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OLEFINS

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1.0 SCOPE

This data sheet applies to the process of thermal cracking of hydrocarbons (e.g., ethane, propane, naphtha) to produce ethylene and propylene, the lightest olefins. The process unit can include both gas and liquid feeds, cracking furnaces, hot and cold sections, compressors, cryogenic fractionation, byproducts, and storage.

The recommendations in this data sheet are intended to prevent or minimize the effects of equipment failures, fires, and explosions involving these process units.

This data sheet does not cover the following technologies:

- Aromatic hydrogenation
- Membrane dehydrogenation of ethane
- Oxydehydrogenation of ethane
- Oxidative coupling of methane
- Methanol and ethanol to ethylene
- Dehydration of ethanol
- Ethylene from coal
- Disproportionation of propylene

1.1 Hazards

Olefin manufacturing facilities have inherent fire and explosion hazards due to handling liquified petroleum gas, flammable vapor, and ignitable liquids in combination with large fuel-fired and rotating equipment.

Additionally, these facilities are often highly integrated with process streams interconnected between multiple pieces of critical equipment. A fire (jet, 3D, pool), explosion (including vapor cloud explosion), or mechanical breakdown in one section of the process can create a cascading effect that may impact a multitude of upstream and downstream equipment.

FM loss history shows the leading cause of loss is mechanical or electrical breakdown, and/or loss of utilities, which can result in a fire or explosion.

1.2 Changes

January 2023. Interim revision. Minor editorial changes were made.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Introduction

Use FM Approved equipment, materials, and services whenever they are applicable and available. For a list of products and services that are FM Approved, see the *Approval Guide*, an online resource of FM Approvals.

2.2 Construction and Location

2.2.1 For construction and location of specific processes or equipment, such as cracking furnaces, compressors, transformers, tank farms, etc., follow the guidance in the applicable FM Property Loss Prevention Data Sheet. See Section 4.1 for a list of applicable data sheets.

2.2.2 Conduct a comprehensive facility siting study in accordance with Data Sheet 7-14, *Fire Protection for Chemical Plants*. Ensure the following considerations are included as well as equipment spacing and accessibility for safety critical emergency isolation valves, maintenance, replacements, emergency, and firefighting activities.

A. Locate control rooms, central and remote process I/O rooms, central utilities, motor control center (MCC) substations and emergency response facilities outside of areas exposed to blast damage. Where this is impractical, design these facilities with blast-resistant construction sufficient to withstand the expected blast loads.

B. Locate control buildings, cracking furnaces, ground flares and other fuel-fired equipment in the prevailing upwind direction of the main process plant.

2.2.3 Use noncombustible construction for modular-style buildings (e.g., motor control centers, remote instrumentation enclosures, power distribution centers). Ensure the following are addressed in the design:

- Wind effects
- Fire and explosion exposures
- Noncombustible insulation

2.2.4 Provide containment and emergency drainage for processing units where an ignitable liquid pool fire exposure or lube oil systems exist, in accordance with Data Sheets 7-14, *Fire Protection for Chemical Plants*, and 7-83, *Drainage Systems for Ignitable Liquids*.

A. Arrange drainage to avoid accumulation under pressure vessels or critical equipment. Walls, dikes, trenches, or channels are permitted to assist in draining the area. A minimum of 1% slope should be provided from the center of processing units or under critical equipment towards the perimeter of the unit.

B. For LPGs, if slope and containment are adequate, drainage is not needed. These materials are expected to vaporize before they can be effectively drained. Ground slope, walls, dikes, trenches, and channels should be arranged to avoid pooling under LPG storage or process vessels. Additional guidance is available in Data Sheet 7-55, *Liquified Petroleum Gas (LPG) in Stationary Installations*, and API 2510.

2.2.5 Provide damage limiting construction (DLC) for buildings with a room explosion hazard (e.g., compressor enclosures that might be required in cold climate regions for cracked gas, ethylene [C2], or propylene [C3]) in accordance with Data Sheet 1-44, *Damage Limiting Construction*.

2.2.6 Install and locate cable trays and safety critical cables in accordance with Data Sheets 7-14, *Fire Protection for Chemical Plants*, and 5-31, *Cables and Bus Bars*. Locate cable trays at the top of pipe racks, above process piping. Conduct process hazard analysis (PHA) for the routing and location of safety critical cables.

2.2.7 Install piping systems containing LPGs, flammable gases, and ignitable liquids at pipe rack bottom levels with utility service piping above. Provide fireproofing in accordance with 2.4.2(H).

2.3 Process Hazards/Safety

2.3.1 Establish a formal and complete process safety program in accordance with Data Sheet 7-43, *Process Safety*. Implementation is expected to be at the highest level of all chemical occupancies.

2.3.2 Conduct a global process hazard analysis (PHA) considering all modes of operation, including normal and emergency. Ensure the following scenarios are also evaluated:

- · Sudden site-wide utility and support service outages including nitrogen
- Load shedding schemes
- Natural hazards (wind, flood, earthquake, and freeze conditions) with post storm depressurization needs, unstable chemical handling (if any), and long-term utility interruption that include the ability to depressurize the plant
- Emergency isolation valves
- Major site-wide fire and explosion scenarios and how this impacts the site hazards
- Cyber attacks
- · Sudden major raw material pipeline and product pipeline disruptions

2.3.3 Conduct a flare header sizing study for combined relief cases such as external fire and loss of support services (power, steam, instrument air, etc.). Ensure revalidation is performed after changes.

