SAFETY IN NAPHTHA CRACKER PLANT

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Safety and Hazards Management)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"SAFETY IN NAPHTHA CRACKER PLANT"**, in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Safety and Hazards Management, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand (India), is an authentic record of my own work carried out during the period from June 2010 to June 2011 under supervision of **Dr. I. D. Mall**, Professor & Head, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter, embodied in this dissertation for the award of any other degree or diploma.

Date: 18-06-11

Place: Roorkee

VADISELA SURESH KUMAR

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

Naphtha cracking process is used to convert complex hydrocarbons to simple hydrocarbons like ethylene, propylene, etc. by using steam as heating medium. Pyrolysis or steam cracking is the primary process utilized to manufacture olefins from large hydrocarbon molecules. This gas-phase reaction takes place in metal alloy tubes within a fired furnace. Lower olefins (ethylene and propylene) are industrially produced by the steam cracking of hydrocarbons. The steam cracking operation involves heating the hydrocarbons in radiant coils in the presence of steam in a furnace. The heat is transferred to the coils by radiation, and the coils are made of high alloy materials capable of withstanding the high temperatures above 800 °C in the bulk fluid. To avoid undesired side reactions, which would lower the selectivity of ethylene in the process, the reactants must be cooled down as quickly as possible. This step is carried out in transfer line exchangers immediately after the radiant cracking zone. The products are cooled down and separated to yield olefins and other co-products.

The present dissertation work has been conducted in Naphtha Cracker plant, at Panipat where ethylene and propylene are the main products. The various hazards that are possible to take place in the naphtha cracker plant have been identified during the study and various preventive measures have been suggested.

Hazard and operability (HAZOP) study is the most widely used and preferred approach in the chemical plant to accomplish hazard assessment qualitatively and quantitatively. The HAZOP study requires the examining the process P&ID systematically, identifying every conceivable deviation from design intent in the plant using a 'guideword' approach; determining all possible abnormal causes and the adverse consequences of that deviation. Deviation or changes in the process parameters (such as temperature, pressures and levels of chemicals, etc.) of naphtha cracker plant may lead to serious accident and undesirable product since the product quality is sensitive; therefore qualitative and manual HAZOP study has been carried out as a dissertation work for better performance of the process system as well as safety.

The present HAZOP report shows the possible abnormal causes and consequences of hazards in the plant. A brief result discussion is also performed based on the present HAZOP study report and also preventive corrective measures and recommendation has been made to improve safety performance of the process and the production line as well.

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CHAPTER 1 INTRODUCTION

Petrochemicals have become an indispensable part of our life. Petrochemical Industries started growing since Second World War and today the Petrochemical products have taken an important role in our daily life. The per capita consumption of petrochemical products in India is around 4 kg against the world average of 20 kg.Light olefins and diolefins such as ethylene, propylene, butenes and butadiene are considered as the backbone of the petrochemical industry (Khan et al., 1997). They are providing key feedstock to chemical industry for making of thousands of different chemicals with people usually encounter as end or customer products. It is closely linked with socio-economic needs of people which include packaging to agriculture, automobiles to telecommunication, construction to home appliances, health care to personnel care, pesticides to fertilizers, textile to tyre cord, chemicals to dyes, pharmaceuticals and explosives. Ethylene itself forms a basic building block for a large number of petrochemicals and is quoted as king of chemicals (Mall, 2007). The petrochemical industry is the large segment within the US $1600 billion global chemical industry having as whooping share of around 40%.

Petrochemical industry is concerned with the manufacture of various products and comprises multiple processing units at one specific location adopting different technologies, equipments, unit processes and unit operations from the basic feed stock. It leads to generations of a wide spectrum of emission of air pollutants, mainly of volatile organic compounds. Some of these pollutants are toxic and even carcinogenic, while others are responsible for damage to materials. Some pollutants also have potential for photochemical oxidant creation, global warming, ozone depletion or malodour creation. Besides, volatile organic compounds, there is generation of various types of inorganic hazardous air pollutants and conventional air pollutants.

Olefins (ethylene and propylene) are industrially produced by the steam cracking of hydrocarbons. This technology has been around for as long as the early 1940s when the first commercial plant came into operation (Cai et al., 2002). The steam used in this process is basically an inert gas and it serves the purpose to increase olefin selectivity and reduce coke formation by reducing the naphtha partial pressure (Salari et al., 2010). The steam cracking operation involves heating the hydrocarbon (which could be ethane, propane, butane, naphtha or gas oil) in radiant coils in the presence of steam in a furnace. The heat is transferred to the coils by radiation, and the coils are made of high alloy materials capable of withstanding the high

temperatures above 800°C in the bulk fluid. To avoid undesired side reactions, which would lower the selectivity of ethylene in the process, the reactants must be cooled down as quickly as possible. This step is carried out in transfer line exchangers (TLEs) immediately after the radiant cracking zone. The products are cooled down and separated to yield olefins and other co-products. The heavier the feedstock the more the co-products.

1.1 NAPHTHA CRACKER PLANT

In Naphtha Cracker Plant, low aromatic Naphtha cracks into lighter hydrocarbons in cracking heaters, which are then individually separated by fractionation to produce mainly polymer grade ethylene and polymer grade propylene. It also produces Hydrogen, Methane off gas, Pyrolysis Fuel Oil (PFO) and other products like raw C_4 mix, raw Pyrolysis Gasoline that are further processed in associated Units. Ethane and propane, produced in the process, are recycled back to cracking heater. The raw C_4 mix from naphtha cracker plant is processed in Butadiene Extraction Unit (BDEU) to extract Butadiene product. The raffinate from BDEU (or raw C_4 mix from naphtha cracker plant when BDEU is not operating) is hydrogenated in C_4 Hydrogenation Unit and hydrogenated C_4 is recycled back to naphtha cracking heater. The raw pyrolysis gasoline is hydrogenated in two stages in Pyrolysis Gasoline Hydrogenation Unit (PGHU). The hydrogenated C5s, separated in this unit, are recycled back to naphtha cracking heater. Hydrogenated C6-C8 cut is routed to BEU to extract Benzene. Partially hydrogenated C9+ product is routed to refinery storage. In BEU, Benzene is extracted from C_6-C_8 cut by extractive distillation and routed to storage tank.

The naphtha cracker is designed to produce polymer grade ethylene and polymer grade propylene by thermal cracking of naphtha and hydrogenated C4/C5/C6 recycle streams from C4 hydrogenation, pyrolysis gasoline hydrogenation and benzene extraction units respectively. Ethane and propane are recycled to extinction.

A steam cracker is comprised of the following three sections: Pyrolysis, Primary fractionation/compression and Product recovery/separation.

1.1.1 PYROLYSIS SECTION

This is the heart of a steam cracker. Naphtha first enters the convection section of a pyrolysis furnace, where a series of heat exchangers are located and it is preheated to 650 ^{0}C. Then, naphtha is vaporized with superheated steam and is passed into long (12–25 m), narrow

(25– 125 mm) tubes, which are made of chromium nickel alloys. Pyrolysis takes place mainly in the radiant section of the furnace, where tubes are externally heated to 750–900 ^{0}C (up to 1100 ^{0}C) by fuel oil or gas fired burners. Depending on the severity, naphtha is cracked into smaller molecules via a free-radical mechanism in the absence of catalysts. The free radicals lead to the formation of light olefins in the gaseous state. After leaving the furnace, the hot gas mixture is subsequently quenched in the transfer line exchangers (TLEs) to 550–650 ^{0}C, or sometimes lower to 400 ^{0}C. TLE will then be followed by a series of heat exchangers and temperatures can drop down to 300 ^{0}C. These heat transfer activities avoid degradation by secondary reactions and at the same time generate high pressure steam for driving compressors, etc. However, heat exchangers are prone to fouling and therefore need both scheduled and unscheduled shutdowns.

1.1.2 PRIMARY FRACTIONATION/COMPRESSION

Primary fractionation applies to naphtha and gas oil feed only. In the primary fractionation section, gasoline and fuel oil streams (rich in aromatics) are condensed and fractionated. While this liquid fraction is extracted, the gaseous fraction is desuperheated in the quench tower by a circulating oil or water stream. The gaseous fraction is then passed through four or five stages of gas compression with temperatures at approximately 15–100 ^{0}C, then cooling and finally cleanup to remove acid gases, carbon dioxide and water. Most of the dilution steam is condensed, recovered and recycled. Products of this section are fuel oil and BTX, or aromatic gasoline which contains benzene, toluene and xylene. A common problem with compression is fouling in the cracked gas compressors and after-coolers. The build-up of polymers on the rotor and other internals results in energy losses as well as mechanical problems. Wash oil and water are used to reduce fouling.

1.1.3 PRODUCT RECOVERY/FRACTIONATION

This is essentially a separation process through distillation, refrigeration and extraction. Equipment includes chilling trains and fractionation towers, which include refrigeration, de-methanizer, de-ethanizer and others. De-methanization requires very low temperatures; undesired acetylene is removed through catalytic hydrogenation or extractive distillation. Similarly, C_3 compounds, or propane and propylene, are re-boiled with quench water at approximately 80 ^{0}C and separated in the C_3 splitter. Ethane and propane are recycled as

feedstock. Methane and hydrogen are separated at cryogenic temperatures. As fuel grade by-products, they are often used as fuel gas in the pyrolysis process, but they can also be exported. Butadiene, other C_4 compounds and aromatic gasoline are separated in the end. The total product yields from naphtha cracking differ depending on the paraffin and aromatic content of the naphtha and on the severities.

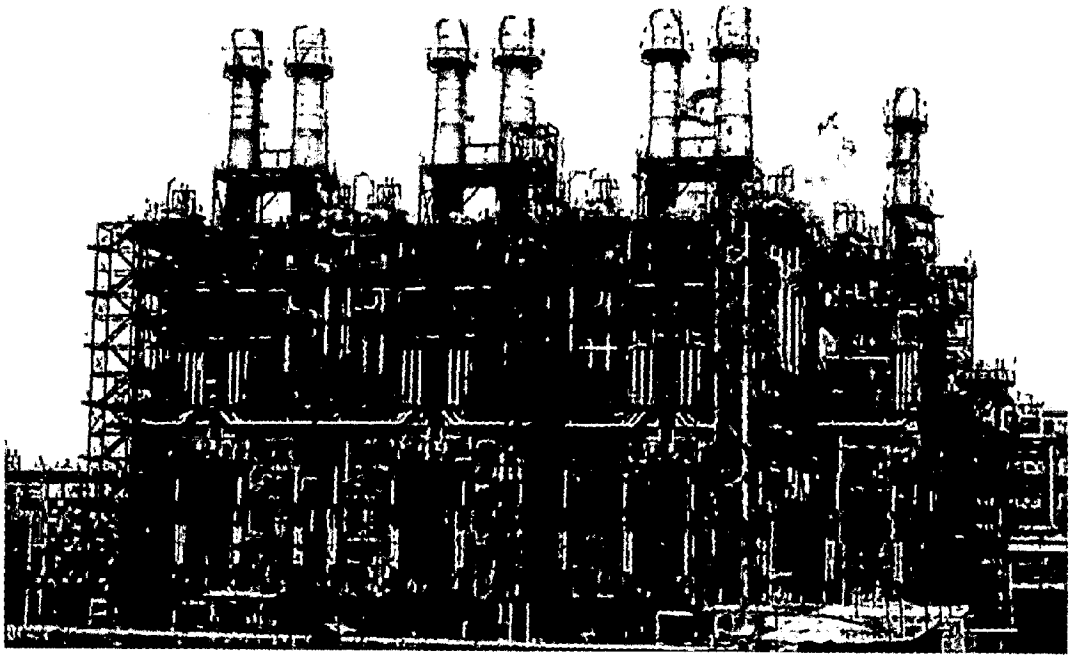

Figure 1.1 NAPHTHA CRACKER

The Naphtha Cracker Plant consists of following processing areas:

- Cracking Heaters Feed System
- Pyrolysis Module
- Charge Gas Oil Quenching
- Gasoline Fractionation, Pyrolysis Gas Oil and Pyrolysis Fuel Oil Stripping
- Charge Gas Water Quenching
- Process Water Stripping and Dilution Steam Generation
- Charge Gas Compression, Gasoline Stripping, Condensate Stripping and Condensate Stripper Bottoms Drying

- Acid Gas Removal by Caustic Wash
- Spent Caustic Pre-treatment by Gasoline Wash
- Charge Gas Drying and Dryer Regeneration Facilities
- Cracked Gas Chilling
- Demethanization and Methane Refrigeration
- Methanation and Hydrogen Purification
- Deethanization, Acetylene Hydrogenation, and Ethylene Drying
- Ethylene Fractionation
- Ethylene Product System
- Depropanization
- MAPD Hydrogenation and Propylene Fractionation
- Debutanization
- C4 Hydrogenation
- Pyrolysis Gasoline Hydrogenation
- Propylene and Ethylene Refrigeration

The Naphtha Cracker Unit is designed to produce the following by-products:

- Hydrogen
- Methane off gas
- Raw mixed C_4
- C_4 LPG
- Hydrogenated C_6-C_8
- Partially hydrogenated C9+ product
- Pyrolysis fuel oil (combined PGO + PFO)

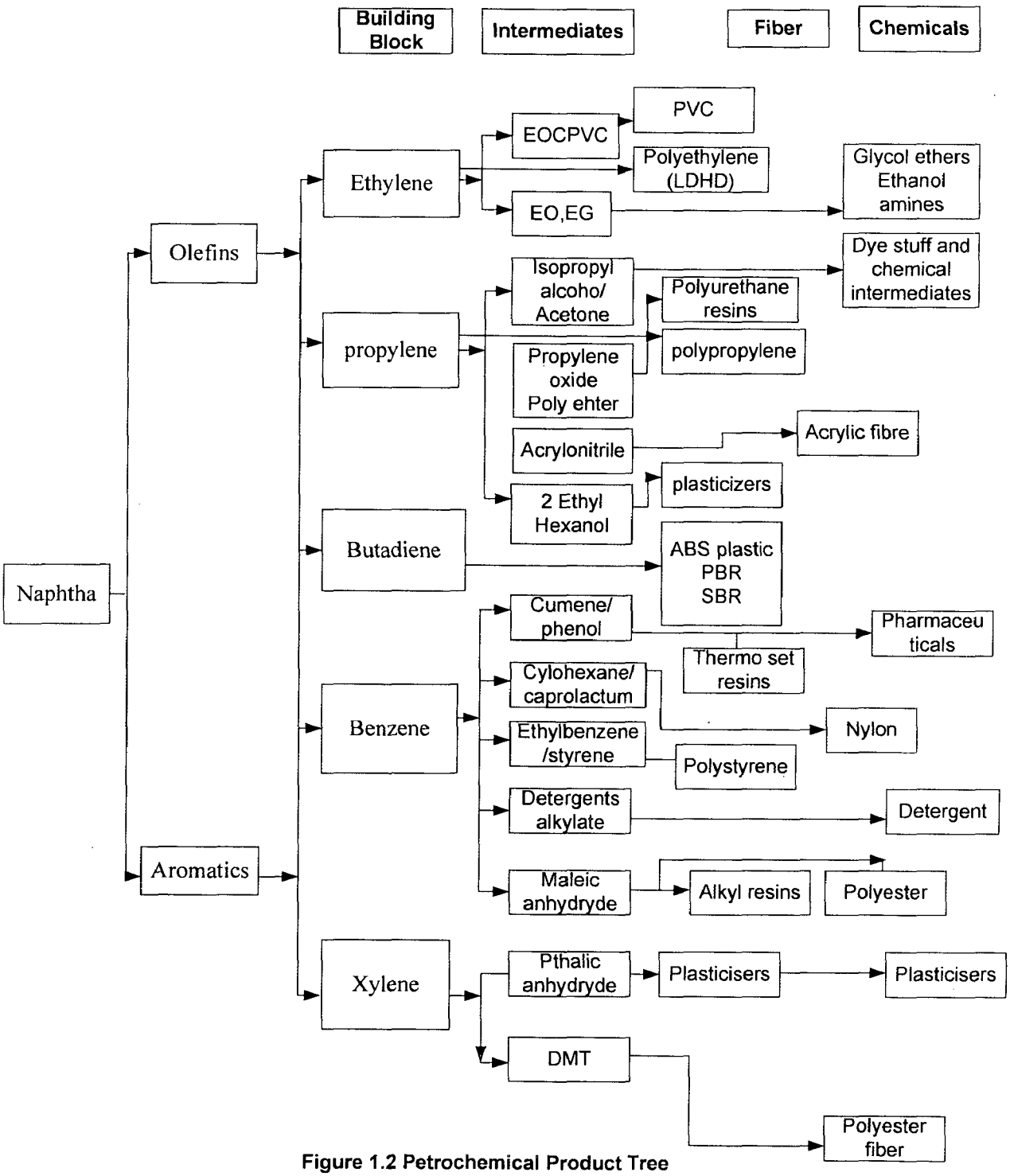

Figure 1.2 Petrochemical Product Tree

1.2 OBJECTIVES

1. To study the cracking of naphtha by steam cracking process in Naphtha Cracker Plant.
2. To study the Hazards and Safety measures during the Naphtha cracking process.
3. To present a comprehensive and literature review about HAZOP study.
4. To carry out HAZOP study in Naphtha Cracker plant.
5. To suggest the preventive corrective action based on the HAZOP study result.
6. To give future recommendations based on HAZOP study report.

CHAPTER 2 LITERATURE REVIEW

This section gives the literature review of about the naphtha cracker plant, its process of operation, hazards taking place during the process and HAZOP study in the naphtha cracker plant.

2.1 NAPHTHA CRACKER PLANT

Thermal cracking of naphtha and other hydrocarbons is one of the most important processes in the manufacture of olefins and aromatics, the building blocks of the chemical and petrochemical industries. Hydrocarbon feed stock mixed with the process steam are introduced in to tubular reactors (cracking coils) with short residence time and high temperatures. The process steam is basically an inert gas and it serves the purpose to increase olefin selectivity and to reduce coke formation by reducing the hydrocarbon partial pressure (Niaei et al., 2008).

A steam cracker is comprised of the following three sections:

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- Product recovery/separation

2.1.1 PYROLYSIS SECTION

This is the heart of a steam cracker. Naphtha first enters the convection section of a pyrolysis furnace, where a series of heat exchangers are located and it is preheated to 650 ^{0}C. Then, naphtha is vaporized with superheated steam and is passed into long (12–25 m), narrow (25– 125 mm) tubes, which are made of chromium nickel alloys. Pyrolysis takes place mainly in the radiant section of the furnace, where tubes are externally heated to 750–900 ^{0}C (up to 1100 ^{0}C) by fuel oil or gas fired burners. Depending on the severity, naphtha is cracked into smaller molecules via a free-radical mechanism in the absence of catalysts. The free radicals lead to the formation of light olefins in the gaseous state. After leaving the furnace, the hot gas mixture is subsequently quenched in the transfer line exchangers (TLE) to 550–650 ^{0}C, or sometimes lower to 400 ^{0}C. TLE will then be followed by a series of heat exchangers and temperatures can drop down to 300 ^{0}C. These heat transfer activities avoid degradation by secondary reactions and at the same time generate high pressure steam for driving compressors, etc. However, heat exchangers are prone to fouling and therefore need both scheduled and unscheduled shutdowns.

