)

Guide Word	Deviation	Cause	Consequence	Action
Low	Oxygen take up	• Malfunctioning of Damper • Improper burning • Fuel pressure too high • Tube Rupture	• Increased fuel loses • Lesser heat transfer	• Confirm damper opening in field. • Check the draft of the furnace • Call and verify the damper through instrumentation • Check burner air register opening. • Confirm damper opening from DCS, may be low opening • Choked burners pulled and repaired • Adjust the loads as per outlet temperature • Check NG pressure on DCS

High	Oxygen take up	• Malfunctioning of Damper • Improper burning. • Fuel flow too low • Furnace peep hole opening or any leakage from Furnace shell	• Fuel Losses. • Furnace temp may decrease. • Due high (-ve) draft fire may extinguish	• Confirm damper opening in field. May be too high. • Adjust air register. • Check burner air register opening. • Confirm damper opening from DCS, may be high opening • Close all peep holes of furnace. • Adjust air to burner. Inspect Furnace shell for possible leakages. Verify by cross matching O2 and draft.

SUMMARY

The project was done in three phases;

1. Literature review and data collection.
2. Design, simulation and economic analysis
3. Thesis.

Phase 1

During the phase 1 of our project, we gathered all the necessary data about furnace design, operation of VCM plant and ways to prevent coking. For this we studied a number of research papers online and contacted the industry to provide us the required data. The IPO office was a great help during this process.

Phase 2

After we had studied the design used presently in Engro Polymers, we selected the modification that best suited them and which has the minimum capital and running cost. We designed the burner and furnace and simulated the area under study on Aspen HYSIS. All the calculations by the software were consistent with our manual calculations.

Phase 3

During phase 3, we compiled all the information the we got from the literature review, data obtained from the industry and our calculations to write a thesis about the decoking process and how the plant can be made more efficient by using the burner modification we suggest.

CONCLUSION

The solution that we present is replacing the single nozzle needle flame burners with multi nozzle inclined flame burners. The advantage of it would be that instead of impinging the reaction tubes at one particular point and developing a highly non uniform flux, multi nozzle inclined flame burners would have interacting flames which would form a radial uniform heat flux thus eliminating any hotspots and would reduce maximum coking. The burner comprises of three nozzles inclined at an angle of $\mathbf{8 \pm 1^0}$towards each other. Installation of these burners in place of needle burners is expected to decrease the coking by 70%. This would increase the production by 33 ton per month and reduce the shutdown coking time from 12 times a year to only 4 times a year.

REFERENCES

[1] Hadiseh Karimi .Bolaji Olayiwola ,Hany Farag ,Kimberley B. McAuley "Modelling coke formation in an industrial ethane-cracking furnace for ethylene production." (2009)

[2] Li, C. ;Hu, G. ;Zhong,W. ;Hui, C.; Qian, F.; Comprehensive Simulation and Optimization of an Ethylene Dichloride Cracker Based on the 1-D model Lobo–Evans Methodand Computational Fluid Dynamics. Industrial & Engineering Chemistry Research. 52 (49(2012).

[3] Susana Broeiro Bento, "Ethylene Dichloride Cracker Modelling and State Estimation" (2017).

[4] C. Li, G. Hu, W. Zhong, W. Du, and F. Qian. Coke Deposition Influence Based on a Run Length Simulation of a 1,2–Dichloroethane Cracker. Ind. Eng. Chem. Res., 52:17501– 17516, 2013.

[5] K. E. Howlett. The pyrolysis if 1,2– dichloroethane. Transactions of the Faraday society, 48:25–34, 1952