2.3.4 Conduct an auto-refrigeration study to determine potential scenarios and equipment/piping that can be affected. Include in the study a means of detection as well as proper response and corrective actions. See Appendix A for additional information.

2.4 Protection

2.4.1 Provide fixed fire protection in accordance with Data Sheet 7-14, Fire Protection for Chemical Plants.

2.4.1.1 Provide monitor nozzles to ensure all areas of the process unit can be reached by a minimum of two nozzles at their maximum rated capacity, but not less than 1,000 gpm (3,800 L/min) combined.

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2.4.1.2 Provide a minimum water supply duration of four hours. The water supply should be capable of maintaining discharge and pressure requirements until the ignitable liquid flow can be shutoff and the area drained, or the ignitable liquid is consumed. Also consider the depressurization time for the largest inventory in the cold section.

2.4.1.3 Develop hose demands as part of the site-wide fire preplan.

2.4.2 Provide FM Approved fireproofing rated for a two-hour hydrocarbon fire exposure, or active fire protection for load-bearing structural steel and vessel supports with the potential for a 3D spill, long-duration pool, or spray fire, in accordance with Data Sheet 7-14, *Fire Protection for Chemical Plants*. Ensure the following critical process equipment are included:

A. Feed vaporizers/dryers.

B. Cracking furnaces. For liquid-fed or combined liquid/gas-fed plants, consider fireproofing for the furnace section where liquid feeds are vaporized. (See also Data Sheet 7-72, *Reformers and Cracking Furnaces*.)

C. Quench oil column and related quench oil coolers.

D. Pyrolysis gasoline separators/decanters.

E. Gas compressors (cracked gas, ethylene [C2], propylene[C3]) with lube oil systems, inter-stage suction tanks and inter-stage exchangers.

F. Separation columns in hydrocarbon fractionation areas with associated reboilers, condensers, and reflux drums/rundown tanks.

G. Hydrogenation reactors [acetylene, methylacetylene, and propadiene (MAPD)].

H. Pipe racks. Consider fireproofing or active fire protection up to the level containing LPG, flammable gas, or ignitable liquid piping.

2.4.3 Provide fire pumper suction headers within 200 to 300 ft (61 to 91 m) of the cold section to allow for onsite and/or mutual aid mobile equipment. For location of these headers, consider exposure to pooling ignitable liquids, and LPGs floating into containment areas around the cold section.

2.4.4 Provide fire protection for process control and I/O rooms where combustible construction and combustible loading is present in accordance with Data Sheet 7-110, *Industrial Control Systems*.

2.4.5 Provide a gas detection system throughout the cold section, hot section, quench section and compression section of the olefins unit. Install systems to alarm to a constantly attended location at the lowest practical level below the lower explosive limit (LEL). Follow manufacturer's guidelines for the installation of these systems. See Data Sheet 5-49, *Gas and Vapor Detectors and Analysis Systems*, for additional information.

2.5 Equipment and Processes

2.5.1 General

2.5.1.1 Provide adequate overpressure protection to process and storage vessels. Refer to Data Sheets 7-49, *Emergency Venting of Vessels*, and 7-88, *Outdoor Ignitable Liquid Storage Tanks*, for additional information.

2.5.1.1.1 Provide a means to depressurize equipment in the cold section and direct them to flares, capture devices, or other safe location.

2.5.1.1.2 Design waste gas and emergency relief systems to prevent, withstand and/or mitigate an autorefrigeration event.

2.5.1.2 Install automatic emergency isolation valves (EIVs) or emergency block valves (EBVs) to minimize the duration of a depressurization in an emergency shutdown. Install EIVs based on a hazard analysis, considering potential releases that exceed 10,000 gal (38 m³) (LPGs).

2.5.1.3 Do not use leak clamps in hydrocarbon service. If installed, do all of the following:

A. Include them in the management of change (MOC) program to ensure proper hazard analysis and manager approval is applied.

B. Establish a maintenance plan for regular inspection of the leak clamp in accordance with the manufacturer's recommendation, but not to exceed a quarterly duration.

C. Create a tracking system to ensure leak clamps are removed and reliable engineered repairs are made at the next outage (minor or major).

2.5.1.4 Provide real-time monitoring, alarms, and operational interlocks to ensure safe operation of process vessels and equipment. Install instruments and devices to facilitate online inspection, calibration, and maintenance. See Data Sheet 7-45, *Safety Controls, Alarms and Interlocks*, for additional information.

2.5.2 Cracking Furnaces

2.5.2.1 For cracking furnaces, follow the guidance in Data Sheet 7-72, Reformer and Cracking Furnaces.

2.5.3 Compressors

2.5.3.1 For compressors, follow the guidance in Data Sheet 7-95, Compressors.

2.5.3.2 Perform cleaning operations to remove any excessive accumulation from blades and vanes immediately after established vibration levels are exceeded.