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2.2 COKE FORMATION

Coke formation and equipment fouling in steam cracking furnaces in the ethylene industry still remain a major operation problem (Cai et al 2010).The amount of coke deposited on reactor walls depends on the type of feed, the operating conditions and the composition of reactor tube alloy. Coke accumulation on the inner surface of the cracking coils and on the TLX hampers the heat transfer from the furnace to the process gas and increase the pressure drop over

the coil. As a result of coke formation, thermal cracking furnaces have to be removed from service regularly for decoking, thus lowering the on-stream time and therefore the production capacity. Decoking is carried out, by using a mixture of steam and air to burn out the coke. This process is very undesirable to the plant owner because of the following reasons: frequent decoke means lost ethylene production, high operating and maintenance costs and shortened life of the coil because of the constant thermal cycling of the coil. However, there is an incentive for the operator to try to reduce coke formation or deposition in the minimum level (Niaei et al 2008). The development and use of additives appears to be the most effective and practical method in the coke formation reduction (Salari et al 2010). Significant reduction in the coking rate was achieved by adding benzyl diethyl phosphite to the feed. Sulphur addition is believed to minimize the overall coking rate by suppressing the catalytic activity of the metal wall. The reduction in the rate of coke formation during naphtha pyrolysis is due to the addition of Dimethyl disulfide (DMDS). This study shows that the rate of coke formation during naphtha pyrolysis can be reduced by using high sulphur content feed. The sulphur present in the feed can reduce the rate of coking in two ways, it can either react with the metal surface to form metal sulfides, thus passivating the reactor wall, or it can take part in the homogeneous gas phase free radical reaction (Salari et al., 2010).

2.3 PYROLYSIS FURNACE

An industrial pyrolysis furnace is a complicated piece of equipment that functions as both a reactor and high-pressure steam generator. The pyrolysis reactions proceeds in tubular coils made of Cr/Ni alloys. These coils are hung vertically in a firebox. Depending of furnace design, there may be between 16-128 coils per firebox. Burners are arranged on the walls and on the floor of the firebox for indirect firing. This section is called the radiant section because the radiant heat is recovered. At the end of the pyrolysis, the reaction needs to be quenched rapidly to avoid further decomposition of the desired olefins. This is achieved by either indirect cooling using a quench exchanger or direct cooling by injecting quench oil into the gas effluent. The heat carried by the flue gas is recovered at the convection section of the furnace. This section consists of a series of "tube banks" where the heat is recovered for superheating steam, preheating the hydrocarbon feed, boiler feed water and dilution steam.

The coils in pyrolysis furnaces used to produce ethylene, propylene and other valuable hydrocarbons are subjected to high temperatures and very hostile operating conditions. Nickel

and iron present on the metal surface are believed to catalyze the production of coke and especially filamentous coke, through the formation of metal carbides. Coke formation in naphtha cracking reactors decreased the product yields, heat transfer and reactor life. Although the time and money for decoking operations are increased Metallurgists have known for years that a highly efficient engineering material would result if the high temperature corrosion resistance of aluminium could be combined with the mechanical advantages of steel. Unfortunately, the adding aluminium to the steel melt as an alloying element is difficult. Also, the addition of more than eight atomics percent aluminium to a bulk alloy creates a brittle material at room temperature, which is difficult to use as a structural component. Then much research is based on surface coating to solve these problems. Much research on the formation of coke catalyzed by surfaces is based on attempts to solve these problems. Significantly effort has been expended to identify ways to passivate metal surface under high temperature pyrolysis conditions. The formation of metal oxide layers on alloy is reported to passivate the surface and reduce coking. Effect of run time and temperature on morphology of coke formation in different metal surfaces was studied on the system. Chemical vapour deposition to coating chromium and nickel is used. The authors conducted an experiment in the laboratory for the study of steam cracking and deposition of coke, with an arrangement containing micro pump of water, micro pump of naphtha, preheater of water, preheater of naphtha, electrical furnace, steam cracking reactor, small coupon suspended in the reactor, condenser system for output gases and electrical furnace for control system. Several metal surfaces were used in varying run time and the rate of coke formation was investigated. Amount of coke formation on nickel coated coupons were very high. But chromium coated coupons not also has non catalytic effect but also passivate catalytic activity of iron and nickel. The rate of coke formation on silicon coated coupons during the first hours decreases the catalytic activity of metal wall and other coking mechanisms. The catalyzing intensity of coke deposition decreases in the order Nickel>Chromium>Silicon. The rate of coke formation increased with temperature for nickel and chromium coating. But in silicon coating rate of coking in high temperature reduced significantly. On the aluminized coupons the rate of coke formation during the first hours not also decreases the catalytic activity of metal wall but also decrease the other coking mechanisms. It seems alumina was constructed protects reaction involving iron and nickel. Furthermore, in the first hours operation the coking rate decreased significantly but with aluminum-magnesium coupons coated, the rate of coke formation were

essentially constant entire the operation. Results obtained from zinc plates coated confirm that decoking is taking place during pyrolysis so that increasing temperature, rate of decoking is speeder than rate of coking. The investigations show that the rate of coke deposition during naphtha pyrolysis can be significantly reduced by passivating the surface with a coating of aluminum and aluminum-magnesium, nickel, silicon, chromium and zinc, so that aluminum-magnesium surface is resisted to coking in high temperature. The results obtained from zinc coated show decoking carry out during thermal cracking, so that with increasing run time and temperature rate of decoking was speeder than the rate of coking (Salari et al., 2007).

2.4 ACCIDENTS AND ANALYSIS OF CAUSES AND CONSEQUENCES

The major hazards with which the chemical industry is concerned are fire, explosion and toxic release. Of these three, fire is the most common but explosion is more significant in terms of its damage potential, often leading to fatalities and damage to property. Toxic release has perhaps the greatest potential to kill a large number of people and cause an area to be toxified for several months to several years. Accidents involving hazardous chemicals can be broadly categorized into two major groups: fixed installation accidents and transportation accidents. The fixed installation accidents consider all accidents occurring in industries during different stages of operation, while transportation accidents consider accidents occurring during transportation, loading or unloading of chemicals. Of the 3222 accidents OCCURRED DURING 1926 TO 1997, 54% are fixed installation accidents, 41% are transportation accidents and 5% miscellaneous accidents. The authors discussed about different accidents in chemical/petrochemical industries like Maharashtra accident, Visakhapatnam disaster, Mexico City disaster etc. and other major accidents in chemical process industries and concluded that:

- Most of accidents take place due to malfunctioning of a component of equipment and/or minor negligence of personnel during operation or maintenance.
- The damage potential of an accident depends upon the chemical in use, causative factors, operating conditions and site characteristics.
- The damage potential in terms of the area affected is a maximum for toxic release and depends upon the type of chemical, meteorological conditions and site characteristics.
- The number of fatalities per accident is highest for those involving explosions.
- Pipeline transport of chemicals is comparatively safe, provided that the line is carefully maintained and its route does not pass through populated areas. I With an increase in

density of industries in a complex, the probability of accidents as well as that of the domino effect increase sharply (Khan et al., 1999).

2.5 HAZARDS IN INDUSTRIES AND DEVELOPMENT OF MAXCRED

The history of the chemical process industry is replete with major accidents. Information on majority of such accidents which had catastrophic implications, causing massive losses of property, human lives, and environmental quality is not available in detail. Increasing population and developmental needs keep putting ever-increasing pressure on the available land space. Even industries which were earlier set up in remote areas away from human dwellings now find themselves being enveloped by residential colonies. The risk posed by industrial accidents is thus increasing even in situations where the quantities of the hazardous materials being handled, or the manner in which they are being handled, remains the same as before. Unlike the normal release of gaseous, liquid or solid wastes from industrial processes-which take place slowly and are controllable- accidental toxic releases, explosions, or fires occur all of a sudden leaving no chance for people to escape, let alone control the accident. Special techniques, tools and management strategies are therefore required to handle the hazards or accidents in chemical process industries. The most feasible way to deal with such accidents is to anticipate them and take all possible steps to prevent them. Even to devise any meaningful emergency preparedness plan one needs to forecast what can happen and then take all such steps to minimize the adverse impacts if an accident does occur.

Khan and Abbasi developed a computer-automated tool MAXCRED (MAXimum CREdible accident analysis) with which one can rapidly and quantitatively simulate accidents in any chemical process industries. MAXCRED is a software package enables simulation of accidents and estimation of their damage potential. MAXCRED has been developed to provide a more versatile and accurate tool for rapid risk assessment than is possible with existing packages. The authors chose a petrochemical industry area in pune which is engaged in manufacturing of wide variety of chemicals. The industry also stores various hazardous chemicals in bulk quantities. The study analyses the hazards associated with the storage of various chemicals in the industry using MAXCRED. The authors developed eight scenarios of 'credible' accidents, i.e. accidents likely to occur given the history of failures in chemical process industries as Ethylene storage, Propylene oxide storage, Propylene storage, Propylene dichloride storage, Ethylene oxide storage, Propylene glycol storage, Glycerin storage, Chlorine storage and carried out

MAXCRED simulation for each scenario and revealed that scenario eight represents the worst possible disaster which has the largest area of lethal impact (Khan et al., 1998).

2.6 BUTADIENE PRODUCTION

1,3-Butadiene (butadiene) is a colorless gas at room temperature with a characteristic hydrocarbon odor. It is a hazardous chemical due to its flammability, reactivity and toxicity. Butadiene is a major product of the petrochemical industry and an important building block for many consumer and industrial products. The largest use of butadiene is in the production of synthetic rubbers. International Symposium Evaluation of Butadiene and Chloroprene Butadiene is traded globally, and global demand is expected to grow at about 3% through the end of this decade. In 2004, the global demand was expected to exceed 9 million metric tons.

In the steam cracking process, the feedstock is fed to a pyrolysis (steam cracking) furnace where they are combined with steam and "cracked" at temperatures between 1450 and 1525 ^{0}F (790–830 ^{0}C). This steam cracking produces a pyrolysate composed of hydrogen, ethylene, propylene, butadiene and other important olefins plant co-products. The pyrolysate is quenched to remove the high-boiling components; compressed to remove the C_5 and higher components as a raw pyrolysis gasoline; and then dried. The resulting material (predominantly hydrogen and C_1–C_4 components) is taken through a series of distillation steps to separate the hydrogen, methane, ethylene (and other C_2 components) and propylene (and other C_3 components), leaving the crude C4s or crude butadiene. Light crackers use ethane and propane as the feedstock and produce very low quantities of C4s and heavier co-products, including butadiene. Heavy crackers use Naphtha's, condensates, or gas oils as feed stocks and produce much greater quantities of butadiene and heavier co-products. For this reason, most light crackers do not have butadiene recovery units. The crude butadiene produced in the light crackers is either recycled to the cracking furnaces or is collected for transfer to a butadiene recovery unit. Butadiene is stored under pressure as a liquefied or compressed gas. Most butadiene is used in the production of polymers or chemical intermediates which go into the production of polymers. Butadiene is a major product of the petrochemical industry and is used in numerous valuable and beneficial consumer and industrial products. Almost all butadiene is produced as a by-product of the ethylene production steam cracking process. The major end uses are in styrene–butadiene rubber and polybutadiene, which represent 54% of butadiene production. Tire production is the single most important use of these butadiene-based rubbers (White, 2007).

2.7 COMPRESSION SYSTEM CHECK VALVE FAILURE HAZARDS

Catastrophic equipment failure due to overpressure can potentially occur in the event of compression system discharge, interstage, and/or suction check valve failure, coincident with compressor shutdown. Depending on system design and application, overpressure values approaching or exceeding 300% of equipment design are possible. Comparatively, for some equipment even limited overpressure can result in catastrophic vessel failure due to brittle fracture. Additional hazards associated with compression system fail-to-check scenarios include risks associated with excessive flare loading and compressor rotor reverse rotation. In the case of an ethylene refrigeration compressor at a typical ethylene plant, rotor reverse rotation can potentially exceed over-speed limits.

Craig et al. (2011) summarized the risk assessment results based on analysis performed on the three primary compression systems within six different ethylene plants. The methodology used to assess associated risks and system dynamics is presented. Alternative methods for mitigating risks are also discussed along with check valve reliability data. An overview of applicable overpressure protection requirements defined in the ASME Boiler and Pressure Vessel Code is provided. This paper will be of interest to anyone that designs or operates multistage compression systems in the chemical, petrochemical or refining industries (Craig et al., 2011).

2.8 CONTROL OF VOCs

Volatile Organic Compounds (VOCs) are among the most common air pollutants emitted from chemical, petrochemical, and allied industries. VOCs are one of the main sources of photochemical reaction in the atmosphere leading to various environmental hazards; on the other hand, these VOCs have good commercial value. Growing environmental awareness has put up stringent regulations to control the VOCs emissions. In such circumstances, it becomes mandatory for each VOCs emitting industry or facility to opt for proper VOCs control measures. There are many techniques available to control VOCs emission (destruction based and recovery based) with many advantages and limitations. Therefore, deciding on a particular technique becomes a difficult task. This paper describes various available options for VOCs control (Khan et al., 2000).

2.9 optHAZOP

The optimal and effective HAZOP (optHAZOP) signifies the application of hazard study in such a way that the duration of the study should be optimum. Most of the hazards should be identified and assessed; better efficiency, good reliability of results, and the time of applicability should be such that the recommendations made by the study can be followed easily and economically. Khan discovered that the optHAZOP study procedure is same as HAZOP study procedure that uses an expert knowledge base (called information base).This information base is a large collection of facts, rules, and information regarding various components of process plant. Along with the use of information it also follows some basic recommendations to give effective and reliable results.

2.9.1 *INFORMATION BASE*

The information base is an expert knowledge base consisting of information for process deviations, their causes, and their immediate consequences for various components (process/equi pment/pipeline, etc.).The information regarding various aspects of the process plant is developed based on past experience, experimental study and the operational study.

2.9.2 *TIME OF APPLICABILITY*

The best time for HAZOP study is just after the basic design. As the basic design is the final step of plant/process development and it can be executed only when all relevant information regarding the chemicals, process equipment and operating conditions has been made available.

2.9.3 *INFORMATION REQUIRED*

As the HAZOP study is based on the brainstorming discussion of the available information regarding process, material and equipment used in the process, all the relevant information needed for the study should be collected before starting the HAZOP study. The total information needed for the HAZOP study can be characterized in three main groups namely-chemicals, process equipment, and off-and-on-site information (Khan et al.1997).

2.10 HAZOP

The basic idea of a pipeless batch plant is to move the process vessel between fixed stations for mixing, separation and other activities. Mushtaq and Chung made an arrangement of many units, such as movable reactors and functional stations, which work cooperatively by avoiding collision or conflict. The elimination of their pipe work for the transfer of material offers a great flexibility for change, and allows a company to respond quickly to market demands

and technological advances. Other benefits include reduced product loss, ease of cleaning, and reduced inventories. However the flexibility that the pipeless plant offers, which allows changes to be made quickly and easily introduces new hazards. They also suggests that changes always need to be considered carefully before being implemented, as a change in a small section of a system could affect the safety of the whole system (Mushtaq and Chung,2000).

2.11 HAZOPExpert models

Manual hazards analysis techniques and methodologies that can be leveraged by an intelligent systems approach to reduce the time, effort and cost involved, and to improve the consistency and thoroughness of the analysis. Such systems are not meant to replace the human team but to assist them in improving the overall efficiency and productivity of the team. Of the various PHA (Process Hazards Analysis) methodologies, the HAZOP analysis is the prime one for automation using intelligent systems due to its wide spread usage in the process industry and its systematic and comprehensive nature. The ITOPS, HAZOPExpert intelligent system developed at Purdue University are now well beyond proof of concept and are ready for industrial applications and commercial exploitation.

2.11.1 *HAZOPExpert models*

HAZOPExpert is a model-based, object oriented, intelligent system for automating HAZOP analysis in the continuous processes. The results of a HAZOP study may vary from plant to plant; the model approach is systematic and logical, with many aspects of the analysis being the same and routine for different process flow sheets..Hence, focusing on these routine cause and effect analysis by developing generic models which can be used in wide variety of flow sheets thus making the expert system process-independent. It is also recognized that the process-specific components of knowledge, such as the process material properties and process P&IDs, have to be flexibly integrated with the generic models in an appropriate manner.

2.11.2 *HAZOP-Digraph (HDG) models*

The initial version of HAZOPExpert was modified in to HAZOP-Diagraph (HDG) model based framework to facilitate model development and refinement by the users as well to tackle more complex process configurations. The HDG models are modified, signed, directed graphs (SDG) developed for the purpose of hazard identification. Hazard-Diagraphs provide the infrastructure for graphically representing the casual models of chemical process systems in a transparent manner to the user. The knowledge about finding the abnormal causes and adverse

consequences are incorporated in these digraphs. The HDG models of the process unit s re used for propagating the process variable deviations and for finding abnormal cause and adverse consequences by interacting with the process specific knowledge. The HDG models are developed in a context-independent manner so that they are applicable to a wide variety of flow sheets. The user can build a new HDG model or add more knowledge to the existing HDG model using the graphical HDG model developer (Venkatasubramanian et al., 2000).

2.12 HAZOP

Qualitative models of equipment units and their use in automatic HAZOP analysis is mainly based on qualitative reasoning and the equipment models is essentially qualitative. Infact, qualitative unit models have to contain the knowledge to perform the HAZOP analysis of a chemical plant. In other words, equipment units must be considered form the point of view of their functionability, both in the normal and abnormal states, In particular ,qualitative models must contain the information needed to propagate variable deviations from one unit to the previous one or to the next one and to evaluate the effects of operative faults and failures.

Bartolozzi et al. (2000), build the model library including the most common chemical units: this allows analyzing every plants configuration. The models that Bartolozzi et al. (2000) developed is similar to those proposed by Lees et al. (1997) to simulate the propagation of faults in chemical process plants, consisting of mini fault trees. This models of equipment units included in the library were set up specifically for the automatic HAZOP analysis; separate types of qualitative models, named "cause models", "HAZOP models", and "consequence models", is also in order to take into account the different phases of the HAZOP analysis and the distinct mental; model

Used by the analysts during the methodical application of the guide words of the HAZOP analysis to the main variables of the plant units (Bartolozzi et al., 2000).

2.13 KRM (Knowledge-based Risk Management)

It is a general frame work for safety and quality oriented process modelling and monitoring. It connects an object oriented model of the plant behaviour to a set of databases for the conditional retrieval of relevant information. This frame work has many applications, for example, in quality management, acquisition of experience, detailed diagnosis, 'living' safety analysis, etc.

