

Guidelines – Petroleum works

Issued by: Inspection Department – Operations Section

1.0 Introduction

The petroleum industry covers a very wide range of operations from simple primary separations to complex petrochemical products. This note covers only refining separation processes, which can again be simple primary distillations or complex secondary treatments such as catalytic cracking, hydrogenation, alkylation units and vacuum distillation, etc.

These notes apply to works in which:

- Crude or stabilized crude petroleum or associated gas, or condensate handled, stored or refined; or
- Any product of such refining is subjected to further refining or to conversion; or
- Natural gas is refined or odourized; or
- Used lubricating oil is prepared for reuse by any thermal process.

These notes are intended to provide a basis for consultation between works managements and the Authority so that the latter can take into account the types of plant and their capacities when deciding on requirements, leaving flexibility to make allowances for special local circumstances.

An industrial accident involving a refinery happened at the Texas City Refinery. On 23 March 2005, an explosion occurred at a petroleum refinery in Texas City, Texas, that belonged to British Petroleum. It is the third largest refinery in the United States and one of the largest in the world, processing 433,000 barrels of crude oil per day and accounting for 3% of that nation's gasoline supply. Over 100 were injured, and 15 were confirmed dead, including employees of the Fluor Corporation as well as British Petroleum. British Petroleum has since accepted that its employees contributed to the accident. Several level indicators failed, leading to overfilling of a knock out drum, and light hydrocarbons concentrated at ground level throughout the area. A running diesel truck nearby set off the explosion.

PCFC has published a Health and Safety Manual dealing with requirements for the protection of employees and neighbours from risks of injury, health, fire and electricity hazards, and this should be studied in conjunction with these notes.

The health, safety and environmental problems of the petroleum industry are many and varied and long experience has brought solutions for the design, construction, operation and standardization of refineries to make them acceptable. Such requirements and standards are embodied in national and international agreements with organizations such as the American



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National Fire Protection Association (NEPA), the American Petroleum Institute (API), and Stichting CONCAWE of Western Europe. All new refineries are required to design and plan their equipment to those standards.

2.0 Emission Limits and Controls

- 2.1 The emissions of combustion products from furnaces shall be maintained free from visible smoke or fumes and in any case shall not be more than one hundred fifty (150) mg/m³ during normal operation.
- 2.2 Carbon monoxide from a catalytic cracker shall be burnt in an efficient appliance.
- 2.3 Particulate matter from catalytic crackers shall not exceed an emission concentration of one hundred fifty (150) mg/m³.
- 2.4 The aim shall be completely to destroy hydrogen sulfide but an emission concentration of five (5) ppm v/v can be tolerated for a short time. SO₂ / NO_x shall not exceed five hundred (500) mg/m³.

3.0 Operational Controls

3.1 Liquid Effluents

All crude oil refineries produce substantial quantities of aqueous effluents which have been in contact with sulfur-containing hydrocarbon streams and are contaminated with hydrocarbons, hydrogen sulfide and mercaptans. These sour water effluents must be freed from foul-smelling substances, normally by steam stripping in a distillation column, or equivalent. The liquid effluent, perhaps containing water-soluble organic compounds and phenols from catalytic aeration to produce an aqueous stream fit to discharge. Oil/water separators on oil refineries should be covered to reduce evaporation and prevent the free emission of oily vapours from the surface. The standards for discharge of liquid effluents are discussed in detail in the water environment section.

3.2 Catalytic Crackers and HF Alkylation Units

- a. Most modern oil refineries now use catalytic crackers and HF alkylation units to meet demands for low-lead and lead-free petrol and great care has to be taken in the design of these massive units to prevent hazards and nuisance from solids and gases.
- b. Carbon monoxide from cracking plants must be burnt before discharge.
- c. Particulate matter separators can be designed to reduce dust emissions to below one hundred fifty (150) mg/m³ by inertial separation, otherwise more energy consuming units such as electrical precipitators may have to be used.