2.5.3.3 Configure vibration monitoring equipment to alarm at established set points and automatically trip on excessive axial and/or radial vibration. Establish appropriate vibration alert (cleaning needed), alarm and trip settings in accordance with the compressor manufacturer's recommendations and/or operational history.

2.5.3.4 Provide radial vibration monitoring systems with high vibration alarms and high-high vibration trips.

2.5.3.5 Equip large motors that drive process compressors with suitable online condition monitoring in accordance with Data Sheet 5-17, *Motors and Adjustable Speed Drives*.

2.5.4 Steam Turbines

2.5.4.1 For steam turbines follow the guidance in Data Sheet 13-3, Steam Turbines.

2.5.4.2 Provide steam turbines that drive process compressors with throttle/stop valves to facilitate online exercising.

2.5.4.2.1 Provide electronic overspeed protection systems that facilitate simulated online testing.

2.5.5 Acetylene Converters

2.5.5.1 Provide interlocks to shut down feed if high temperature is detected, or if excessive acetylenic compounds are detected in the converter discharge.

2.5.5.2 Provide an interlock to shut off hydrogen flow in the event of high bed temperature or improper ratio control.

2.5.6 Cold Fractionation Section

2.5.6.1 Provide nitrogen purge through the cold box that include a flow meter or other means of flow detection to ensure nitrogen flow is maintained. Interlock the purge system to send an alarm to the control room on loss of or low nitrogen flow.

2.5.6.1.1 Provide the exhaust nitrogen stream with a hydrocarbon detection system which alarms to the control room upon detection of 25% of the lower explosive limit (LEL) by volume of hydrocarbons.

2.5.6.2 Develop a program to assess whether the cold-box is exposed to nitrous oxide buildup. If it is confirmed, conduct testing of the cold-box liquids for nitrous oxide crystals prior to turnarounds or when the cold-box has to be opened and/or inspected.

2.6 Operation and Maintenance

2.6.1 Operation

2.6.1.1 Implement an alarm management policy and conduct GAP surveys of the existing alarm and trip settings to reduce recurring, non-critical alarms and trips. See Data Sheet 7-110, *Industrial Control Systems, for additional guidance.*

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2.6.2 Maintenance

2.6.2.1 Establish an asset integrity monitoring program in accordance with Data Sheet 9-0, *Asset Integrity*. Include the following critical equipment in the program:

- Cracking furnaces
- Auxiliary boilers
- Vessels and piping
- Steam turbines (Consider turbines that drive large process compressors as specialty mechanical-drive steam turbines. See also Data Sheet 13-3, *Steam Turbines for maintenance and testing guidance.*)
- Compressors
- Fans
- Transfer-line exchangers
- Heat exchangers
- Electrical systems
- Large motor
- Critical process pumps, especially underground can type, which can be affected by corrosion and leakages
- Cold boxes (These can be affected by mercury embrittlement, especially those with LNG streams. Detail assessment is recommended to detect mercury depositions and early embrittlement signs.)
- Refrigeration systems

2.6.2.1.1 Ensure equipment where a high-temperature hydrogen attack (HTHA) could occur is included in the program. This includes equipment exposed to a hydrogen environment with temperatures over 350°F (180°C) and 50 psi (3.4 bar) such as, primary quench exchangers (e.g., transfer-line heat exchangers (TLEs)), acetylene converters and cracking furnace tubes.

2.6.2.2 Inspect, test, and maintain safety controls, alarms, and interlock in accordance with Data Sheet 7-45, Safety Controls, Alarms, and Interlocks.

2.6.2.3 Implement a positive material identification (PMI) program for alloys.

2.6.2.3.1 Perform an independent inspection of 100% of alloy replacement and construction parts using a PMI analyzer. For fasteners, welding rods, gaskets, etc., testing less than 100% of the batch is acceptable, but each batch should be sampled.

2.7 Training

2.7.1 Establish operator training programs in accordance with Data Sheet 10-8, Operators.

2.8 Contingency Planning

2.8.1 Ensure a viable equipment contingency plan and/or equipment breakdown sparing is in place to reduce downtime caused by equipment breakdown. See Data Sheet 9-0, *Asset Integrity*, and the following data sheets for additional information:

- Data Sheet 5-4, Transformers
- Data Sheet 7-72, Reformer and Cracking Furnaces
- Data Sheet 7-95, Compressors
- Data Sheet 13-3, Steam Turbines
- Data Sheet 13-17, Gas Turbines

2.9 Ignition Source Control

2.9.1 Locate analyzer houses, motor control centers (MCC), and remote instrumentation enclosures (RIE) outside of main process units and electrically classified hazardous areas. These areas often contain electrical equipment which are not rated for hazardous areas.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Loss History

A summary of FM losses for this occupancy is presented in Figure 3.1-1.



Fig. 3.1-1. Losses by peril (2000-2020)

Equipment breakdown represented 36% of the total losses, with cracking furnaces being the main equipment affected. Fire was the initial cause in 29% of the losses, while electrical breakdown caused 28%, with transformers as the main equipment involved.

During the 20-year period, large losses (>US\$50 million) with extended business interruption periods were observed at this occupancy. For most of these losses, the cost of this period accounted for 60%-80% of the total loss.