KRM is a software system for documenting, handling and utilizing qualitative safety information. It consists of separate modules meant for various user categories in an industrial organization. The modules are integrated with each other and it is possible to run them in the same environment on the same physical machine. Then important goal of KRM system is to facilitate the exchange of information between process designers and operating personnel. Currently, the usual practice in process industry is that safety documentation created in investigations during the design phase is available to the operating personnel only in the form of a folder with no well-organized updating. Feedback from plant operation to the designers is not usually organized well either.KRM is able to contribute to the flow of information between different groups in the plant. KRM has two main objectives: analysis support and operator support. Deviation and their potential causes and consequences are the basic concepts in the knowledge-based operator support methodology of KRM. An advantage of KRMHAZOP is that it creates a structured database of HAZOP results (Heino et al., 1994).

2.14 EXPERTOP

The object-oriented architecture of EXPERTOP consists of (a) knowledge base,(b) inference engine and (c) graphical user interface.

2.14.1 *Knowledge-base module*

Knowledge base is a collection of information set up in a pre-defined format which can be retrieved and used for HAZOP study. The knowledge base is created in two segments in order all the equipment, process/ambient conditions, and typical problems that have been encountered in various industries. The knowledge base is developed in terms of rule network, where equipment is specified as the derived objects of the main equipment object class. These derived objects have sub objects, functions and attributes attached to them. The knowledge base has the following four main features: (1) general process causes (2) general process consequences (3) process specific causes and (4) process specific consequences.

2.14.2 *Inference engine module*

The inference engine is a type of controller, which acts as a manager of the knowledge base, according to the user intention and requirements of the problem study. The user interface enables the user to easily and swiftly interact with various modules of the software. It also provides on-line help for each option.

2.14.3 *Graphical user interface module*

This opinion provides a mode of external interface between the knowledge and the user. This option enables the user to draw industrial flow diagrams (process flow diagrams).It further extends the facility to select particular equipment from the process flow diagram with associated parameters and interacts with the knowledge base to carry out the HAZOP study. This option provides a means of modification or upgradation of knowledge base according to the need and experience of the expert user (Khan et al., 2000).

2.15 TOPHAZOP

TOPHAZOP is as a knowledge-based software tool for conducting HAZOP in a rapid and efficient yet inexpensive manner. This TOPHAZOP consists of the following main modules: knowledge-base, inference engine, and user interface.

2.15.1 *Knowledge-base*

Knowledge-base is a collection of information set up in a pre-defined format which can be retrieved and used for HAZOP study. The knowledge-base is created in two segments in order to cover all the equipment, process/ambient conditions, and typical problems that have been encountered in various industries. The knowledge-base is developed in terms of rule networks with equipment specified as the derived objects of the main equipment object calss.These derived objects have various sub-objects, functions an attributes attached to them. The knowledge-base has the following four main features: general process causes, general process consequences, process-specific causes and process-specific consequences.

2.15.2 *User interface*

This option provides a mode of external interface between the knowledge and the user. This option enables the user to choose particular equipment from the set of equipment and associated parameters and interacts with the knowledge-base to carry out the HAZOP study. This option also provides a means of modification or upgrading of the Knowledge-base according to the need and experience of the expert user. The user interface has two options: analysis and modifications. Choosing one of these options will link the user to the appropriate module of knowledge and ion keying in the necessary information the results of the HAZOP study will be obtained. The user has the liberty to check and modify the knowledge-base or add new

information to it. The output of TOPHAZOP is in the form of normal HAZOP reports and can be directly used in the presentation of the HAZOP study.

Remarks

The TOPHAZOP proposed by Khan et al. is knowledge-based user friendly software for conducting HAZOP studies in a comprehensive, effective and efficient manner within a short span of time. TOPHAZOP overcomes several major limitations of the existing HAZOP procedure. The software has an in-built knowledge-base which is extensive ad dynamic. It incorporates process units, and works out numerous modes of failure for certain input operational conditions. It drastically minimizes the need of expert time. The knowledge-base has been developed in two segments: process general knowledge, and process-specific knowledge. The process specific knowledge segment handles information specific to a particular process unit in a particular operation, whereas the process-general knowledge segments handle general information about process units. Further advancements are possible in the TOPHAZOP system in terms of incorporating: more complex process units, more efficient search methods, ability to handle more complex process situations such as reverse flow, recycle loop, purging, etc., and user interactive flow charting options (Khan et al., 1997).

CHAPTER 3 NAPHTHA CRACKER PLANT

The Naphtha Cracker Plant comprises of two sections

(1) Hot section

-Convection zone

-Radiant zone

-Quench section

(2) Cold section

-Demethanizer

-Deethanizer

-Acetylene hydrogenation unit

-Ethylene separation

-Depropanizer

-C3 hydrogenation

-Debutanizer

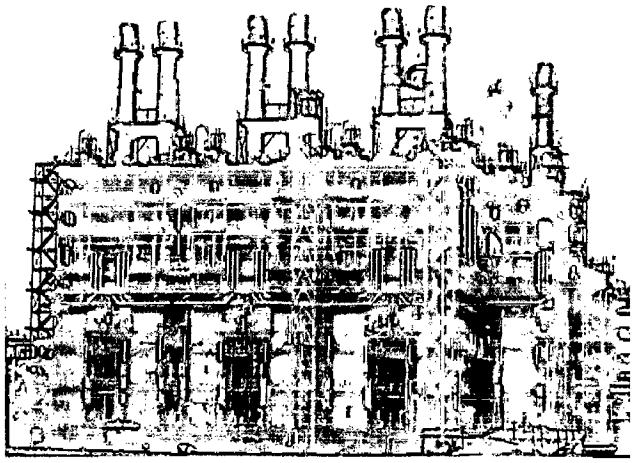

Figure 3.1 NAPHTHA CRACKER

Majority of the ethylene is produced by the thermal cracking of petroleum feed stocks (hydrocarbons) at high temperatures without catalyst. Thermal cracking is the process of cracking Naphtha into ethylene and propylene and other co-products. Steam cracking is a technology for cracking; the process is based on addition of steam. The feedstock is vaporized by pre-heating, mixed with steam, and passed into a furnace. The yield of products depends on the feedstock, the temperature used (between 700 and 900 °C), and the time spent in the furnace ("residence time"), which ranges from 0.1 to 1second.

Steam is used as a diluent to inhibit coking in the tubes and to increase the percentage of ethylene formed. The amount of steam varies with the molecular weight of the hydrocarbon feedstock and varies from 0.3 kg steam/kg ethane to 0.9 kg steam/kg gas oil. Lower molecular weight feed stocks, such as ethane and propane, give a high percentage of ethylene. Higher molecular weights feed stocks, such as naphtha and gas oil, are used if propylene is required in significant quantities. Naphtha and gas oil also generate a high proportion of raw pyrolysis gasoline (RPG). Lower temperature and shorter residence time favour this reaction. The basic method is that the hydrocarbon feedstock, mixed with steam, is passed through a metal tubular

heater coil that is heated to 750-930°C. The product is then cooled to 300°C. The entire reaction time is about 1 second. Cooling of effluent takes place in a quench boiler – the recovered heat being used to generate steam.

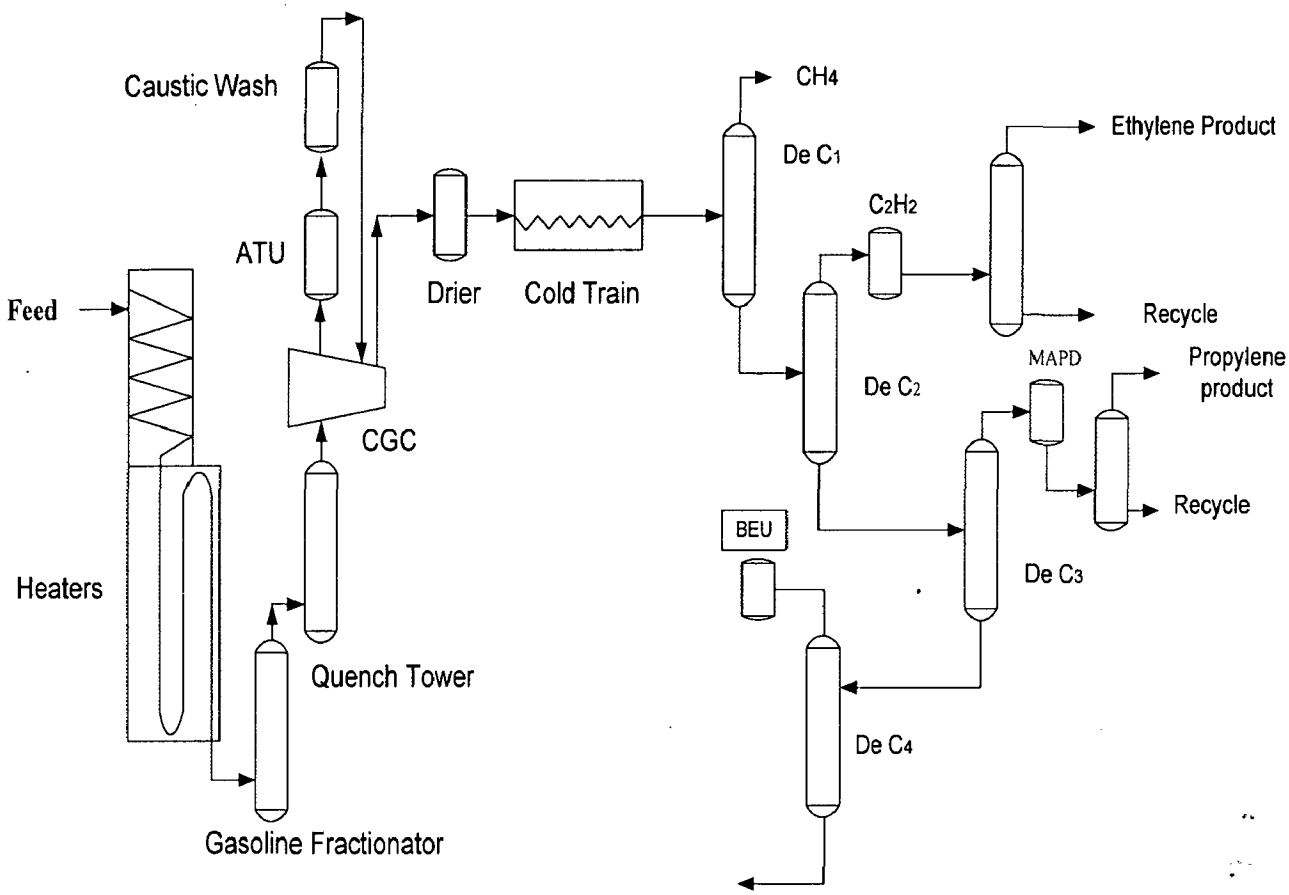

Figure 3.2 Process Flow Sheet of Naphtha Cracker Plant

Naphtha normally refers to a number of different flammable liquid mixtures of hydrocarbons, i.e. a distillation product from petroleum or coal tar boiling in a certain range and containing certain hydrocarbons. It is a broad term covering the lightest and most volatile fraction of the liquid hydrocarbons in petroleum. In petroleum engineering, full range naphtha is defined as the fraction of hydrocarbons in petroleum boiling between 30°C and 200°C. It consists of a complex mixture of hydrocarbon molecules generally having between 5 and 12 carbon atoms. It typically constitutes 15–30% of crude oil, by weight. Light naphtha is the fraction boiling between 30°C and 90°C and consists of molecules with 5–6 carbon atoms.

Heavy naphtha boils between 90°C and 200°C and consists of molecules with 6–12 carbons. It is used in the petrochemical industry for producing olefins in steam crackers and in the chemical industry for solvent (cleaning) applications. Common products made with it include lighter fluid, fuel for camp stoves, and some cleaning solvents. Naphtha is a very flammable liquid used as a solvent for various chemical industries. It is used as a cleaning fluid and can be found in washing detergents. It can also be used in shoe polishes.

3.1 FEEDSTOCK CHOICE

A wide range of alternative feed stocks such as naphtha, ethane/propane, alcohol, and LPG, NGL and gas oil can be used for production of Petrochemicals. In India, naphtha and C_2/C_3 fractions from natural gas are the main feedstock used. LPG is normally used as domestic fuel, while gas oil is not used because it is heavier fraction and needs complex processing. In India, some refineries crack LPG in their fluid catalytic cracking units to produce propylene. It is apparent that about 59% of India's cracking capacity is based on natural gas, whereas 40% is based on Naphtha feedstock. Industrial alcohol which was an attractive feedstock in the days of alcohol price control is no longer an important feedstock and accounts for only 0.8% of the total ethylene production in the country. The major factors, which affect the choice of feedstock, are the relative yields of olefins and aromatics desired energy costs, investment levels, availability and relative pricing. Natural gas and NGL yield a much higher proportion of ethylene. Hence, they are preferred when the polyolefin's output of a cracker is sought to be maximized. On the other hand naphtha is preferred when a wider range of output products (including propylene and butadiene derivatives) is desired.

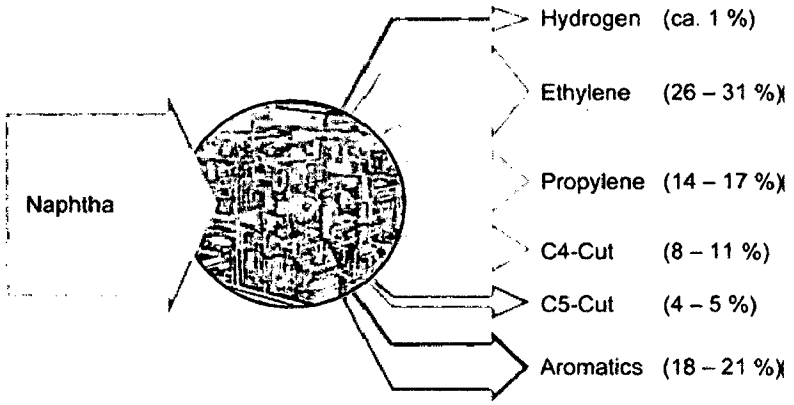

Figure 3.1.1 Derivatives of Naphtha

3.2 PRODUCTION IN REFINERIES

Naphtha is obtained in petroleum refineries as one of the intermediate products from the distillation of crude oil. It is a liquid intermediate between the light gases in the crude oil and the heavier liquid kerosene. Naphtha's are volatile, flammable and have a specific gravity of about 0.7. The generic name 'naphtha' describes a range of different refinery intermediate products used in different applications.

3.3 PROPERTIES

- Molecular weight range is 100–215 g/mol;
- Specific gravity range is 0.75–70.85 g/cm^3;
- Boiling point range is 160–220 °C (320–430 °F);
- Melting point: <-30°C;
- Flash point: >= 44°C
- Auto-ignition temperature: 355 °C
- Explosive limits, vol% in air: 0.6-8.0
- Vapour pressure is < 5 torr (5 mm Hg).
- Naphtha's are insoluble in water;
- Colourless (kerosene odour) or red-brown (aromatic odour) liquid;
- Incompatible with strong oxidizers.

3.4 PRODUCTION OF OLEFINS

As the current global capacity for light olefin production has exceeded 150 million tons, steam cracking is now the most energy consuming process in the chemical industry (Ren et al., 2008).Olefins are major building blocks for petrochemicals. Because of their reactivity and versatility-especially the light olefins like ethylene, propylene, butadiene, etc., there has been tremendous growth in the demand of olefins. Olefins are finding wide applications in the manufacture of polymers, chemical intermediates and synthetic rubber. Ethylene itself forms a

basic building block for a large number of petrochemicals and is coated as king of chemicals. World ethylene capacity was 109.4 million tonnes per annum (I.D.Mall, 2007). Light olefin demand typically grows faster than GDP. Steam cracking is the major source of production olefins.

3.5 ETHYLENE

Ethylene is sometimes considered as the "king of petrochemicals". This is because more commercial chemicals are produced from ethylene than from any other intermediate due to its several favorable properties as well as technical and economical factors. Ethylene has a simple structure with high reactivity. It is a relatively inexpensive compound, which can be easily produced from any hydrocarbon source through refinery process like steam cracking and in high yields. In addition, there are less by-products generated from ethylene reactions with other compounds than from other olefins. Valuable chemicals can be produced from ethylene by reacting with many inexpensive reagents such as water, chlorine, hydrogen chloride, and oxygen. Ethylene can be polymerized by free radicals or by coordination catalysts into polyethylene, which is the largest-volume thermoplastic polymer (Yan et al., 2009). Also, the copolymerization of ethylene with other olefins can produce copolymers with improved properties. Ethylene is the industrial gas produced in the largest quantity worldwide. It is considered to pose a low risk for potential adverse impacts in the work place and to the public when risk management controls are in place to minimize an accident release from closed equipment systems designed for the safe handling, processing, storage, and transport of these products. However ethylene is flammable and explosive when in contact with direct heat, sparks or flames. Ethylene is shipped as a compressed or a gas under high pressure by pipe line to other industrial processors that produce other chemicals or polyethylene plastic resins. Potential exposure in the work place or releases to the environment is strictly controlled to well below applicable regulatory limits.

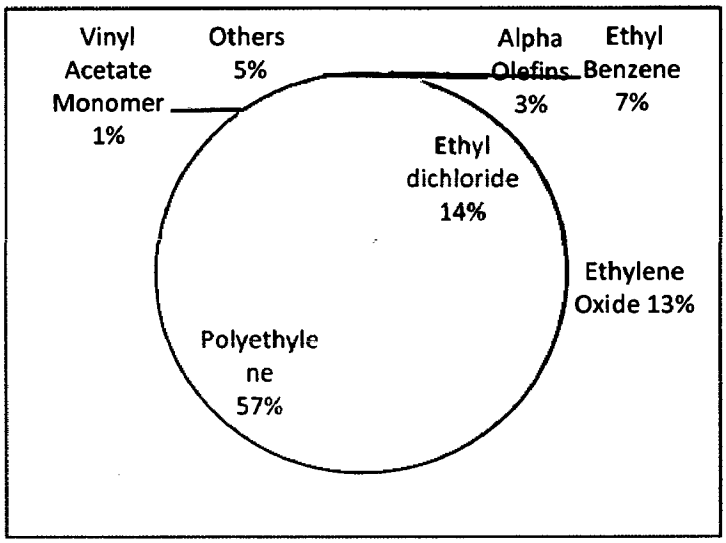

Figure 3.5 World Ethylene End Use

3.6 PROPYLENE

Propylene, which is second to ethylene as the largest-volume hydrocarbon intermediate for the production of chemicals, has been regarded as "the crown prince of petrochemicals" (Khan et al.1999).Like ethylene, propylene is a reactive compound that can react with many common reagents such as water, chlorine, and oxygen. However, propylene has different reactivities toward these reagents as its structure is different from that of ethylene. For instance, instead of yielding propylene oxide as in the case of ethylene, the oxidation of propylene using oxygen produces acrolein. This is due to the ease of oxidation of allylic hydrogen's in propylene.