Outside FM, losses for the petrochemical industry presented by Marsh in their 2020 report (Figure 3.1-2) showed explosions as the lead cause, with 58% of the total number of losses. Olefin plants accounted for more than 20% of the total number of losses in this industry during this 45-year period.



Fig. 3.1-2. Petrochemical industry losses presented by MARSH (1974-2019)

3.2 Illustrative Losses

3.2.1 A transformer suffered a catastrophic electrical failure followed by oil spray and fire, creating a complete shutdown of the plant due to loss of cooling water and electrical supply. Several pieces of equipment were damaged, including tubes in the cracking furnaces.

3.2.2 A fire in a cracking furnace was initiated by quench oil that back-flowed and entered the firebox through fractured radiant tubes. Quantities of burning oil flowed through drains at the bottom of the firebox, causing the fire to spread up the entire exterior side of the furnace that houses 8-10 rows of natural gas-fired burners.

3.2.3 A fire in a cracking furnace was initiated on the transfer line that connected the cracking furnaces to the gasoline fractionator, damaging furnaces steel structure, piping, electrical systems, and instrumentation. All process units in the plant were shut down as a result of the fire. The plant restarted operations almost a month after the fire.

3.2.4 A fire and explosion occurred at the flare system, causing damage to power and control wire cable trays, vessels, and piping, shutting down one of the ethylene plants. Damage to tubes in 4 of the 7 cracking furnaces also occurred as a consequence of the uncontrolled shutdown.

3.2.5 During a large storm, lightning struck one of the substations, causing damage to a relay, with a subsequent plant shutdown. The sudden loss of power resulted in a trip of fuel for burners and flow of product into the cracking furnaces. With furnace tubes in excess of 2,000°F (1,100°C) without proper feed, tube rupture started to occur.

3.3 Process Description

Olefins are unsaturated hydrocarbon compounds containing at least one carbon-to-carbon double bond, also referred as to alkenes. Olefins are basic building blocks for many chemical syntheses. They are very versatile and reactive materials, widely used to manufacture polymers, chemical intermediates, fibers, synthetic rubber, etc. The two most important olefins are ethylene, and propylene, as they form the backbone of the petrochemical market.

Light olefins are mainly produced by steam cracking, where a liquid or gas hydrocarbon feedstock is used. Common liquid feeds are gas oil and naphtha whereas gas feeds are ethane, propane, and butanes. The choice of the feedstock for olefin production depends on the availability of raw materials and the desire range of downstream products. Naphtha has made up about 50-55 percent of ethylene feedstock sources since 1992. The cracking of liquid or gas feedstocks follows the same basic principles; however, adjustments considering the different technologies available and process conditions needs to be made for each feedstock.

There are several different configurations of olefin plants in operation; nonetheless, they all operate using different processes within two basic sections, which are commonly known as hot and cold sections (Figure 3.3). The hot section is where the cracking reactions occur to form different olefin products. These reactions take place in furnaces with a short time residence under the addition of steam. The hot gases containing the olefins products are quenched. For liquid feedstocks, the first quench uses oil that recovers fuel oil, and the second quench uses water where aromatics are recovered. Gas feedstocks use water quench. The light C2/3/4 olefin gases are then compressed, washed in a caustic tower, and dried before they are sent to the cold section for separation.

Before being fed to any of the fractionation towers in the cold section, the dried cracked gas must be cooled and partially condensed in the cold box to be later separated into the desired products by using a complex sequence of separation and chemical treatment steps.



Fig. 3.3. Olefin process

3.3.1 Gaseous Feed Olefin Units

These units use light, gaseous feedstocks like LPG (liquefied petroleum gas, mostly consisting of propane and butanes), or NGL (natural gas liquids, mostly consisting of ethane, propane, butanes) to generate olefins. These raw materials are mostly obtained from wet natural gas sources and refinery waste gases. The feed gas can also include contaminants such as carbon dioxide, acetylene, arsenic, mercury, carbonyl sulfide, nitrogen oxides, oxygen, and the like, which must generally be removed or treated. Mercury (Hg) contamination can lead to corrosion of aluminum heat exchangers in the cold process sections.

The most important products from olefin plants are ethylene and propylene. Gaseous feed cracking furnaces typically have a capacity of 1.5 to 2 times more than liquid feed furnaces (up to 280,000 – 330,000 ton (250,000 – 300,000 tonnes) compared to 140,000 – 220,000 ton (130,000 – 200,000 tonnes) per furnace) related to the ethylene output. Light (gaseous) feedstocks generally offer higher yields of these products compared to heavy (liquid) feedstocks and therefore require lower amounts of feedstock. The highest yield (more than 50 wt% of ethylene) can be achieved with an ethane feedstock, but ethane is very stable compared to other feed materials requiring higher temperatures at the furnace coil inlet to achieve a good conversion rate. While it is possible to crack ethane in all types of furnaces (with lower temperatures at furnace coil inlet), sometimes separate furnaces for ethane cracking are used to avoid large ethane recycle streams in the process plant (especially in naphtha feed units).

Major differences between gas feed and liquid feed olefins plants are based on the creation of byproducts. With gas feed, less amounts of heavy byproducts (pyrolysis gasoline, benzene, etc.) are generated, but more light byproducts (hydrogen, methane, etc.). While the basic process principles are the same in gaseous and liquid feed plants, the front-end section of a gaseous feed plant is less complex compared to a liquid feed

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plant since this is the part of the process where heavy fractions are separated from the cracked gas stream. In gaseous feed units, heavy hydrocarbons can be removed from the cracked gas stream in the water-quench column (see Figure 3.3.1).



Fig. 3.3.1. Simplified process flow diagram of a gaseous feedstock ethylene plant

Another difference with gaseous feed units is given in the hydrogenation step (to remove acetylene), which can also be done directly with the cracked gas stream (during or after compression, as well as before or after drying). This is not desired in liquid feed units, where valuable C4 byproducts like 1,3-butadiene are created in the cracking process, which would be completely co-hydrogenated to butane and butene.

3.3.2 Liquid Feed Olefin Units

These units use heavy feedstocks such as naphtha (mixture of hydrocarbons with a boiling range of 86°F to 390°F (30°C to 200°C); the most important feedstock worldwide used in roughly 50% of the heavy feedstock units), or gas oil (crude oil fractions; atmospheric gas oil (AGO) with a boiling range of 360°F to 660°F (180°C to 350°C) and vacuum gas oil (VGO) with a boiling range of 660°F to 1100°F (350°C to 600°C)], to generate olefins. These raw materials are mostly obtained as byproducts from petroleum refineries.

Heavy (liquid) feedstocks generally offer lower yields of ethylene and propylene products compared to light (gaseous) feedstocks and therefore require higher amounts of feedstock. More amounts of heavy byproducts (pyrolysis gasoline, benzene, etc.) are generated, but less light byproducts (hydrogen, methane, etc.). Aromatic components in the feedstock are stable under normal cracking conditions and remain unchanged or condense to higher molecular mass materials as byproducts.

As mentioned in section 3.3.1, especially in naphtha feed units, separate furnaces for recycle ethane cracking might be used to avoid large ethane recycle streams in the process plant.

While the basic process principles are the same in gaseous and liquid feed plants, the front-end section of a liquid feed plant is more complex compared to a gaseous feed plant (see Figure 3.3.2). Heavy hydrocarbons need to be removed in an oil-quench column and fractionation cycle and additional installations are required in the water-quench, the compression and the drying sections to treat the relatively high amounts of pyrolysis gasoline. Large hot oil and pyrolysis gasoline systems are present at liquid feed units, which increases the fire hazards related to ignitable liquids in the front-end process area compared to a gaseous feed plant.



Fig. 3.3.2. Simplified process flow diagram of a liquid feedstock ethylene plant

As mentioned in section 3.3.1, there is less flexibility for the hydrogenation step in liquid feed units. This needs to be accomplished in the C3 or C2 streams in order not to lose valuable C4 byproducts.

There is a higher need for pure hydrogen in liquid feed units compared to gaseous feed units due to various hydrogenation and hydrotreatment steps for heavy byproducts (pyrolysis gasoline, etc.). Therefore, a more complex hydrogen recovery and purification step is required in liquid feed units. The hydrogen demand in gaseous feed units is much lower, and the hydrogen-methane mixture is typically directly sent to the fuel gas system.

3.3.3 Hot Section

The hot section is where the cracking reactions occur to form the different olefin products. Steam cracking of naphtha or LPGs is the most common way of producing these chemicals. Generally, the hot section includes the following:

- Cracking. Takes place in cracking furnaces and is considered the main segment in an olefin plant.
- Primary fractionation. Quench oil and water is used to separate pyrolysis oil and gasoline.
- Compression.
- Caustic scrubbing and drying. Scrubbing with caustic followed by molecular sieve adsorption to remove sulphur compounds, mercaptan, etc.

3.3.3.1 Cracking Section

Steam cracking is the thermal cracking and reforming of hydrocarbons in the presence of steam at high temperature, short residence time, and rather low pressure in a fired tubular furnace. Typical olefin plants can have several furnaces, where the feedstock mixed with steam is cracked at temperatures that varies depending upon feedstock type and cracking conditions.

Figure 3.3.3.1 shows a typical modern cracking furnace arrangement. They usually have one or two rectangular fireboxes with vertical radiant coils located centrally between two radiant refractory walls. Firebox heights of up to 50 ft (15 m) and widths of 6-9 ft (2–3 m) is standard design practice in the industry.

Reformers consist of two main zones, convection and radiant. In the convection zone, hydrocarbon feedstock is preheated and mixed with steam. Requirement of steam will depend upon the type of feedstock; the lighter hydrocarbons require less steam as compared to heavier feedstock.

In the radiant zone the reaction of the preheated mixture of hydrocarbon feedstock and steam take place in the radiant coils. The addition of dilution steam enhances ethylene yield and reduces the coking tendency in the furnace coils. The temperature of the hydrocarbon and steam mixture entering the radiant chamber is usually in the range of 930 to 1,300°F (500 to 700°C). However, lower or higher temperatures can be used depending upon feedstock type.

The products obtained from the cracking reaction consists of a wide range of saturated and unsaturated hydrocarbons. Cracking reactions are endothermic; therefore, heat supplied by firing fuel from sidewall and/or floor burners are required for hydrocarbon conversion. Sidewall burners usually give uniform heat distribution, but 40 to 200 burners are required in a single furnace. Newer sidewall furnace designs include floor burners, so this arrangement requires a fewer number of burners. The selection of burners depends on the type of fuel (gas and/or liquid), source of combustion air (ambient, preheated, or gas turbine exhaust), and required NOx levels.