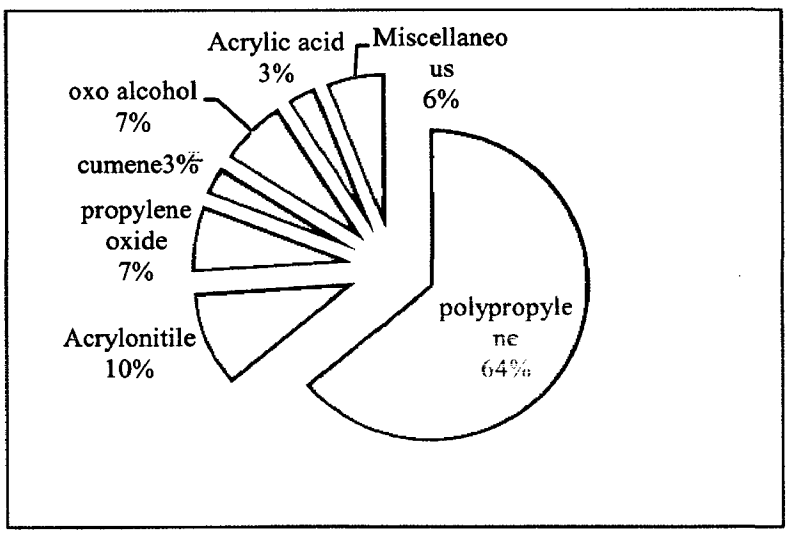

Figure 3.6 World Propylene End Use

3.7 STEAM CRACKING FOR THE PRODUCTION OF OLEFINS

Light olefins (e.g., ethylene and propylene) are the most important basic petrochemicals, which are used to produce plastics, fibers and other chemicals. Most light olefins are produced by steam cracking (Ren et al.2008).Cracking is a process to break larger molecules of hydrocarbons into smaller ones by heating. The steam cracker remains the fundamental unit of the global petrochemical industry and is at the heart of any petrochemical complex and produces a large number of products and by products such as olefins namely ethylene, propylene, butadiene, butane and butenes, isoprene, etc., as well as pyrolysis gasoline. These products serve as basic feed stock for many chemicals, intermediates which are used in the production of polymers, synthetic fibres, synthetic rubbers, pesticides, pharmaceuticals, dyes, explosives and other organic chemicals. The choice of feed stock for olefin production depends on the availability of raw materials and the range of downstream products. Naphtha has made up about 50-55 percent of ethylene feedstock sources since 1992.The complexity of steam cracking and production of olefins depends on the feedstock. Olefins plants are complex and costly with both complexity and cost that increases with heaviness and feedstock. Heavier feedstock produces a wide variety of olefins requiring more complex separation and recovery process. Although earlier production of olefins was from lighter feedstock like ethane, propane and naphtha, heavier feedstocks are also gaining importance because production of ethylene from heavy liquids will increase as demands grow. Present uncertainty in petrochemical feedstock market requires that ethylene plant must be designed for variety of products.

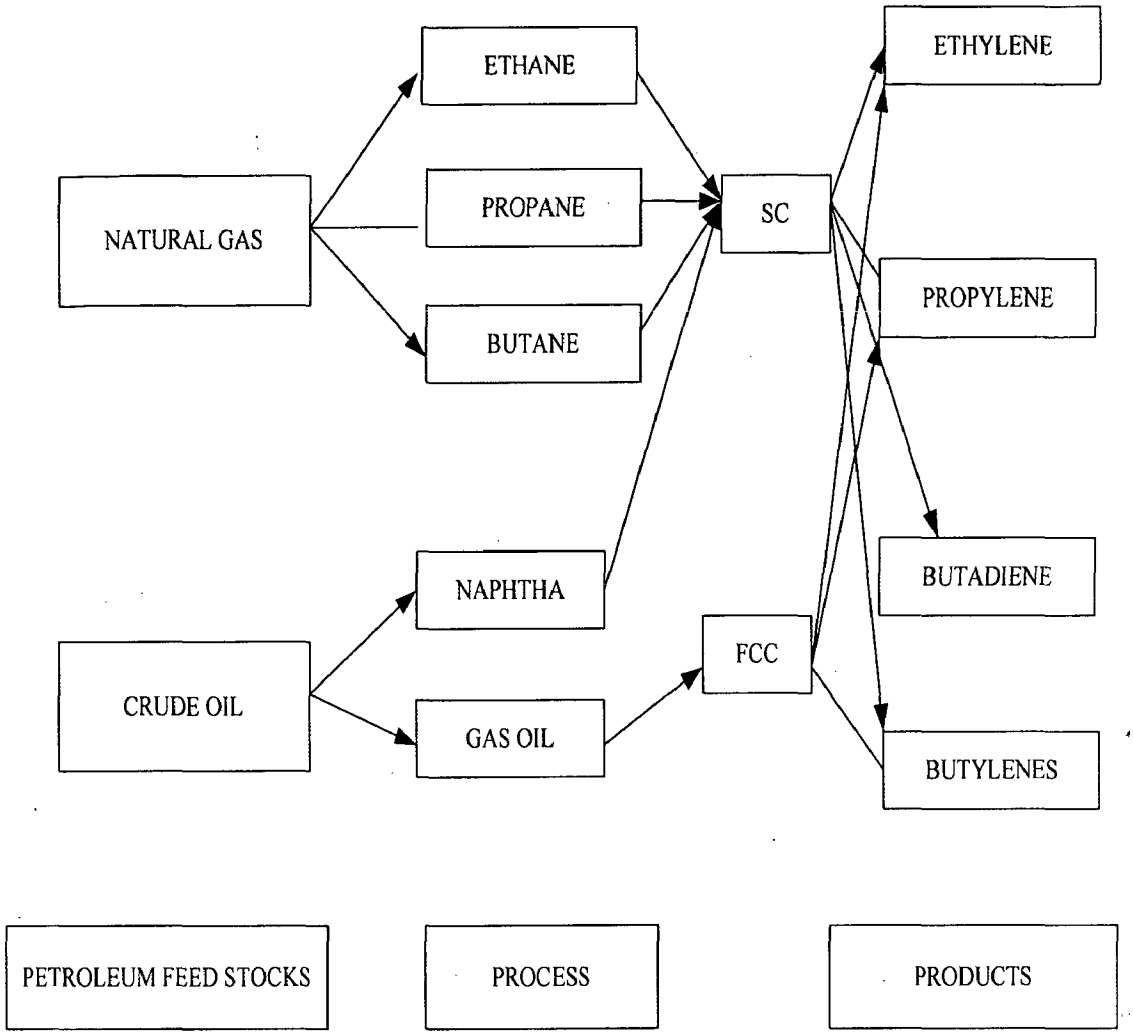

Figure 3.7 Main Important Current Sources of Olefins

3.8 STEAM CRACKING (SC)

Currently, the main source of light olefins specifically, ethylene and propylene, is steam cracking, which involves the pyrolysis of a paraffin feedstock which can have a wide range in number of carbon atoms and can even include mixtures of hydrocarbons. SC has a worldwide production of more than 150 million metric tons of ethylene and propylene annually. This process is known as a non-catalytic, radicals-promoted, thermal cracking process, which is performed in the presence of steam at high temperature. Steam acts as a diluent to lower the hydrocarbon partial pressure and suppresses to a significant degree the formation of coke deposits throughout the reactor ($C + 2H_2O \rightarrow CO_2 + 2H_2$).The SC reaction is highly endothermic, and the typical temperatures for this process range from 700 to 900 ^{0}C, and higher,

according to the type of feedstock used. The residence time ranges from a few seconds to a fraction of a second. The product spectrum for steam cracking is rather large. Light olefins are primarily produced, but a cut of C_4 fraction containing paraffin's, olefins, and butadiene's is also formed. A third cut, that of C_5 and higher hydrocarbons, contains pentanes/pentene and BTX (i.e. benzene, toluene, and xylenes).The light fraction is in the gaseous state, so that to isolate them, the product stream is passed through a series of units which in turn removes a single compound from the stream. Thus, there is a demethanizer, a deethanizer and so on until only the liquid fraction remains. The products in the liquid fraction are separated by distillation. Coke and heavy oils are also formed in lesser quantities but have the unfortunate quality of forming deposits throughout the system, which must be removed. Cyclic alkanes can be formed and subsequent dehydrogenations also produce aromatics. Diolefins are also produced and are very reactive. They can combine with olefins to produce larger molecules by Diels-Alder cycloaddition reaction. Condensation of aromatics leads to coke particles. Offers some examples of the reaction mechanism of steam-cracking using ethane as example.

3.9 STEAM CRACKER PROCESS OVERVIEW

The steam cracking section comprises of two sections, a hot section and a cold section. The cracking of hydrocarbons and separation of light cracked gases from heavier fraction pyrolysis gasoline takes place in the hot section while the cracked gases ethylene, propylene, butadiene and other fraction takes place in the cold section which operates below 0^0C .

3.10 HOT SECTION

The cracker furnace is divided into three sections: convection zone, radiation zone and quench section. The hydrocarbon feedstock is preheated by quench water and steam before entering the convection zone of the furnace where it is further preheated and mixed with superheated steam, which is added as diluents. The steam minimizes the side reaction responsible for the formation of the coke during pyrolysis and improves the selectivity to produce desired olefins by lowering hydrocarbon partial pressure. Requirement of steam will depend upon the type of feedstock; the lighter hydrocarbon requires less steam as compared to heavier feedstock. The hydrocarbon and steam preheated in convection zone in the upper part of the furnace enter the radiant section of the furnace at about 650 ^0C and total pressure of 1.7 bar, where pyrolysis of feed takes place. The coil length in the radiant section varies from 60m for a naphtha cracker to 85m for an ethane cracking unit. The residence time varies for different

feedstock is around 0.15-1.2 s. The effluent leaves at about 830-870 ^{0}C and total pressure of 1.7 bar. The burners are either gas fired and are radiant and are of the long flame type. The flue gas temperature may be of the order of 1200 ^{0}C with the inner tube skin temperature of 1008 ^{0}C.The reaction is highly endothermic and heats flux ranges from 55-85 kj/m^2.The radiant coil outlet temperature is controlled to achieve desired ethylene, propylene yield. Pyrolysis of any hydrocarbon feedstock is always accompanied by coke formation, which deposits on the walls of the tubular reactor. Under typical operating conditions, the coke formation in the naphtha pyrolysis is about 0.01 wt percent of the feed. Furnace effluent is rapidly quenched in the USX double pipe exchangers and multi-tubular TLX heat exchanger in which t is cooled to 350 ^{0}C.The effluent is further quenched by direct contact with quench oil before entering the quench oil tower, which besides cooling the furnace effluent, the separation of gasoline and lighter products from the fuel oil also takes place. Quenching is essential in order to restrict the polymerization reactions. Ethylene cracking effluent must be quenched uniformly and rapidly for high product yield and to stop secondary olefin reactions which cause coke formation and shorten unit run length. Quenching is basically performed in two ways directly by oil or water or indirectly by a quench cooler or transfer line exchangers. The basic requirement for cracked product quench coolers are: rapid and uniform cooling, small pressure drop, maximum heat recovery, long continuous run length and low maintenance. The cracked gas over heads of the quench oil tower is further cooled in quench water tower by direct contact with water and is finally sent to primary fractionating column. The gases are separated at the top and are sent to compression section for separation and purification of cracked products. The effluent from primary fraction column is compressed in five stages on centrifugal compressors containing inter coolers and then to a separator drum. The condensate from separator drum enters a stripper where high fractions are recovered. The gas before entering the final stage compression is desulphurised by passing through a caustic scrubber containing 10 percent caustic where the separation of sulphur compounds and CO_2 takes place. The removal of CO_2 from gas is essential in order to meet the product quality in which the ethylene should be less than 1 ppm. Removal of CO_2 also protects the downstream catalytic operation. The removal also avoids corrosion and formation of ice in the cold section. Spent caustic is then sent to caustic decoiling drum, degassing drum and spent caustic oxidation unit for removal of hydrocarbons like benzene and

polymers. The cracked gases are dried in dehydrators containing molecular sieves before entering the cold section.

3.11 COLD SECTION

The dried cracked gas after removal of sulphur compounds, CO_2 and moisture are sent to cold section where it is cooled to -165 ^{0}C in cascade refrigeration system using propylene and ethylene. The cold section contains demethanizer, deethanizer, acetylene dehydrogenation unit, ethylene separation, depropanizer, C_3 hydrogenation and debutanizer.

3.12 PROCESS DESCRIPTION

3.12.1 HEATER SECTION

Pyrolysis or steam cracking is the primary process utilized to manufacture olefins from large hydrocarbon molecules. This gas-phase reaction takes place in metal alloy tubes within a fired furnace. Pyrolysis proceeds as a series of free radical reactions and the complexity of the mechanisms increases with the nature of the feedstock (4). This is the heart of a steam cracker. Naphtha first enters the convection section of a pyrolysis furnace, where a series of heat exchangers are located and it is preheated to 650 ^{0}C. Then, naphtha is vaporized with superheated steam and is passed into long (12–25 m), narrow (25–125 mm) tubes, which are made of chromium nickel alloys. Pyrolysis takes place mainly in the radiant section of the furnace, where tubes are externally heated to 750–900 ^{0}C (up to 1100 ^{0}C) by fuel oil or gas fired burners (Ren et al., 2006).

Naphtha feed received from storage tanks is filtered and mixed with Hydrogenated C4, C5 and C6 recycle streams and then preheated against quench water and sent to SRT liquid cracking heaters. Naphtha and C_4, C_5, C_6 recycles are fed to the Short Residence Time (SRT) liquid cracking heaters where naphtha and C_4, C_5, C_6 recycle feeds get cracked. There is one gas-cracking heater where ethane and propane recycles are cracked. Dilution steam is added to each of these coils to reduce coke deposition. Each heater is provided with motor driven induced draft fan located above the convection section that discharges flue gases through an individual stack. There are Transfer Line Exchangers (TLE) for each SRT cracking heater. The cracked gases are cooled in TLEs and the heat recovered from cracked gases is used to generate Super High Pressure (SHP) steam .The effluent from heater is routed to Gasoline Fractionators. All the

heaters are operated on Fuel Gas which is mainly the methane rich off-gas, produced in the unit. Make-up / back-up fuel is LPG.

3.12.2 GASOLINE FRACTIONATION

The heater effluent from SRT heater is further cooled in Gasoline Fractionator. Gasoline and lighters are taken out as an overhead vapor and sent to Quench Tower. The fractionator bottom is Pyrolysis Fuel Oil (PFO), which is sent to the PFO Stripper. Pyrolysis Gas Oil (PGO) is drawn from the fractionator as a side stream and after steam stripping in PGO stripper, it is sent partly as purge oil for instrumentation and the rest is blended with PFO and sent to storage.

3.12.3 CHARGE GAS QUENCH AND PROCESS WATER STRIPPING

Gasoline fractionator overhead and enter the Quench Tower where the gases are partially condensed by direct countercurrent contact with recirculating water. An olefin plant closed loop quench water system is designed to cool cracked gas to approximately 90 °F to 100 °F prior to cracked gas compression. The quench tower removes most of the dilution steam as well as pyrolysis oil, heavier hydrocarbons, and coke fines from the cracked gas. An oil-water decanter is used to separate hydrocarbons from the hot quench water exiting the tower. Emulsification problems in the decanter can result in an excessive amount of hydrocarbons being carried back to the quench water tower. These hydrocarbons can lay down residue on the quench tower internals, both trays and packing, and can cause severe fouling problems. The result of this type of fouling is reduced heat transfer in the column, increased pressure drop, reduced capacity, and reduced run time(29). The quench tower overhead is sent to Charge Gas Compressor while the water and condensed gasoline is sent to the Quench Water Settler for gasoline separation. Part of the gasoline from settler is sent back to Gasoline Fractionator as reflux and the balance is sent to Gasoline Stripper.The water from the Quench Water Settler is sent to Process Water Stripper for steam stripping. The water from stripper bottom is used for steam generation in Dilution Steam Drum.

3.12.4 GASOLINE STRIPPER

The gasoline, separated in quench water settler, is sent to the Gasoline Stripper along with gasoline from the Charge Gas Compression section The Stripper overhead is sent back to the Quench Tower while the bottom is used as wash gasoline for spent caustic pre-treatment.

3.12.5 CHARGE GAS COMPRESSION AND CONDENSATE STRIPPING

Quench Tower overhead vapour (charge gas) is compressed from in a 5-stage centrifugal compressor. Condensate from 3rd stage discharge drum recycled to 2nd stage suction drum via 3rd stage suction drum where hydrocarbon and water get condensed. While hydrocarbon is sent back to Gasoline Stripper, water is recycled to 1st stage suction drum and then pumped to Quench Tower.

3.12.6 ABSORPTION OF ACID GAS IN AMINE ABSORPTION UNIT

Charge gas from the charge gas compressor is heated against quench water and then fed to the bottom section of Mono Ethanol Amine (MEA) Acid Gas Absorber. Super heated charge gas shall be introduced to acid gas absorber to avoid HC condensation. Lean MEA coming from regenerator is introduced to middle of absorber .Charge contacts with lean MEA by counter current flow; MEA absorbs both H_2S and CO_2 in charge gas. Then, rich MEA is sent to gasoline wash column.

Treated charge gas from the top of acid gas absorber is sent to Caustic/water wash tower for further removal of trace amount acid gas. Rich MEA from acid gas absorber is introduced to top of gasoline amine contactor. Dissolved light HC in rich MEA is vaporized in top compartment and is routed to wet flare. Wash gasoline coming from gasoline stripper bottom and regenerator reflux drum is introduced to contactor bottom and contacted with rich MEA. HC in MEA is removed by wash gasoline and the gasoline is sent to gasoline/amine separator. Finally, rich MEA washed by gasoline is sent to regenerator through rich/lean amine exchanger. Thus Acid gases are removed from charge gas by Amine wash, caustic and water wash.

After 5th stage discharge, the charge gas is progressively cooled by both process and refrigerant cooling. Partially condensed liquid / vapour mixture flows to Dryer Feed Drum.

3.12.7 CHARGE GAS DRYING AND CHILLING

The charge gas from Dryer Feed Drum overhead is dried in a two bed molecular sieve drying system which is then progressively chilled to –131°C by both process and refrigerant cooling.

3.12.8 DEMETHANIZER

The condensed liquids from the charge gas chilling train are sent to the appropriate feed locations of the Demethanizer. Demethanizer bottom product is sent directly to the Deethanizer as the top feed.

3.12.9 DEETHANIZATION, ACETYLENE HYDROGENATION AND ETHYLENE FRACTIONATION

The demethanizer bottoms product is feds to the deethanizer to separate C_2 from C_3+ material. Deethanizer overhead is partially condensed and collected in reflux drum. The liquid is pumped back as reflux. The vapour form reflux drum goes to a two-bed acetylene converter having silver promoted palladium catalyst for selective hydrogenation of acetylene to ethylene and ethane. The ethylene product is withdrawn as a side draws from the tower and sent to the ethylene product surge drum.