Cracked gases leaving the radiant coils can reach temperatures in the range of 1,400 to 1,700°F (750 to 900°C). Thus, rapid reduction of gas temperature in the transfer line exchangers (TLEs) to 930 to 1,200°F (500 to 650°C) is required, depending on the feedstock, to avoid losses of valuable products by secondary reactions.

3.3.3.2 Quench Section

Quenching instantaneously stops further reaction. Depending upon the feedstock, water or oil is utilized as the quenching medium, with oil commonly used for heavier feedstocks. Quench oil is a heavy grade hydrocarbon.

The cracked gas from the furnace must be cooled down as fast as possible to avoid over-cracking (decreases olefin yield) and prevent formation of side products. As shown in Figure 3.3.3.2, quenching happens in three steps: transfer line exchanger (TLE or TLX), the quench oil tower, and the quench water tower.

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Fig. 3.3.3.1. Typical cracking furnace

Cracking furnaces are equipped with transfer line exchangers (TLEs). After leaving the cracking furnace, the hot gas mixture is initially cooled in the transfer line exchangers (TLEs) to generate high-pressure steam. This steam is recycled for use in the steam cracking process.

When a gaseous feedstock (ethane, propane) is processed, the cracked gas is directly quenched with circulating quench water after the heat recovery in the transfer line exchangers (TLEs). Water quenching cools the gas very rapidly to near ambient temperatures by direct contact with water in a vertical quench tower. Condensable hydrocarbons are also removed in this step. The flow is countercurrent with the gases entering on the bottom of the quench tower and cooling water entering on the top. Cooled cracked gases from the water quench tower overhead are caustic scrubbed and then go to compression. The majority of the dilution steam and some of the heavier hydrocarbons are condensed and exit the tower bottoms.

When a heavier feedstock (C4 hydrocarbons, naphtha) is processed, the cracked gas is usually cooled by direct contact with quench oil. After the TLEs, the cracked gas stream enters the bottom of the primary fractionation (gasoline fractionator or quench oil tower). As the gas fraction flows to the top of the tower, it is contacted with a countercurrent flow of circulating oil and, at the top of the column, with a heavy pyrolysis gasoline fraction obtained from the subsequent water quench tower. In addition to cooling the gases, the quench oil removes entrained hydrocarbon liquids from the pyrolysis products. The overhead gases from the fractionator go to the water quench tower; the outlet temperature of the oil quench tower is typically in the range of 680-970°F (360-520°C). Oils (gasoline and fuel oils rich in aromatics) in the bottom of the TLEs. Excess oil is removed from the fractionation system and sent out as product. Pyrolysis oil is generally produced as



Fig. 3.3.3.2. Quench section for liquid feedstocks

one fraction, containing all hydrocarbons boiling above 390°F (200°C). Some plants produce two fractions, pyrolysis gas oil (PGO, boiling point in the 390°F-750°F [200°C-400°C]) and pyrolysis fuel oil (PFU, containing the heavier components).

Almost all modern olefin plant designs employ indirect quenching, by which valuable high-pressure steam is generated, and direct quenching is only used for very heavy feeds.

A general problem in all quench towers is the separation of hydrocarbons and water. Tarry material, which is present in small quantities and has a density similar to water, tends to accumulate in the system and to stick to the surface of the column internals. On-line or off-line washing with high-boiling, aromatic-rich solvents is applied to extend the on-stream time of the system up to five years. There is also a strong tendency for formation of emulsions, leading to fouling problems in the generation of dilution steam and in the processing of wastewater from the system. Emulsification is avoided by careful control of the quench water system pH. Numerous options exist in the design and operation of the quench column and primary fractionator units for removing pyrolysis tars, recovering various heavy hydrocarbon streams, and isolating quench oil for recycle.

Occasionally, there may be an incomplete separation of gasoline and water in the water quench tower. This will result in gasoline in the dilution steam. If gasoline is in the dilution steam, the steam will have a hydrocarbon smell. When gasoline is detected, the steam should be blocked in/isolated until the dilution steam system is back to normal (i.e., no gasoline in dilution steam). Gasoline put into the heater can cause a fire and equipment damage.

Decoking is also required for quench towers.

3.3.3.3 Compression Section

After cooling and purification of the cracked gas in the primary fractionator and/or in the quench tower, the effluent is separated into desired products by compression in conjunction with condensation and fractionation at gradually lower temperatures.

Compression is typically performed by a turbine-driven centrifugal compressor in four to five stages with intermediate cooling (Figure 3.3.3.3). The number of stages depends primarily on the cracked-gas composition, the temperature of the cooling medium, and the highest temperature allowed for interstage discharge.



Fig. 3.3.3.3. Compression section process

Interstage cooling and temperature control keep the cracked gas below 210°F (100°C) to prevent diolefin polymerization and subsequent equipment fouling. Various injection systems, using aromatic rich oil or water, are applied to reduce fouling of compressor internals and intercooling equipment.

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.

Interstage cooling usually employs water coolers to minimize inlet temperature in the subsequent stages.