3.12.10 DEPROPANIZATION

Deethanizer bottoms and condensate stripper bottoms are the feed to depropanizer to separate C_3 components from C_4 and heavier components. After condensation of depropanizer overhead, part of the condensate is used as reflux and balance is fed to Methyl Acetylene and PropaDiene (MAPD) converter. Depropanizer bottom product, containing C_4 and heavier material, is sent as Debutaniser feed.

3.12.11 MAPD HYDROGENATION

In this section Methyl acetylene (MA) and Propadiene (PD) present in the depropanizer overhead are removed by selective hydrogenation to propylene and propane in a single bed MAPD reactor.

3.12.12 DEBUTANISER

Depropanizer bottom flows to the debutaniser where the raw C_4 product is separated. The debutaniser net overhead product, consisting of mixed C4s, is pumped to the Butadiene Extraction Unit or to C_4 hydrogenation unit when BDEU is not in operation. Debutaniser bottom product is combined with gasoline from the gasoline stripper and sent to Pyrolysis gasoline hydrogenation unit (PGHU) for hydrogenation.

3.12.13 BUTADIENE EXTRACTION UNIT

Butadiene Extraction Unit (BDEU) is designed to separate C_4 hydrocarbon mixture containing butanes, butadienes, C_3 and C_4 acetylenes.

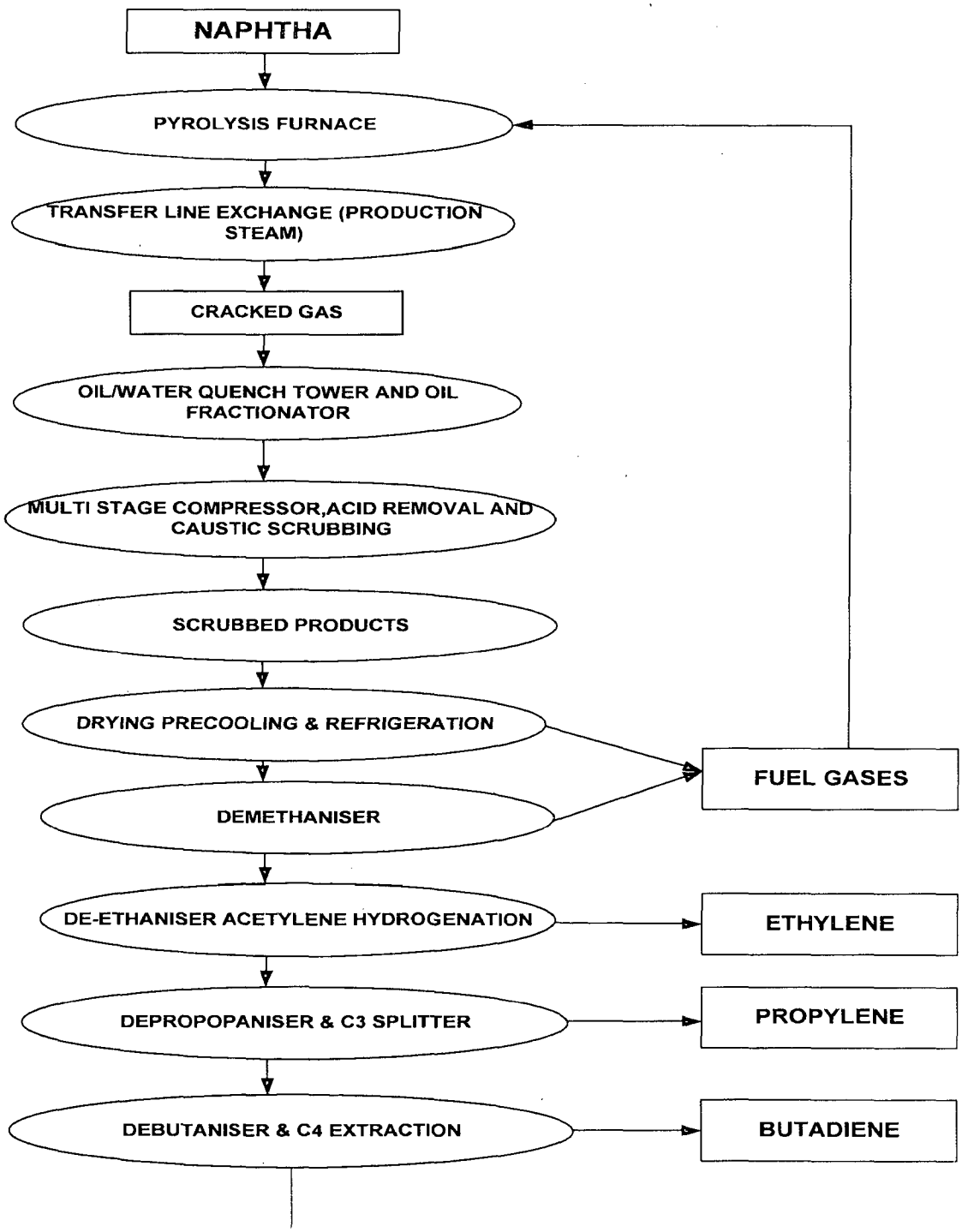

Figure 3.12 FLOW DIAGRAM FOR A NAPHTHA STEAM CRACKER

CHAPTER 4

HAZARDS AND SAFETY MEASURES IN NAPHTHA CRACKER PLANT

Major hazards associated with naphtha cracker plant are discussed in subsequent sections in this chapter.

4.1 LOSS OF HYDROCARBON FEED

Loss of hydrocarbon feed to the heater will result from a failure of the feed pumps and corresponding failure of the automatic start of the spare feed pumps. Loss of hydrocarbon feed to the heater will trip an interlock that will initiate trip of that heater. This will cause the Hydrocarbon feed valve to that particular heater to close. The dilution steam flow will remain at the last controlled value as long as it is above the minimum preset value equivalent to 90% of normal flow. In some cases it may be necessary to increase the dilution steam flow to the maximum valve opening to absorb sufficient heat.

Following emergency action steps should be taken

- Hearth firing and dilution steam should be adjusted to maintain the temperature at a maximum of 750- 760 ^{0}C.
- For induced draft heaters,cooling is accomplished with ambient air by manipulating the ID fan speed.
- The cooling of the heater should be accomplished at a rate not to exceed 100 ^{0}C per hour until the coil outlet temperature reaches 400 ^{0}C.The dilution steam should be shut off at this point and the heater allowed to cool to ambient temperature.
- On loss of hydrocarbon feed, high pressure steam production will be greatly reduced.
- In preparing the heater for decoking, the steam purge lines should be kept open before closing the transfer line block valve and opening the decoking line valve.

4.2 LOSS OF DILUTION STEAM

This failure is normally a result of some other failure, such as total steam, and is unlikely to occur by itself. Medium pressure steam is provided as emergency makeup for the dilution steam system. However, it is possible that some malfunction of the dilution steam control system causes a total shutoff of dilution steam to the heaters.

Following actions should be taken manually

- The heater should be totally shut down manually by activating the trip switch. Hydrocarbon feed to the heater process coils will be automatically tripped when the shutdown is activated.
- The BFW should be continued through the preheat coil. This is ensured by the minimum stop on the BFW level control valves.

4.3 LOSS OF FUEL

Failure of the fuel to the cracking heater can result from a loss of either the plant fuel or a failure of the backup fuel system to maintain pressure or by some malfunction in the fuel distribution system to the heaters. In this case, low pressure in the fuel gas header will result in an automatic closing of solenoid operating valves feeding fuel gas to the wall and hearth burners of the heater. Even if fuel pressure is recovered within a few moments after shutdown, it is not safe to reopen the fuel in to a hot fire box. No attempt should be made to relight the burners before purging because of the possibility of the accumulated gas. A large amount of fuel could enter the fire box inlet without immediately igniting, mix with air and then possibly explode when contacting the hot tube or refractory. The safe action is to completely close all burners and pilots. Before lighting pilots, the heater box is thoroughly checked to ensure that it is gas free. After malfunction has been corrected, the heaters that are near or beyond the midpoint of their cycle should be decoked before being brought to cracking service.

4.4 RADIANT COIL FAILURE

Coil rupture is first observed at the stack where heavy smoking or even a flame will be visible. This condition could result in severe damage; therefore, the heater must be shut down immediately.

Figure 4.4.1 COILS IN THE HEATER

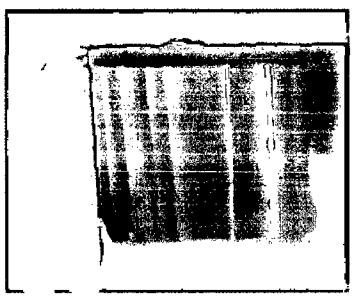

Figure 4.4.2 COILS DURING OPERATION

The following safety measures must be taken in case of tube rupture

- The firing and the hydrocarbon feed to the particular heater should be immediately cut. The heater trip will maintain the dilution steam flow at the last controlled rate and all the hearth and wall fuel valves should be closed.
- With a large rupture, hydrocarbons could back in from the transfer line. These hydrocarbons are a source of fuel, which will cause dangerous positive pressure with resulting flaming out of the fire box.
- To avoid backing in hydrocarbons from the main transfer line into the fire box the ruptured tube, the transfer line block valve should be immediately closed.
- The heater should be cooled and all the flow should be cut off.

4.5 CONVECTION SECTION HYDROCABON FAILURE

A rupture of coil in this section would result in burning the hydrocarbon mixture in the convection section. This will be indicated by black smoke out of the stack. If the burning is occurring in the convection section, the it results in the high temperatures. The heater should be taken offline as rapidly as possible.

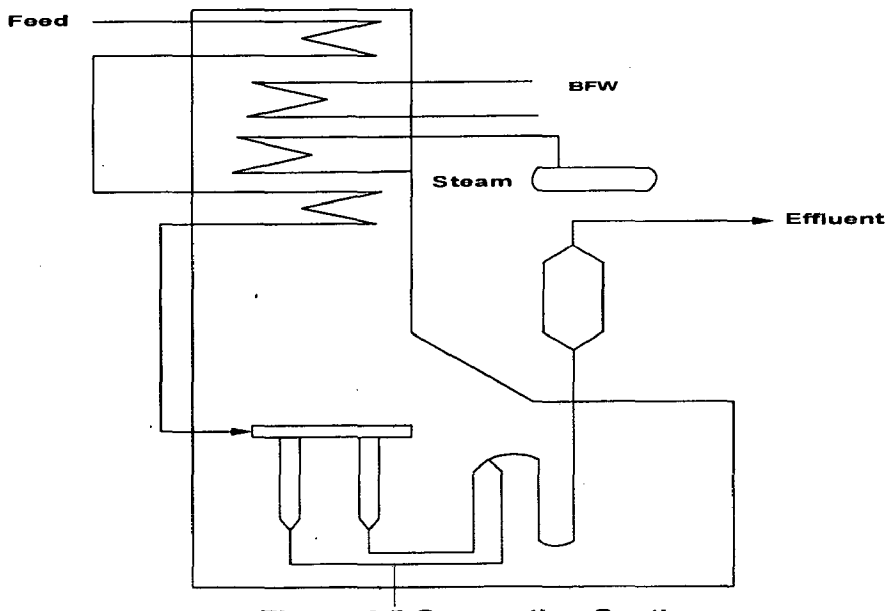

Figure 4.5 Convection Section

4.6 BFW PREHEAT COIL FAILURE

A BFW preheat coil rupture in the heater will be evidenced by the loss of SHP steam drum level and by the steaming stack effluent, as BFW enters the hot convection section in contact with hot flue gases and heater surfaces. This situation could result in a positive firebox pressure and is again a potentially hazardous situation. In most severe case, as the steam drum level drops, the steam drum level controller will cause the BFW level control valve to go wide open to supply as much water in to the system as is leaking through the rupture. The steam drum itself will depressure if the rupture is big due to leakage through the check valve.

Safety measures to be taken

- The fires and the hydrocarbon feed should be cut completely from the heater.
- The BFW control valve should be closed immediately.
- The dilution steam flow is adjusted in conjunction with the heater cool down and the heater should be isolated by closing main transfer line valve.

4.7 TLE TUBE FAILURE

A process tube rupture in the TLE will result in large quantities of high pressure boiler feed water flowing in to the process stream. A rupture will be evidenced by a sudden rise in BFW flow that heater, by a sudden drop in the TLE outlet temperature and by an upset condition in the gasoline fractionators.

Safety measures to be taken

- Trip the heater manually to shut down mode.
- The steam drum should be depressurized to atmosphere through the steam preheat coil and block in the continuous blow down valves to avoid back flow of the MP steam from the continuous blow down system .
- The level in the steam drum after depressuring must be controlled by closing the control valve and manually operating the globe valve upstream of the control valve.BFW flow through the preheat coils must be maintained.
- The main transfer line block valve should be closed switching the dilution steam heater effluent to the heater decoking system. The heater is cooled in this way to a safe temperature and then the dilution steam should be discontinued.

4.8 LOSS OF INDUCED DRAFT FAN

Loss of induced draft fan will automatically trip the heater to total shut down mode. During the I.D. Fan trip, the following actions occur on the affected heaters:

- The hydrocarbon feed valve will close, the dilution steam flow will continue at the last controlled value. The hearth burner fuel valves will also close.
- In all cases, the dilution steam flow is continued and the heater is cooled.

4.9 LOSS OF BOILER FEED WATER

Loss of boiler feed water to an individual heater will cause a low level in the steam drum and a trip of that heater. For all heaters, the trip will cause the following actions:

- The hydrocarbon feed valve will close and the dilution feed valve will remain in the last controlled position.
- The I.D.Fan damper will remain under normal pressure control. The stack gas temperature should be closely monitored.

4.10 LOSS OF STEAM SUPERHEAT TEMPERATURE CONTROL

This emergency can arise due to either loss of injection water or the failure of the temperature controller. In this situation, if normal operation of the heater is maintained, steam temperature at the super heater outlet will increase to the trip temperature and the tube metal temperature of the coil (in convection section) may approach its design temperature. This is a severe overstress condition for both the super heater tubes and the external piping and must be avoided.

4.11 FIRE IN FIRE BOX

In case of fire in fire box, the following safety measures must be taken:

- The cause of the fire is determined as quickly as possible. The fire box can stand moderate fire within its enclosure.
- If the fire is a result of a massive coil breakage, it will be necessary to block in the feed. A large rupture can cause a positive firebox pressure which is an unsafe condition.
- The stack damper is opened to increase firebox ventilation. This is done slowly if unburned fuel is in the fire box.
- As hydrocarbon feed is removed,increase the dilution flow to permit controlled cooling of the heater as monitored by the outlet temperature.

- If the rupture is massive,the heater is tripped and the heater effluent is switched from the transfer line to the decoke line as soon as the feed can be removed .This will prevent back flow from the transfer lines of the other heaters.

4.12 DECOKING

Coke formation during thermal cracking is a complex phenomenon (Salari et al., 2010).Coke formation and equipment fouling in steam cracking furnaces in the ethylene industry still remain a major operation problem. Ethylene producers have been actively seeking ways to reduce coke formation in order to achieve longer furnace run length (Cai et al., 2006). The steam cracking reactions are always accompanied with the formation of coke which deposits on the walls of the tubular reactors (Salari et al., 2007). Heaters can be decoked on a regular basis for operating flexibility. This offers certain advantages with regard to scheduling of decoking utilities and manpower. A fixed decoking schedule coinciding with the design run length should provide smooth and trouble free operation of the heaters. Lengthening of the run cycle between decoking will minimize the cost of decoking and maximize the heater on-stream factor, thus increasing profitability. Coke formation in naphtha cracking reactors decreased the product yields, heat transfer and reactor life (Salari et al., 2007).

The cracking heaters require decoking when one of the following conditions occurs:

- The maximum radiant tube coil tube metal temperature reaches maximum limit.
- When fouling causes the primary TLE outlet temperature to reach its mechanical limits.
- When the heater is shut down under emergencies such as power failure, dilution steam failure, feed failure, manual or automatic trip. If the radiant coils have been cooled after more than several days operation, and then brought back in to the service without decoking, spalling of coke from the tubes walls usually occurs and can plug the radiant tubes or the primary TLE's. Severe plugging of the primary TLE's may require mechanical cleaning. It is important to decoke coils before cooling, as aged tubes have been found to crack f quickly cooled over a layer of very hard coke. When cracking heavier feeds, palling seems to be a less serious problem than with lighter feed because the coke is softer and spalls in pieces small enough to go through the TLE's. If a shut down occurs on a heater, which has been in operation for less than two days, a full decoking may not be necessary.

Table 4.1 Major accidents in process industries (Khan and Abbasi 1999b).

Sl no	Date	Location	Chemical	Event	Deaths/injuries	Cause	Remarks
1.	Aug. 27,1955	Whitting, Indiana	Naphtha	Explosion	2/30	Contamination of inert gases during startup procedure.	The inert gas was carried was carried through put the recycle system and the oxygen was provided by the accidental and undetected leak from the regenerator to the reactor vessel and due to the skin temperature of the recycle furnace, the explosion occurred.
2.	Feb. 25,1971	Longview, Texas	Ethylene	Explosion	6/40	Breakage of pressurized ethylene gas pipe line and formed a vapor cloud and resulted in an explosion	The explosion broke numerous other pipes and caused the release of many thousands of pounds of ethylene.
3.	Feb.10,1975	Antwerp, Belgium	Ethylene	Explosion	6/13	Leakage of ethylene	The leakage was caused at high pressure due to fatigue failure of a vent connection on the suction of a compressor.
4.	Nov.7,1975	Beek,	Propylene	Explosion	14/108	Failure of propylene	The leak was for about half an

		Netherlands				compressor system which resulted in the opening of flow valves of the cracked compressed gas.	hour. Gas flowed through a pressure control valve and the pressure build up in the depropaniser prevented transport from the feed drum.
5.	July 11,1978	San Carlos, Spain	Propylene	Explosion	215	Accident of the truck containing propylene	An explosion occurred by an overloaded 38ton tank truck carrying combustible propylene gas skidded around a bend in the road and slammed into a wall sending 100 ft high flames into a campsite where 780tourists were present.
6.	May19,1985	Priola, Italy	Ethylene	Fire	23/11	Leakage of propylene which was ignited by hot steam piping	The intense fire rapidly engulfed the adjoining ethylene & propylene distillation columns and spread about 180 ft to the storage area. Five of eight ethylene & propylene tanks got exploded.

7.	Sep.12,1985	Quantum's Morris, Illinois, U.S.	Ethylene	Explosion	7/12	Leakage in the acetylene converter area.	The explosion continued for most of the day which occurred due the failure of acetylene converter preheater.
8.	July 3,1987	Antwerp, Belgium	Ethylene oxide	Explosion	-/14	Decomposition of ethylene oxide and accompanied by a fire ball	This was caused due to the leak of ethylene oxide in to the insulation, leading to self heating and then ignition of the leak resulting in the heating of ethylene oxide in the column itself.
9.	Aug.15,1987	Ras Tanura, Saudi Arabia	Propane	Explosion	-	Leakage of propane gas from one of the two parallel gas fractionation trains.	The release continued for about half an hour and a large vapor cloud formed and ignited which caused damage to the property.
10.	May 5,1988	Narco, Louisiana	Propane	Explosion	7/28	Rupture due to internal corrosion in the depropaniser overhead piping.	Vapor cloud explosion took place which caused extensive damage & intermediate failure of all utilities.