Interstage cooler pressure drops must be kept low, especially in the initial stages, to reduce compressor and energy costs. The water and hydrocarbon condensates may be routed to another compressor stage, to the quench column preceding the compressor, or to a fractionation tower. In liquid cracking most of the gasoline fraction containing the C6 to C8 aromatics is condensed in the interstage coolers of the compressor. After gravity separation from process water this gasoline stream is fractionated in a stripper to remove C4 and lighter components before routing it to a hydrotreating step. Drying is required for all liquid and gas streams subjected to temperatures below 59°F (15°C).

3.3.3.4 Caustic Scrubbing and Drying

Before the cracked gases enter the cold section for separation, carbon dioxide and hydrogen sulfide are removed by a caustic wash (sodium hydroxide) and regenerative solvent (MEA) scrubbing in an acid-gas removal system. Acid gas removal systems are located upstream of the drying unit to prevent formation of ice and hydrates in the fractionation steps. Carbon dioxide can also be absorbed into ethylene, affecting product quality and further processing. Hydrogen sulfide is corrosive and a catalyst poison as well as a potential product contaminant.

Acid-gas removal systems are frequently subject to fouling, especially at high concentrations of C4 and C5 diolefins. This fouling process can be controlled by applying special inhibitors.

3.3.4 Cold Section

The cold section is where cracked gases, once washed and dried, are separated in a series of fractionation columns to obtain final olefins products. Cryogenic separation is the predominant method used.

The separation of the cracked gases in the cold section can be initiated by any of the three main columns (demethanizer, deethanizer, or depropanizer), which depends upon process conditions, energy consumption, etc. The differences are primarily in the sequence of fractionation and hydrotreating steps downstream of cracked gas compression but provide similar overall capabilities for fractionation and hydrogenation.

3.3.4.1 Cold Boxes

Before any separation of the dried cracked gas is performed in any of the fractionation columns, the gas must be cooled and partially condensed in a series of heat exchangers, commonly known as the cold box. The design of the refrigeration and heat-exchange systems, including type of refrigerant and number of refrigeration levels, depend on the temperature and pressure required in the downstream fractionation equipment.

Cold boxes are brazed aluminum plate-fin exchangers, used for the cryogenic heat-transfer services. Exchangers are enclosed by welded sheets of carbon steel (box-shaped) which is filled with insulation (e.g., perlite) surrounding the internal equipment for robust insulative properties. This equipment can be subject to mercury embrittlement, mostly in cases where mercury is a trace component of the feedstock and condensation of liquid or precipitation of solid mercury can occur. (See section 3.4 for additional information)

A cold box will contain multiple heat exchangers assembled closely in series and/or parallel, very often in a single package unit. These are often self-supported structures, having supports for the internal equipment. Flanged inlets/outlet connections are provided for process streams (process gas, refrigerant ethylene, refrigerant propylene, etc.)

3.3.4.2 Fractionation or Distillation Section

The primary process used for separating most of the olefin products to a desire purity is distillation. Separation is either achieved by cryogenic distillation (C2 and C3 splitter), or by high pressure distillation. Extractive distillation can also be used when close proximity of boiling points and azeotrope formation exist (C4 separation). The distillation or fractionation columns in these plants are very large due to the low relative volatility of the alkane/alkylene mixtures that require large reflux ratios.

Deethanizer. In the deethanizer the separation of C2 is initiated by producing an overhead stream of ethane and lighter components (hydrogen, methane, acetylene, ethane, ethylene) and a bottom stream of C3 and heavier materials. The lighter components are hydrogenated to convert acetylene to ethylene and ethane in an acetylene converter, to be further fractionated cryogenically (C2 splitter) to ethylene product and ethane which is recycled to the cracking furnaces.

The bottom product from the deethanizer (hydrocarbons with more than two carbons C3+) is sent to the depropanizer to separate C4 and heavier components.

Demethanizer. The demethanizer is used to separate ethylene from lighter components through progressively chilling and distillation processes. All processes consist of a combination of cooling steps, partial condensation, and a demethanizer tower system. During these operations, a tail-gas stream of hydrogen and methane is produced. Hydrogen can be further processed to be obtained as a product by purification. In naphtha cracking, hydrogen is recovered at high purity because it is needed in the plant itself for various hydrogenation steps. Methane is typically used as plant fuel or sold.

Demethanization typically consumes the greatest proportion of energy from the refrigeration systems in the plant. A special challenge in this process is the provision of the respective chilling duty for individual cooling steps, commonly achieved by a refrigerant cascade.

Ethylene Separation. Ethylene and ethane are separated in the C2 splitter, commonly located after the acetylene converter, where ethylene is obtained with a high purity (over 99%) and residual ethane is recycled to cracking furnaces to be mixed with fresh feeds. Ethylene fractionation consists basically of a low temperature, relatively high-pressure distillation process. This column contains 80 to 150 trays, and typical reflux ratio are in the order of 2.5 to 4.0, depending on feed composition.