11.	Dec.24,1989	Baton Rouge, Louisiana	Ethane and propane	Explosion	-/7	Rupture of pipeline a mixture of ethane & propane.	This led to vapor cloud explosion leading to the extensive damage of two large storage tanks, twelve small tanks and two separator units
12.	Mar.7,1989	Antwerp, Belgium	Ethylene Oxide	Explosion	-/5	Low cycle fatigue had caused a hairline crack in a welded seam on piping t a level indicator system, resulting in a small leak of ethylene oxide.	This led to an accumulation of auto oxidable polyethylene glycols in the insulation that reached a temperature which was sufficient to cause a decomposition of ethylene oxide.
13.	Oct 23,1989	Pasadena, U.S.	Ethylene	Explosion	23/300	Leakage of ethylene	The separation distance between process equipment plants was not according to the regulations and did not allow time for personnel to leave the plant safely during the initial vapor release and the separation distance between the control room and the reactors was insufficient to

							allow emergency shutdown.
14.	Nov.6, 1990	Nagothane, India	Ethane and Propane	Explosion	31/-	A leakage occurred in the pipe line transporting ethane & propane to a gas cracker complex.	Vapor cloud formed & ignited at an offsite gas treatment & compression facility causing the death of 31 people and severe damage to offsite units.
15.	March 12, 1991	Seadrift, Texas	Ethylene oxide	Explosion	1/-	Temperature of the reboiler reached 500^0C instead of 60^0C,combined with unknowing catalytic reaction which resulted in the decomposition of EO.	A low circulation reaction in the reboiler could give in some of the tubes low flow, loss of liquid film & stagnant vapor.
16.	Aug. 8,1994	Exxon's Rouge, U.S.	Naphtha	Explosion	-/7	Quench oil failure	Explosion occurred in quench oil failure resulted in extensive damage to the larger train of the two train steam cracking unit. The fire burned for about 52 hours.
17.	July 27,1996	Channelview, Texas, U.S.	Ethylene	Fire	2/13	Leak in ethylene product pipe line.	Fire continued for less than two hours, until the ethylene burned off. The fire damaged electrical utility service to the

							site
18.	June 22,1997	Texas, U.S.	Ethylene & propylene	Explosion	-/1	Leakage of ethylene	High pressure gas release from cracked gas compressor which resulted in the formation of vapor cloud which exploded on reaching the ignition source.

5.1 DEFINITION

Hazard and operability (HAZOP) methodology is a Process Hazard Analysis (PHA) technique used worldwide for studying not only the hazards of a system, but also its operability problems, by exploring the effects of any deviations from design conditions .HAZOP study is a systematic procedure conducted by a team of experts indifferent disciplines to identify and assess hazard using brainstorming discussions of deviations in operational parameters from normal/standard conditions. These deviations are generated by using standard guide words. Normally, the team of experts of different disciplines will sit together to identify and assess the hazards associated with each and every process/plant component by analyzing the behavior of process process/plant component under deviation from the normal operation. Moreover, HAZOP study is applied to a continuous plant and the modification of this study can also be applied to batch plants (Kletz, 1997).

5.2 CONCEPT

The Hazard and Operability (HAZOP) study was originated in the late 1960's and developed as a practical method for problem identification in the process industries in the early 1970's at the ICI, UK (Kletz, 1999).HAZOP study is one of the most common tools to accomplish hazard assessment qualitatively. It involves a detailed study of each and every part of the entire process line from start to finish with the help of "Piping and Instruments Diagrams" (PID's) covering each and every vessel, conduit, valve, and other control equipment employed in the process line. In HAZOP, these PID's are studied in relation to the operation of the process, the causes that may lead to variations in the plant operation due to human errors, process, or material failures, and the likely consequences. HAZOP thus takes in to consideration the conditions such as temperature, pressure, creep, fatigue, etc., under which the physical parts are used, the aspects of human interaction with piping and instruments, and the possible aberrations that may occur due to human errors, loss of process control, or material failures.

5.3 PRINCIPLE

The basic principle of HAZOP technique is that hazards arise in a plant due to deviations from normal behavior. In HAZOP technique, process piping and instrument diagrams (PID;s) are examined systematically by a group of experts (HAZOP team)and the abnormal causes and adverse consequences for all possible deviations from normal operation that could arise are found for every section of the plant,(Crowl 1990).Thus, the potential problems in the process pants are identified. The HAZOP team is multi disciplinary team of experts who have extensive knowledge on design, operation, and maintenance of the process plants. The HAZOP team members try to imagine ways in which hazards and operating problems might arise in a process plant. To cover all the possible malfunctions in the plant, the imagination of the HAZOP study team members is guided in a systematic way using a set of 'guide words' for generating the process variable deviations to be considered in the HAZOP study.

5.4 GUIDE WORDS

The sets of guide words that are often used are NONE, MORE OF, LESS OF, PART OF, and MORE THAN (Leone.H. 1996).When these guide words are applied to the process variables in each line or unit of the plant, we get the corresponding process variable deviation to be considered in the HAZOP study. A list of guide words with their meaning and the parameters where they can be applied are give below:

5.4 Guide words & meanings in HAZOP STUDY

Guide words	Meaning	Applicable to following parameters
NO/NONE	Complete negation to intention	Flow rate, level, Capacity
MORE	Quantitative increase temperature level	Flow rate, Pressure
LESS	Quantitative decrease	Flowrate,Capacity,Pressure,Temperature,Level
PART OF	Only part of intention is fulfilled	Concentration, Signal
REVERSE	Logical opposition of design intention occurs	Signal, Flow
OTHER THAN	Complete substitution	Concentration, Signal

5.5 HAZOP STUDY PROCEDURE

The HAZOP study procedure consists of four main activities:

1. Selection of study team and procurement of relevant information.
2. Brainstorming discussion.
3. Preparation of uncleared points.
4. Report writing.

Steps 2 and 3 are most crucial since the total study duration is depending on these steps as well as effectiveness and reliability of the results. The report writing step is again a dependent activity on the second and the third step.

5.6 HAZOP STUDY METHODOLOGY

In simple terms, the HAZOP study process involves applying in a systematic way all relevant guide words to the plant in question in an effort to uncover potential problems (Kletz, 1999).The results are recorded in columnar format under the following headings:

5.6 Columnar format of HAZOP study

GUIDEWORDS	DEVIATION	CAUSE	CONSEQUENCE	SAFEGUARDS	RECOMMENDATION

5.7 REQUIREMENTS

5.7.1 Assemble the Data

All relevant documentation should be collected beforehand (Crowl, 1990 and Khan et al. 1997).Typically this might consist of:

- A process flow diagram.
- A comprehensive process description containing operating parameters, flow rates, volumes, etc., as well as brief summary of how each plant item functions.
- P &ID's.
- Cause and effect charts setting out how control and trip system operate.
- Plant layout diagrams.
- Line arrangement either from isometrics or model if required.
- Pressures relief valve design data and design criteria.

5.7.2 Understand the Subject: It is necessary to gain a good understanding of how the plant is meant to operate, by studying the assembled data. A proper note should be made during the course of the study. Without a reasonable understanding of how the plant functions, it will be impossible to plan a sensible study strategy, decide how long the review is likely to take, or who needs to be included in the study team.

5.7.3 Subdivide the Plant and Plan the Sequence: If required, that subdivisions of the plant may be considered since it may be too burdensome for the study team to deal with all aspects and operations in the process simultaneously. Therefore, it must be split in to manageable sections. Also, the sequence in which these sections are studied is important.

5.7.4 Mark the Drawings: When the study strategy has been decided, a recording table is made where the plant items encompassed by each table should be marked in distinctive and separate colors, with the table numbers alongside in the same colour. Lines should be paralleled, and equipment and vessels outlined in the chosen colour.

5.7.5 Devise a List of Appropriate Guidewords: Having completed the work above, it will be a simple matter to formulate a comprehensive list of the guidewords required to cover all aspects of the process to be studied. Some companies, because most of the plant they operate is of a similar nature, will have a standard set of Guidewords. Such a list should be checked to ensure that it covers all aspects of the system to be studied.

5.8 Advantages of HAZOP

- Creative and flexible approach to identifying hazards
- Provides means to reveal hazards and operability problems at design stage
- Minimizes cost required to implement appropriate safeguards in new facilities
- Participants gain a thorough understanding of the system
- Good for new processes
- Methodical assessment of all deviations from design
- Easy to document, +/- 1 hour per section
- Can be performed at design stage and at operation stage

5.9 Limitations of HAZOP

- Requires well defined system or procedure
- Assumes design is correct for normal operations
- Easy to get sidetracked
- Is time consuming
- Requires trained personnel to conduct review
- Provides no numeric ranking of hazards
- Focuses on one-event failure
- Never guaranteed that all accident situations, causes, and effects have been considered
- Different expert's different assumptions/results
- Lack of experience of team members and leader
- Inappropriate team selection
- Inadequate/inaccurate information
- Shortage of technical information.

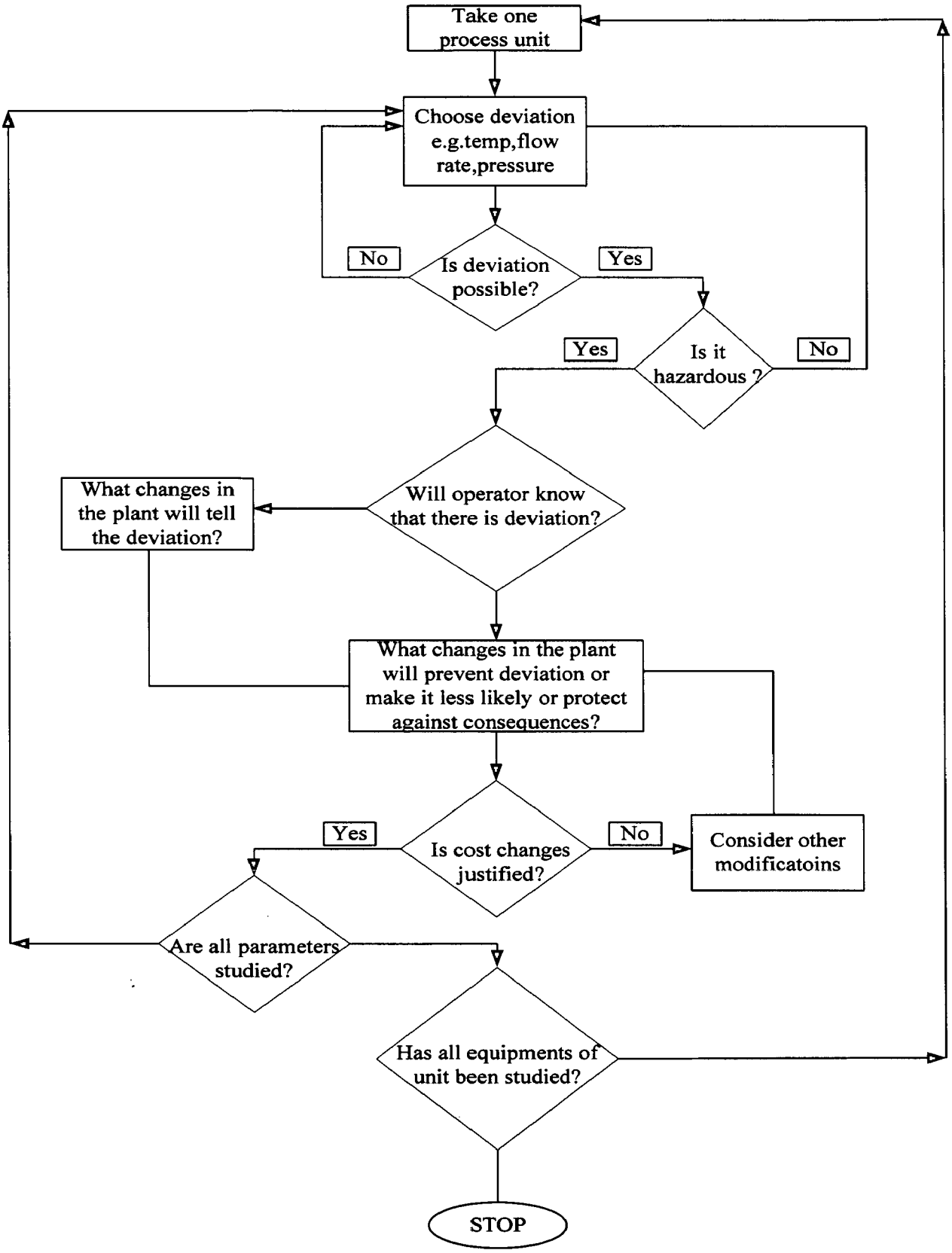

Figure 5.9 Procedure of HAZOP technique (Khan et al. 1997)

Table 5.9 CHARGE GAS COMPRESSOR

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
No	Low Flow	Main oil pump failure	Compressor/turbine bearing damage	Standby pump start	Review requirements for auto start of turbine driven pump when motor driven pump is in motion
More	High flow	PCV malfunction to open	Potential more flow of lube oil to compressor bearings	PSV open	Review to uprate pipe line & remove safety valve
Maintenance hazards		Lube oil treatment	Lube oil has to be clarified/treated while in operation		Provide recommended model details for the clarifier & provide suitable connections in the oil reservoir.
Less	Low Temperature	Decrease in temperature of inlet SHP steam	Potential difference over saturation at LP end of the turbine		Provide low temperature alarm
High	High Temperature	TV does not open on high temperature	Possible high temperature on exhaust hood	High alarm is provided	Provide manual jack on TV

Table 5.10 FUEL GAS VAPOURIZER SYSTEM

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
No	Low flow of L.P.G.	LIC malfunction to close	No LPG vapor available for fuel gas system. Fuel gas header pressure will not be maintained	PALL is provided for heater trip	Provide low pressure alarm.
More	High flow of LPG	LIC malfunction to open	Increase in level of LPG leading to entrainment of liquid LPG to vapor	PSV to take care of such eventuality	Provide High Flow alarm
Reverse Flow	Misdirected flow	LPG offsite pump trip	Reverse flow of fuel gas to LPG line leading to contamination of LPG		Provide a check valve on upstream on LPG liner.
More	High LPG pressure	LIC malfunctions to open	Increase in level of LPG causing entrainment		Provide high flow alarm

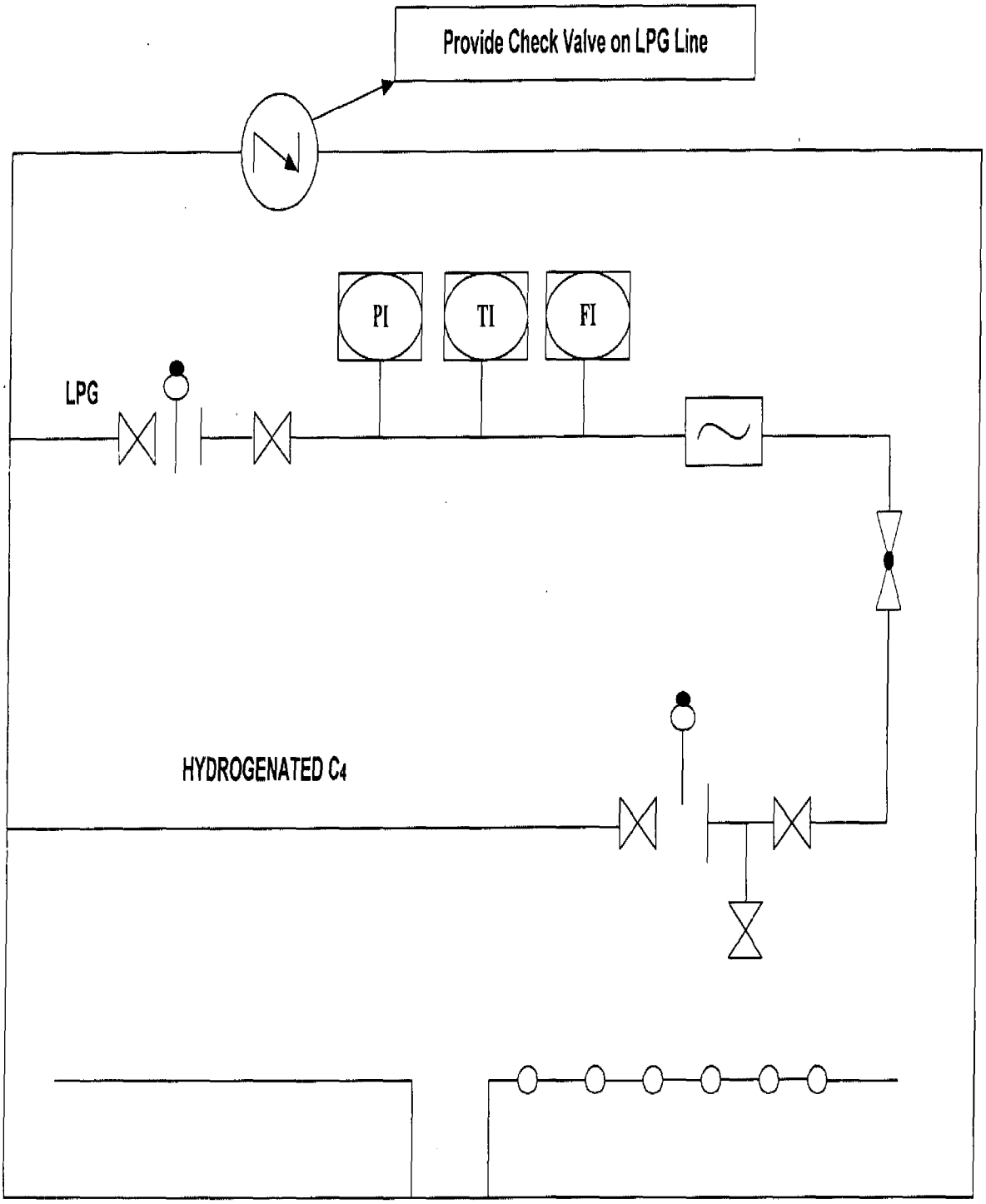

Figure 5.10 FUEL GAS VAPOURISER SYSTEM (REVERSE FLOW)

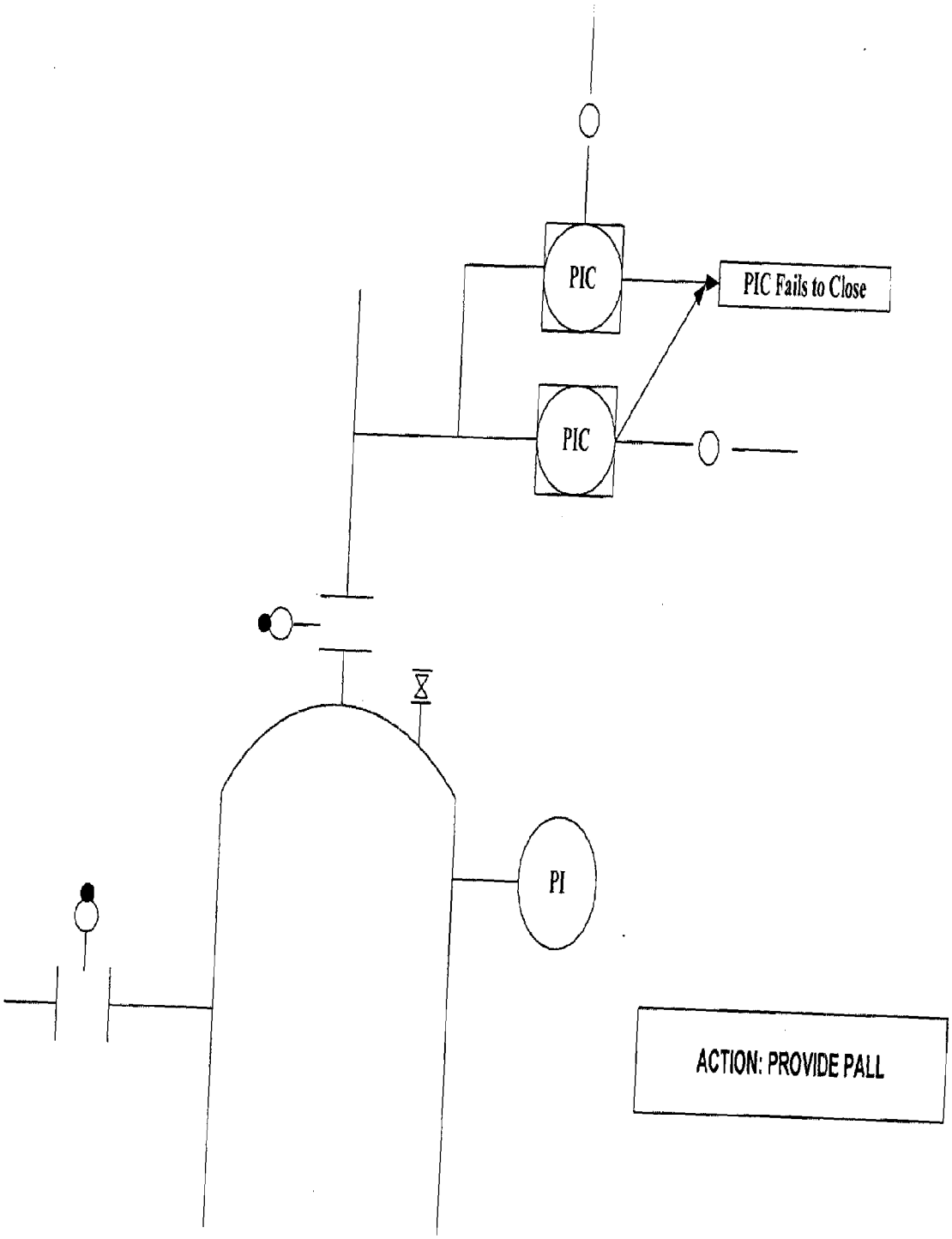

Figure 5.11 FUEL GAS VAPOURISER SYSTEM (NO/LOW FLOW OF LPG)

Table 5.11 DILUTION STEAM GENERATION

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
No	Low flow of MP steam	PIC malfunctions to close	No flow of MP steam leading to low flow of saturated /less superheated dilution steam & upsets in operation		Provide FAL
No	Low pressure	LIC malfunctions to close	No flow of MP steam leading to low flow of saturated /less superheated dilution steam & upsets in operation	PAL provided	Provide FAL
No	Low temperature	PIC malfunctions to close	No super heating of dilution steam		Provide TAL

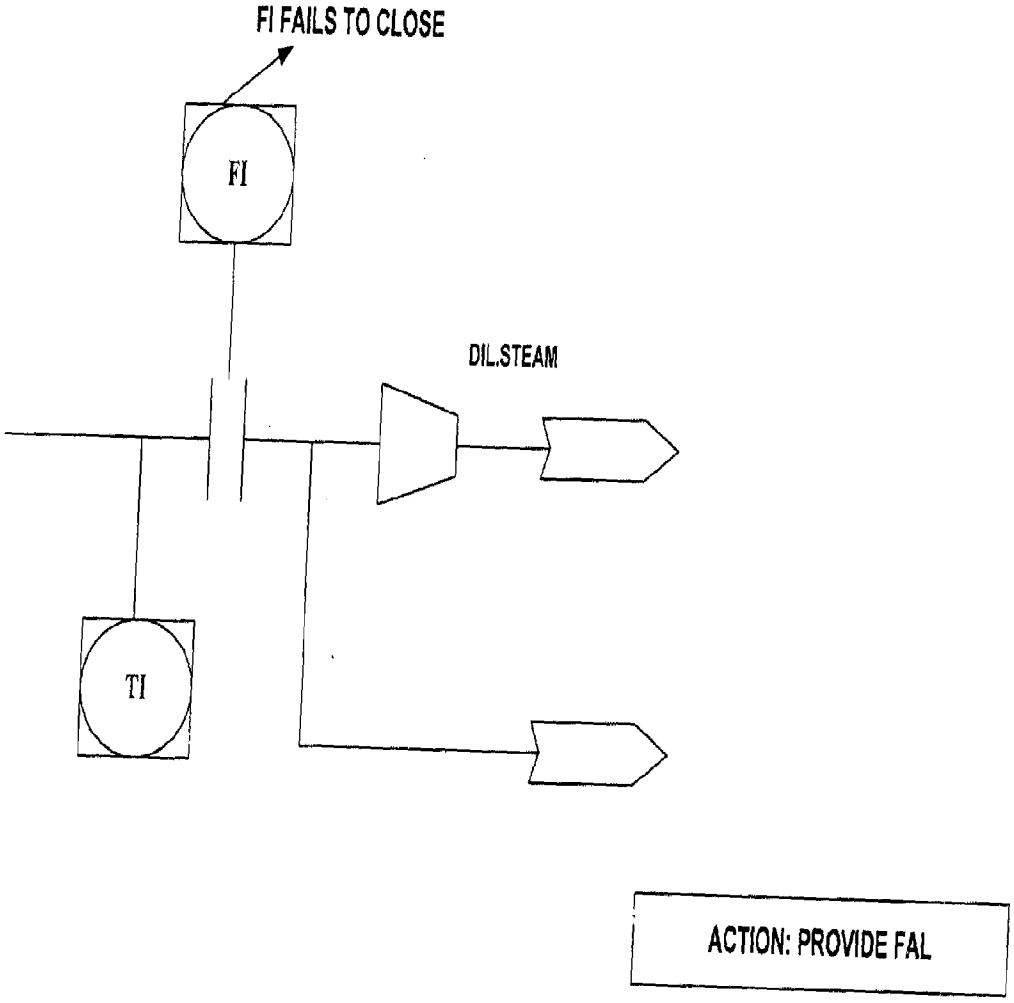

Figure 5.12 DILUTION STEAM GENERATION

Table 5.12 PYROLYSIS GAS OIL STRIPPER

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
No	Low flow of feed	LIC malfunctions to close	No flow of feed leading to accumulation of lighter components in PGO resulting in lower viscosity causing lower bottom temperature		Provide low Alarm
No	Low flow of purge oil	Trip	Loss of purge oil to instruments		Provide PAL
More	High flow of PGO product	FIC malfunctions to open	Pressure of purge oil to instruments may get disturbed		Provide PAL on PIC
More	High flow of LP steam	FIC malfunctions to open	More flow of LP steam leading to higher bottom temperatures		Provide TAH on TI
Low	Low pressure	PIC malfunctions to close	Low pressure in purge oil header going to instruments		Provide PAH on PI

More	High temperature	FIC malfunctions to open	More flow of LP steam leading to higher bottom temperatures		Provide TAH on TI
Low	Low temperature	FIC malfunctions to close	No flow of LP steam leading to lighter components in PGO product leading to lower bottom temperatures		Provide TAL on TI

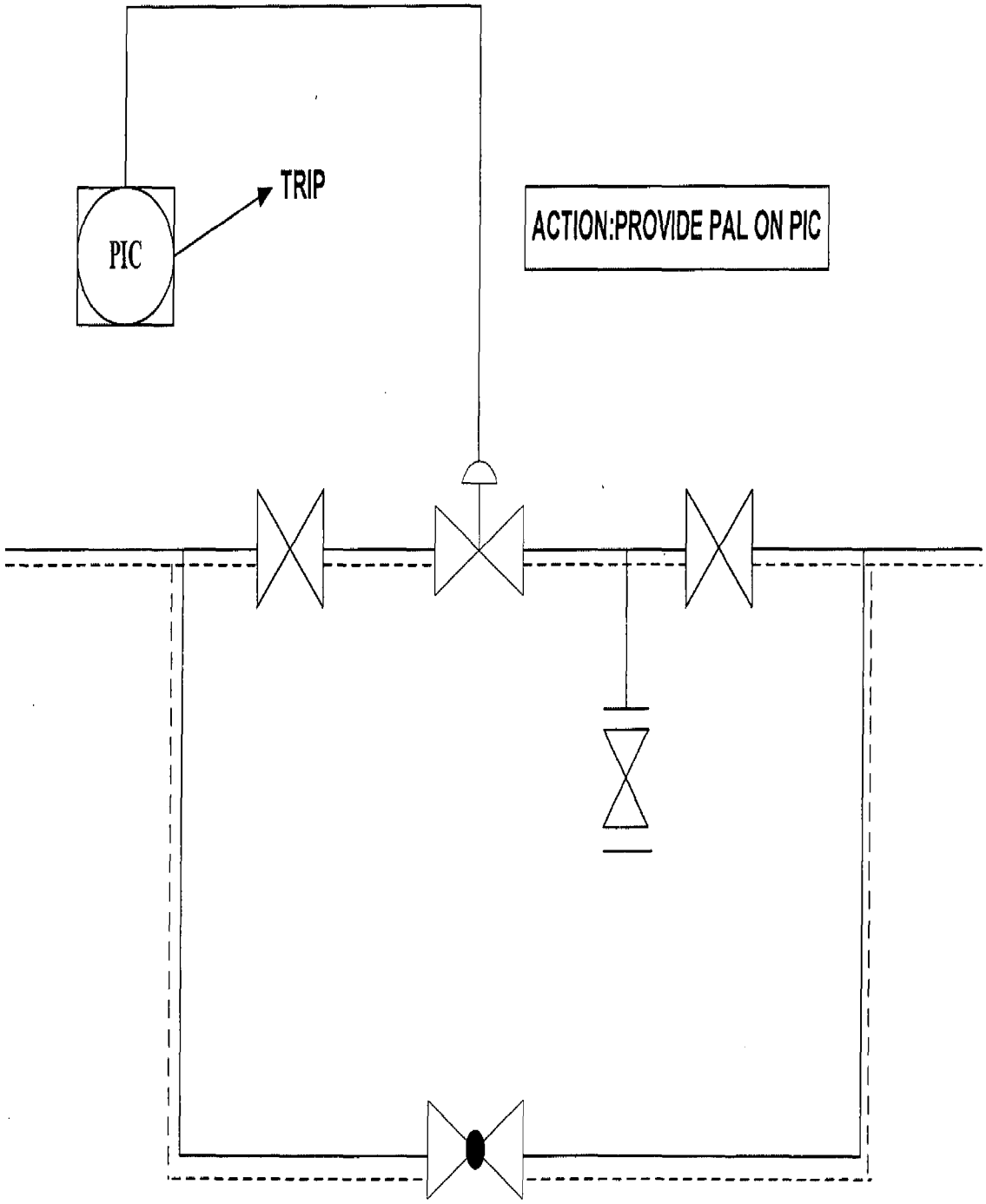

Figure 5.13 PYROLYSIS GAS OIL STRIPPER (NO/LOW FLOW OF PURGE OIL)

Table 5.13 PYROLYSIS FUEL OIL STRIPPER

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
No	Low flow	LIC malfunctions to close	No flow of feed to accumulation of lighter components resulting in lower bottom temperature		Provide low alarm
More	High flow of LP steam	FIC malfunctions to open	More flow of LP steam leading to higher bottom temperature		Provide TAH
More	High Temperature	FIC malfunctions to open	More flow of LP steam leading to higher bottom temperature		Provide TAH
Low	Low Temperature	FIC malfunctions to close	No flow of LP steam leading to lighter components in to PFO product leading to lower bottom temperature		provide TAL
No	No flow of feed	LIC malfunctions to close	No flow of feed leading to accumulation of lighter components in PFO resulting in lower viscosity causing lower bottom temperatures		Provide low alarm

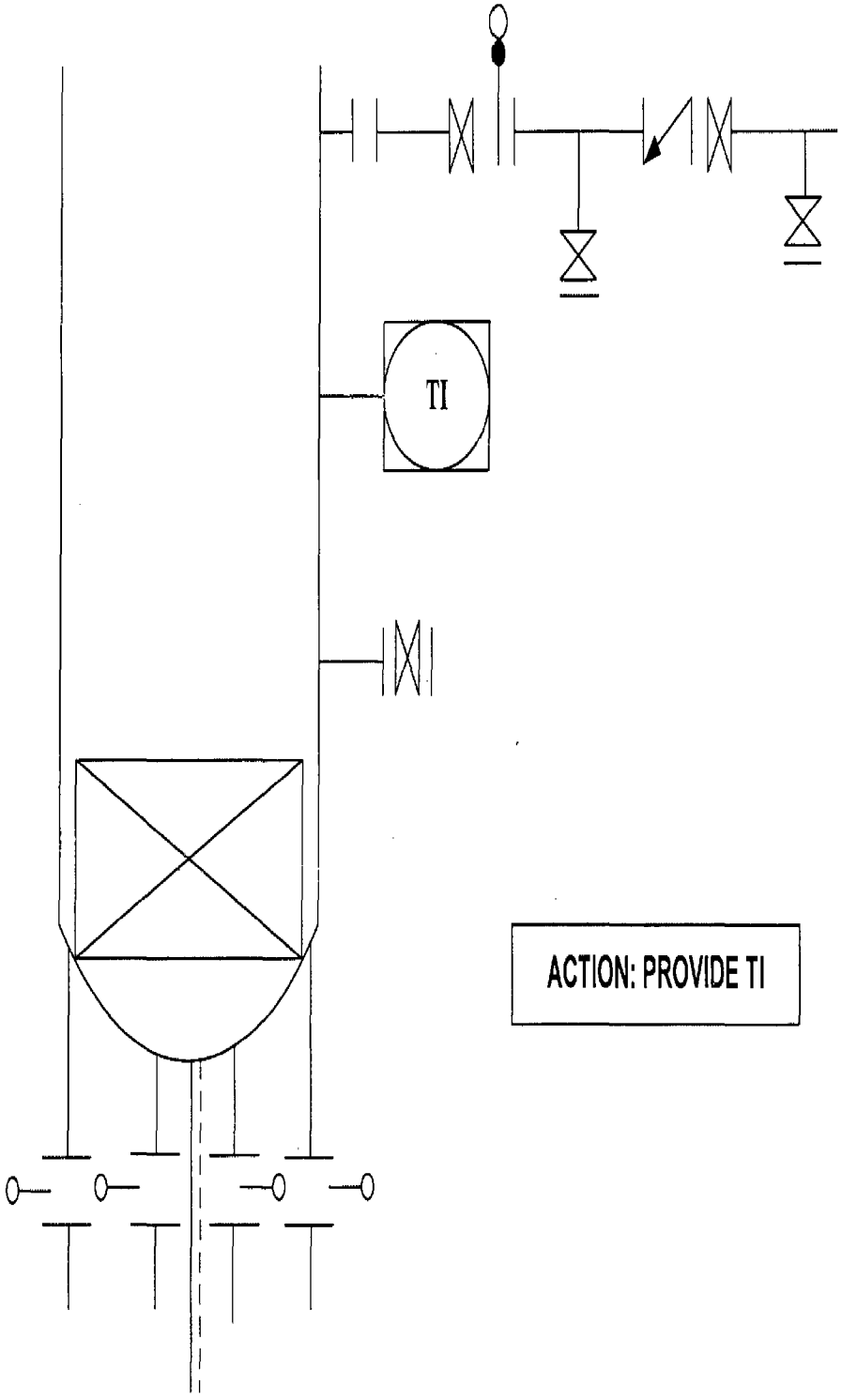

Figure 5.14 PYROLYSIS FUEL OIL STRIPPER (NO/LOW FLOW OF FEED)

Table 5.14 QUENCH TOWER

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
No	Low flow of quench water circulation	TIC malfunctions to close	-Temperature controllability of QW will be affected. -Higher temperature of PFO & PGO is obtained.		Provide TAL
More	High flow	FIC malfunctions to open	More flow of QW leading to low temperature. Flow of QW will be increased leading to lower temperature of QW overhead		Provide TAL
More	High temperature	T IC malfunctions to open	Increase in temperature		Provide TAH
Low	Low temperature	T IC malfunctions to open	-Temperature controllability of QW will be affected & temp. of bottom will decrease. -More flow of QW leading to lower temperature		Provide TAL