Depropanizer. The depropanizer is used to separate cracked gas into propylene-propane and other heavier fractions (C4+). The feed stream of the depropanizer usually comes from the bottom of the deethanizer. In here the overhead components are sent to a propylene-propane splitter (C3 splitter) and the bottom with heavier fractions is sent to a debutanizer. The overhead of the depropanizer is sent to the propylene fractionator. The methylacetylene (MA) and propadiene (PD) are usually hydrogenated before entering the tower. A methylacetylene and propadiene (MAPD) converter is similar to an acetylene converter but operates at a lower temperature and in the liquid phase.

Operating pressure and temperature of the depropanization are low in order to reduce fouling of the fractionator by acetylenic and diolefinic contaminants.

Propylene Separation. Separation of propylene and propane is more complicated than the separation of ethylene and ethane due to the low relative volatility between them. Because of the close boiling points between propylene and propane, typical fractionator requires a large number of trays (up to 200) for high purity propylene product and high reflux ratios (12 to 20).

The propane obtained in the fractionator can be recycled to the cracking furnace to optimized propylene yields or used as fuel.

Debutanizer. In the debutanizer, the feed from the depropanizer bottoms is processed to separate C4 products from light pyrolysis gasoline, C5 materials, aromatics, etc. The debutanizer operates at a moderate pressure of 4-5 bar (0.4 to 0.5 MPa) and is a conventional fractionator with steam-heated reboilers and water-cooled condensers.

3.4 Mercury Embrittlement of Aluminum

Liquid metal embrittlement (LME) is a complex metal fracture mechanism that occurs when ductile metals come in contact with specific liquid metals. Mercury in liquid phase causes, under certain well-defined conditions, metal embrittlement to aluminum.

In situations where mercury is a trace component of feed gas or liquid feeds to crackers, condensation of liquid or precipitation of solid mercury can occur in heat exchanger passes, even with functional mercury removal systems in place.

Olefin manufacturing sites are aware of mercury embrittlement of aluminum; some plants have mercuryresistant/mercury-tolerant design. There are specific standards (ASME Boiler and Pressure Vessel Code, Section VIII, and ALPEMA Standards of the Brazed Aluminum Plate-Fin Heat Exchanger Manufacturers Association).

The Brazed Aluminum Plate Fin Heat Exchanger Manufacturers' Association (ALPEMA) recommends not to exceed the rate of temperature change across any heat exchanger pass beyond 2°C/min or 60°C/hr, as high thermal stresses can damage the aluminum cores. If stream temperature changes are cyclic or recurring, then the allowable rate of temperature change must be less than 1°C/min to prevent thermal fatigue.

Aluminum heat exchangers require close assessment and inspections to predict or detect mercury embrittlement signs for safe operation. It can include computational prediction of mercury deposition, inspection of critical areas, analysis of temperature changes during trips and shutdowns, etc.

3.5 Emergency Isolation Valves (EIVs)

Emergency isolation valves (EIV) or emergency block valves (EBVs) are installed to shutdown the flow of ignitable liquids and flammable gases, in the event of a release or a fire. The installation of these valves is intended to achieve the following objectives:

- Confine the liquids and vapors within the equipment.
- Limit escaping material to a minimum and prevent its spread.
- Stop the transfer of material.
- Quickly drain escaping liquids or vent equipment and systems handling gas to a safe location.

4.0 REFERENCES

4.1 FM

Data Sheet 1-24, Protection Against Liquid Damage Data Sheet 1-44, Damage Limiting Construction Data Sheet 5-1, Electrical Equipment in Hazardous Locations. Data Sheet 5-4, Transformers Data Sheet 5-17, Motors and Adjustable Speed Drives Data Sheet 5-31, Cables and Bus Bars Data Sheet 5-32, Data Centers and Related Facilities Data Sheet 5-49, Gas and Vapor Detectors and Analysis Systems Data Sheet 7-14, Fire Protection for Chemical Plants Data Sheet 7-32, Ignitable Liquids Operations Data Sheet 7-42, Vapor Cloud Explosions

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Data Sheet 7-43, Process Safety Data Sheet 7-45, Safety Controls, Alarms, and Interlocks Data Sheet 7-49, Emergency Venting of Vessels Data Sheet 7-55, Liquified Petroleum Gas (LPG) in Stationary Installations Data Sheet 7-72, Reformer and Cracking Furnaces Data Sheet 7-79, Fire Protection for Gas Turbines and Electric Generators Data Sheet 7-83, Drainage Systems for Ignitable Liquids Data Sheet 7-88, Outdoor Ignitable Liquid Storage Tanks Data Sheet 7-95, Compressors Data Sheet 7-101, Fire Protection for Steam Turbines and Electric Generators Data Sheet 7-110, Industrial Control Systems Data Sheet 7-111, Chemical Process Industries Data Sheet 9-0, Asset Integrity Data Sheet 10-8, Operators Data Sheet 12-2, Vessels & Piping Data Sheet 12-43, Pressure Relief Devices Data Sheet 13-3, Steam Turbines Data Sheet 13-17, Gas Turbines

APPENDIX A GLOSSARY OF TERMS

See Data Sheet 7-111.

Auto-refrigeration scenarios. Where unintentional release or routing of pressurized LPGs from a vessel to a lower pressure state can refrigerate vessels/piping and result in critically low temperatures in the vessels and/or associated piping systems.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

January 2023. Interim revision. Minor editorial changes were made.

January 2022. This is the first publication of this document.