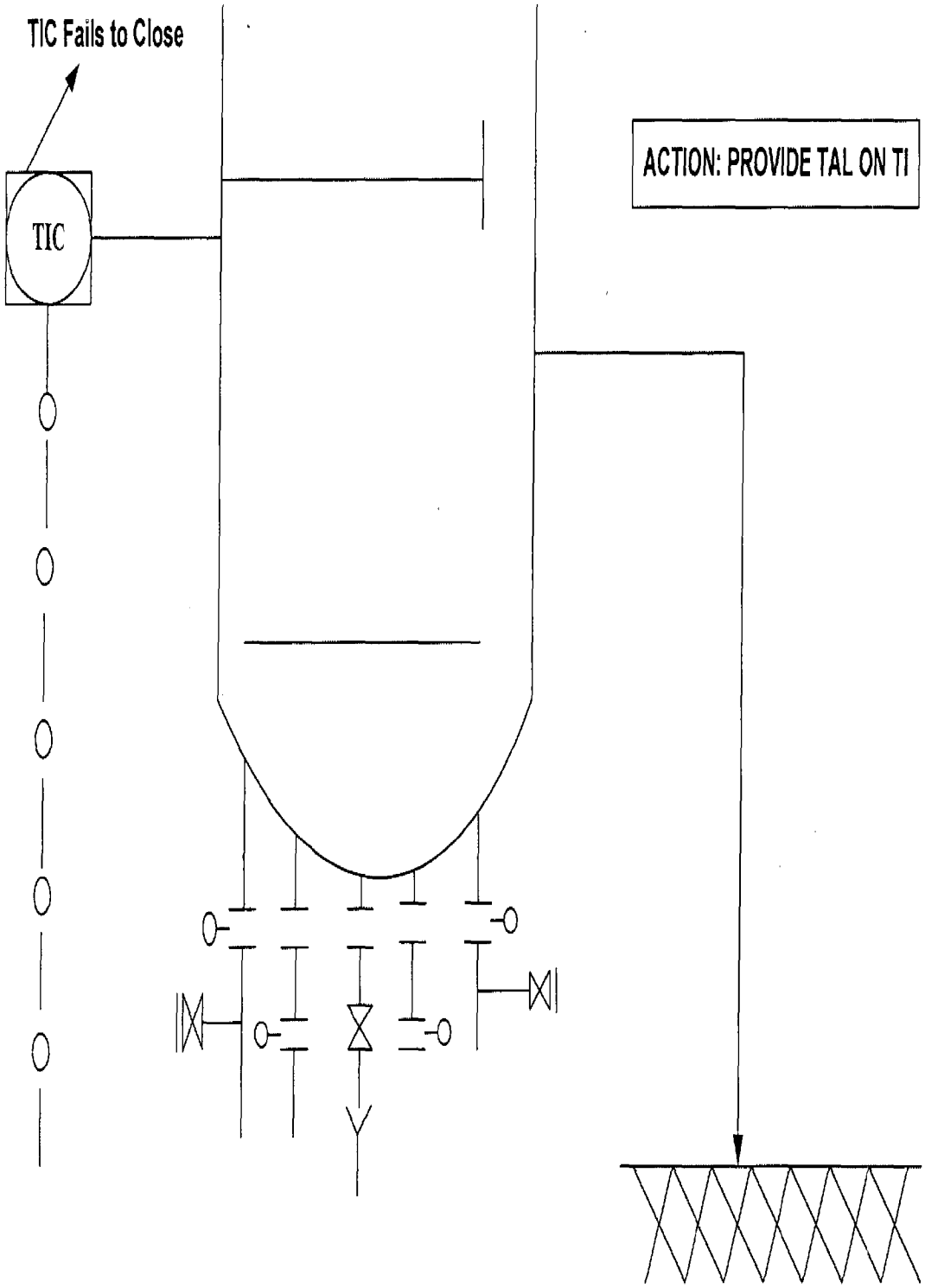

Figure 5.15 QUENCH TOWER

Table 5.15 CAUSTIC WASH TOWER

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
No	Low flow of charge gas	Tripping of compressor	Interruption to production	PIC provided to flare	To ensure compressor trip indication is provided in DGC
No	Low flow of blow down water	LIC malfunctions to close	No spent wash water removal leading to high level water wash section		Provide FAL
No	low flow of spent caustic to OSBL	LIC malfunctions to close	No flow of spent caustic		Provide FAL
More	High flow of spent gasoline	FIC malfunctions to open	More flow of spent gasoline leading to high level		Provide LAH on LIC

More	High flow of spent caustic to OSBL	LIC malfunctions to open	More flow of spent caustic		Provide FAH
No	Low pressure	PIC malfunctions to open	No transfer of spent caustic to OSBL		Provide FAL
High	High level	LIC malfunctions to close	No spent wash water removal leading to high level of water wash section		Provide FAL
Low	Low level	FIC malfunctions to close	No flow of spent gasoline		Provide LAL

Table 5.16 SHP STEAM BLOW DOWN SYSTEM

Guide Word	Deviation	Cause	Consequences	Safeguards	Action
More	high temperature	TIC malfunctions to close	Pump cavitation and possible damage	-	Provide TI with high temperature alarm on pump suction line
More	High flow of HP BFW	TIC malfunctions to open TV	More flow of HP BFW leading to low temperature in downstream of desuperheater		Provide TAL on TI
No	Low temperature	TIC malfunctions to open TV	More flow of HP BFW leading to low temperature in downstream of desuperheater		Provide TAL on TI

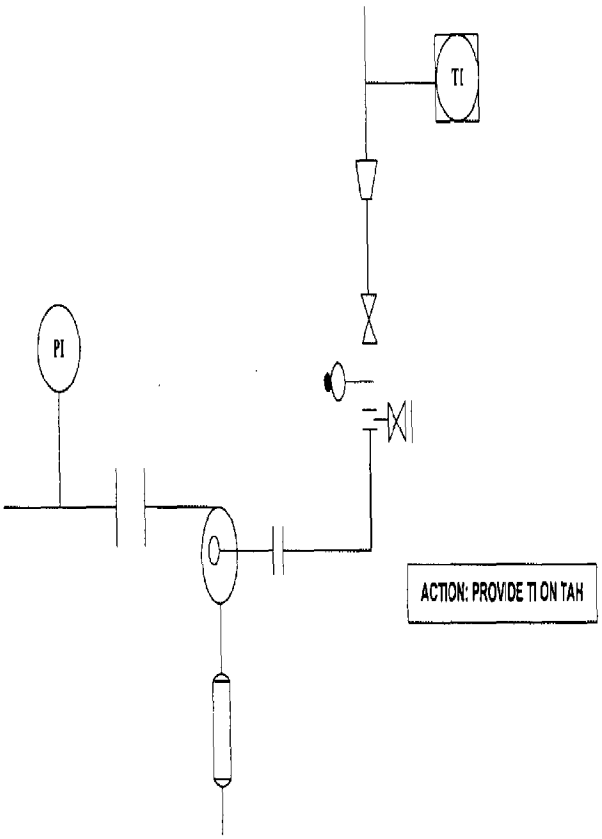

Figure 5.16 SHP STEAM BLOWDOWN SYSTEM

CHAPTER 6 RESULTS AND DISCUSSION

Light olefins (e.g., ethylene and propylene) are the most important basic petrochemicals, which are used to produce plastics, fibers and other chemicals. Most light olefins are produced by steam cracking .Cracking is a process to break larger molecules of hydrocarbons into smaller ones by heating. Naphtha cracking process is used for the production of olefins by using steam as diluent. The process takes place at high temperatures. So there are many possibilities for the hazards to take place. Some of the major hazards identified in the Naphtha Cracker plant are:

1. Loss of hydrocarbon feed
2. Loss of dilution steam
3. Loss of fuel
4. Radiant coil failure
5. Convection section hydrocarbon coil failure
6. BFW Preheat coil failure
7. TLE tube failure
8. Loss of Induced Draft Fan
9. Loss of Boiler Feed Water
10. Loss of Steam Superheat temperature control
11. Fire in firebox

The safety measures for the above hazards are discussed below:

Table 6.1 Hazards and Safety Measures in Naphtha Cracker Plant

SL.NO.	SECTION	HAZARD	SAFETY
1.	Loss of hydrocarbon feed	Tripping of interlock that will initiate tripping of heater.	Hydrocarbon feed valve should be closed immediately.
2.	Loss of dilution steam	Malfunction of dilution steam control system.	Heater should be totally shut down.
3.	Loss of fuel	Possibility of explosion of accumulated gas.	Complete close of all burners.
4.	Radiant coil failure	Heavy smoking or even flame in the heater which causes severe damage to the heater.	Heater must be shut down immediately.
5.	BFW preheat coil failure	BFW enters the hot convection section in contact with hot flue gases and heater surfaces which could result in a positive firebox pressure.	BFW control valve should be closed immediately.
6.	TLE tube failure	Tube rupture in the TLE will result in large quantities of high pressure boiler feed water flowing in to the process stream.	Main transfer line block valve should be closed immediately.
7.	Loss of Induced Draft Fan	Tripping of heater.	Feed valves, burner fuel valves are closed immediately.
8.	Loss of boiler feed water	Loss of boiler feed water will cause a low level in the steam drum and a trip of the heater.	Hydrocarbon feed valve and dilution steam valve should be closed.
9.	Loss of quench oil	Temperature in gasoline Fractionator increase rapidly	Immediate shutdown of the associated heater.
10.	Fire in the fire box	Development of positive pressure.	Close of feed valves, burners, fuel supply and immediate shutdown of the heater.

6.2 RECENT DEVELOPMENTS

Modern pyrolysis furnaces have evolved a great way compared to the early furnace designs. Most industrial furnaces built in the last decade can achieve thermal efficiency up to 98%. High olefins yield has been achieved with novel coil designs, which offer very short residence time. Efficient burners have also been designed to operate at low excess air to save fuel but still meet the NO_x emission limits. The greatest challenge for engineers today is to improve the on-stream factor by reducing the coke formation and to extend furnace life between tube replacements. The following are examples of technologies developed in recent years.

6.3 CHEMICAL TREATMENT

Sulphur-based compounds e.g. mercaptan, Dimethyl sulphide and Dimethyl disulfide, have been traditionally dosed into the pyrolysis coils after a fresh decoke cycle. These sulphur compounds converts the metal oxide sites on the tube wall surfaces into metal sulphides. Although the primary aim is to reduce carburization rate, it also reduces catalytic coking.

Sulphur treatment has limitations as the metal sulphides layer tends to be destroyed by flaking or even liquefied in the case of nickel sulphide. Other chemical additives for the same objective are silicon and phosphorus-based compounds. Each works on the same principle of forming a layer of diffusion barrier. By forming this barrier, catalytic coke is reduced. These techniques are not widely used, as they are relatively expensive.

6.4 TUBE COATING

Tube coatings practice the same principle of diffusion barrier but the pyrolysis coils are pre-coated during manufacture instead of online chemical dosing. These are typically glass ceramic coatings onto the tube walls.

A variant of this technology had a very successful campaign in a Canadian ethylene plant. The on-stream time was improved from an average 33 days to over 500 days before decoking was required. This technology has yet to be commercialized.

A HAZOP study has been carried out for some sections in Naphtha Cracker Plant. After collecting all the relevant information (such as P&ID, PFD, Process description, material properties, safety consideration) and identifying the different chemicals used in the process, the whole process has been divided in to several units (as study nodes), where a unit is defined as a part of plant or process having an independent unit operation and linked with other units to

complete the process. A unit can further be divided in to sub-units so as to study the unit thoroughly.

The sets of appropriate guidewords/keywords (NO, MORE, LESS, REVERSE, PART OF, AS WELL AS, OTHER THAN) are implemented in each of the nodes while conducting HAZOP study in naphtha cracker plant. Since it is a continuous process, a manual and qualitative HAZOP study is preferred effectively. The process units are operated at supercritical conditions, therefore any deviation or changes in the parameter (as temperature, pressure and flow) may lead to serious accident (violent reaction, damage by overheating, etc) and undesirable product since the product quality is sensitive (i.e., highly flammable & toxic).

After studying thoroughly the process description of naphtha cracker plant, it is found that certain deviations generate in the process unit which can cause serious accident and hazards to the environment. Now, let us discuss HAZOP study in each of the selected nodes and a brief result of HAZOP study carried out in Naphtha cracker plant.

6.5 DILUTION STEAM GENERATION

Proper safety operation of the unit process is necessary against hazards. Any deviation or changes in the parameter (as temperature, pressure, and levels of chemicals etc) may lead to serious accident and undesirable product since the product quality is sensitive (i.e., highly flammable & toxic).In view of this effect protective measures have been suggested as back flow protection, high/low alarm for pressure/temperature/level, relief valves should be activated.

Steam drum is used for controlling the parameters. High/low parameter may lead to excess development of pressure. A preventive corrective has been initialized in this system which will trip on high concentrations, high pressure trip/alarm or safety valves. Moreover, any deviation or change in the level in the steam drum may cause hazardous effect such as less water for cooling the reactor, runaway reaction in the reactor or rapid increase of heat load. All these effects can be avoided by implementing measures like safety relief valves, low level alarm & shutdown system, visual observation, proper inspection procedure and corrosion monitoring.

6.6 SUPER HIGH PRESSURE STEAM SYSTEM

The function of this system is to generate super high pressure (SHP) superheated steam using recovered heat from the heater flue gas in the stack and from the heater effluent in the TLE's. The prime objective, therefore, is to maximize the energy efficiency of the plant. Boiler feed water is fed to the BFW preheat coils in the convection sections, where the water is preheated against heater flue gas and then sent to the SHP steam drums. Saturated SHP steam is generated in the TLE's which are fed by thermosiphon action from the steam drum. The steam drum level controller controls boiler feed water flow to the steam drum with a pressure correction to the water density. The BFW flow control valve has a minimum stop set at approximately 20 percent flow. In the event this valve fails closed on signal failure, there will always be a continuous flow of water to the preheat coil to prevent overheating of the BFW preheat coil. This also acts directionally to protect the TLE's from running dry and overheating. At normal steam generation rates, however, the BFW flow (at approximately 20 percent minimum stop point) would not be sufficient to maintain level in the steam drum. A low and high level alarm is provided on each steam drum. There is an automatic heater shutdown on low water level in the steam drum.

A bypass is provided around the BFW control valve to be used manually for start up and low standby when the minimum stop on the control valve results in too high a flow to the drum.

6.7 QUENCH TOWER

Before the various pyrolysis products in the heater effluent can be separated and recovered the heater effluent must be rapidly quenched to stop the pyrolysis reactions. For the liquid feed heaters, the quenching of the heater effluent takes place in two steps. First, the hot effluent is rapidly cooled in the TLE's by heat exchange with high pressure BFW generating Super High Pressure (SHP) steam. The second step involves direct quenching of the TLE effluent in a quench fitting with cooled quench oil. Quenched effluent from the two quench fittings is then sent to the Gasoline Fractionator for further cooling and fractionation.

The amount of quench oil required for the liquid heaters will depend on the operating conditions (feedrate, S/HC, severity), the extent of fouling of the primary TLE's, the quench oil composition/temperature, and the set point of the after quench control.

The cooled quench oil to the fittings is taken from the Quench Oil Circulation Pumps discharge after it is filtered in the Quench Oil Pump Discharge Filters and cooled to 176°C in the Quench Oil/Dilution Steam Exchangers. A minimum flow signal ensures that a minimum quench oil flow is provided to the fitting at all times.

Three (3) of the four (4) quench oil circulating pumps are in normal operation with the fourth pump in auto-start mode based on a low quench oil pressure. In the event of a total quench oil circulation failure, temperatures in the transfer line (downstream of the quench fittings) and Gasoline Fractionator will rise rapidly (approaching the TLE outlet temperature). Thermocouples located downstream of the Quench Fittings will initiate an alarm. Loss of quench oil to a quench fitting requires complete shutdown of the associated heaters to protect the carbon steel metallurgy of the transfer line and the Gasoline Fractionator. Continuing feed to the heaters after loss of quench oil will result in equipment damage and is a potential safety problem.

Make up mater is supplied to the quench section. The changes or deviation of flow process of the makeup water in to the quench section may lead to high/low level of water in the quench section. This cause is due to the failure of flow controller, failure of pump or the line is blocked. A preventive corrective device (such as low & high flow alarm & trip) should be provided.

6.8 CHARGE GAS COMPRESSOR

Quench Tower overhead vapour (charge gas) is compressed in a 5-stage centrifugal compressor. Recycle streams from downstream units, off spec ethylene vapour and internal recycle streams of NCU are reprocessed in the charge gas compressor system.

Anti surge protection is provided for charge gas machine in case of sudden changes of the cracked gas flow rate occurs because of change of the load on the cracking furnace. (e.g. furnace trip) When the cracked gas flow rate changes, the response of FIC (3rd stage to 1st stage anti-surge controller) and FIC (5th stage to 4th stage anti-surge controller) is checked, especially when operating near the surge line. The failure to respond of the anti-surge valves would result in surging and could cause catastrophic damage to the turbine/compressor unit.

6.8.1 Suction Drum High Level

Routine checking of operability of Level Control Valve (LCV) at suction drum of the respective stages is necessary. If the liquid level is too low the LCV could pass gas back to a lower pressure stage, causing unnecessary energy losses. When the liquid level rises abnormally due to the malfunction of the LCV, the liquid could overflow into the compressor, causing vibration and damage to the compressor. Therefore, high level trip interlock systems are provided on each suction drum.

6.8.2 Compressor Discharge Temperature

The estimated discharge temperature of any stage is approximately 88 to 97 °C. Temperatures above this point increase the tendency for polymerization of the cracked gas and fouling of the compressor rotor. To prevent build-up of polymer (which forms in spite of the limitations put on the temperature rise) Wash Gasoline is injected into the suction line of each stage. The Wash oil is a hydrogenated C9+ product from Rerun Tower in PGHU. The wash oil flows as a liquid film through the compressor, reducing the opportunity for polymer to form on the metal surface.

6.8.3 Items Requiring Close Monitoring

- Gas temperature and pressure at the suction and discharge of the respective stages.
- The temperature of metals, bearings, etc.
- Abnormal noise and vibration of the compressor.
- Liquid level in Cracked Gas Compressor.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Pyrolysis furnace is an active research area for improved yields, increased capacity and fuel reduction. Pyrolysis is a series of free radicals reactions utilized in olefins production. High olefin yields are favoured by short residence time, high temperature and low hydrocarbon pressure. Steam is an inert added to reduce carburization and the hydrocarbon partial pressure. The reaction product spectrum can be estimated using empirical methods, rigorous solutions or a combination of both. Coke formation is a challenge to engineers trying to improve the furnace on-stream factor. Several new technologies have been developed to mitigate the coke formation challenge.

HAZOP study in naphtha cracker plant has been carried out successfully by showing all the possible causes and the adverse consequences of failure or malfunction of the process units. A preventive action and process modification has been performed after this HAZOP study, to safeguard the operating system from undesirable accident in future.

HAZOP study is a qualitative approach, therefore it consumes less time and easy to carry out compared quantitative analysis such as risk assessment, LOPA etc., and more, over this HAZOP study not only identifies the hazards, but also increases the operating life and performance of unit process and makes it environmental friendly.

7.1 FUTURE WORK

The present work described and concentrated logically on identifying the possible causes and consequences of variable deviations, but further and analysis may require assessing the hazards. LOPA (Layer of Protection Analysis), PHA (Process Hazards Analysis) etc, are the semi-quantitative analysis which required qualitative analysis (HAZOP study) results for conducting the analysis to assess the hazards.

Further, it is recommended that computer and artificial intelligence should be more extensively used for HAZOP studies as well as plant safety. Already a program (software) such as TOPHAZOP, iTOPS, HAZOPExpert, etc. are being proposed as easy and efficient way of doing hazop study. This is because; such system can facilitate HAZOP reviews at early stages of process development and design. This means that problems can be identified and rectified during

detailed design or while formulating operating procedures. Making changes once a plant is built is very expensive compared with changes at design stage. Early identification of hazards will also lead to effective avoidance or control of such hazards. HAZOP at this stage also help to develop confidence that the desired process is safe. Along these lines, the longer-term aim may well be to move towards process conception and synthesis to create inherently safer designs and operating plants that tend towards zero defects. A more immediate development could be the use of online hazard reviews for the training of the operators for abnormal situation management. The online hazard models can also be adapted for fault diagnosis applications. Intelligent systems are now well poised to make significant contributions to PHA in real life industrial settings thus improving the quality of the analysis while reducing the time and effort involved.

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