3.3 Desulphurization



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Gas and liquid streams can contain hydrogen sulfide and mercaptans which are absorbed in ethanolamine, the latter being regenerated by removing the hydrogen sulfide gas in concentrated form. Sulfur recovery is effected in Claus kiln units by partial combustion to form sulfur dioxide and hydrogen sulfide which react to deposit sulfur. At least 98-99.9% efficiency must be achieved and the final emissions has to be combusted to emit a small amount of sulfur dioxide for discharge at a suitable height. There are times when a Claus kiln has to be out of commission for routine testing or maintenance and at least two kilns have to be used to take care of this situation. Ideally, three Claus kilns should be used, with any two capable of handling the total flow. The final design will depend largely on the scale of operations, which should be odour free.

4.0 Flaring

- 4.1 On all oil refineries, flares are used to burn flammable gases under controlled or breakdown conditions. All plants handling gases and volatile petroleum fractions are connected to the flare system through pressure relief valves or remotely controlled depressurizing valves, so that in the event of a shut down or process disturbances, the flammable gases can be vented to the flare and there burned safely. The system has to be carefully designed with a knockout pot to remove liquid droplets, followed by a water seal of given pressure and a tall flare stack. Waste gases would be burnt in efficient and adequately tall flaring stack by virtue of complete combustion, preferably during night time, using steam assistance. Otherwise, prior agreement/approval of Authority is required. Odourous emissions to be avoided.
- 4.2 One of the difficulties with elevated flares is that of achieving good mixing of the massive amounts of the flared gases with air to produce clean and smokeless combustion. This is achieved by injecting steam into the gas at the tip to cause turbulence and aid in combustion by reacting with carbon and hydrocarbons in the high temperature flame zone. Such treatment with steam is essential and whilst perfection has not yet been achieved, there are several good designs on the market.
- 4.3 When simple hydro-skimming operations are employed in the distillation process, ground-level flares can be used to give better combustion control and smokeless operation, and are less conspicuous, but they are more costly to maintain and a high level flare is still needed for a major emergency discharge. With catalytic crackers and HF alkylation units in use, large quantities of sulfur containing gases and traces of hydrogen fluoride would have to be discharged at high level.

5.0 Liquid Storage

- 5.1 Crude oils vary enormously in their physical and chemical properties. Some are “sweet” and some are “sour”, but all have characteristic odours which can be a nuisance unless proper storing and handling facilities are used. Crude oils must be received and stored either in double-seal, floating roof tanks, or in fixed roof tanks with vapour extraction to a scrubbing system.



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- 5.2 The crude oil tanks must be designed to permit the settling and extraction of water. Such water has to be stripped of volatile matter for destruction, with the water passing to a well-designated oil/water separation system to the satisfaction of the Authority.
- 5.3 There are times when tanks have to be emptied for maintenance, or change of product, and floating roofs have to be supported on legs or pedestals, leaving a vapour space between the roof and the tank bottom. In order to minimize vapour emissions when the tanks are refilled, the legs or pedestals should be as short as is practicable.
- 5.4 The storage of volatile organic compounds with vapour pressures above five hundred seventy (570) mmHg should be accompanied by a vapour recovery system. Below that vapour pressure, pressure/vacuum (P/V) ventilation valves should be fitted to storage tanks. In some cases it is practicable to install a floating, light metal sheet on the surface of the liquid to reduce evaporation.
- 5.5 All storage tanks must be adequately bunded to contain their contents in the event of a catastrophic leakage. They must also be fitted with foam and water connections in case of fire. The bunded area shall be sufficient to contain 110% of the volume of the largest tank within the bund. The floor shall consist of a good quality, impervious surface concrete with 2mm HDPE liner and leak detection system is required.
- 5.6 The storage tanks for volatile organic compounds should ideally be of floating roofs with nitrogen blanketing. The vapours, upon filling, be recovered and routed to flare or recycled.
- 6.0 Chimneys
- 6.1 The quality of oil processed on refineries can vary from time to time as sources change, and also petroleum refineries tend to use their own arising of high-sulfur residues, as well as petroleum gas, to heat their own furnaces. It is good practice to have these residues burnt on oil refineries with waste gases dispersed from tall chimneys and with supervision by well-trained and knowledgeable staff, rather than to allow them to be burnt in numerous works elsewhere. In general, the policy for dispersion of waste products of combustion is to treat a refinery as a point source and to base the chimney heights of the major emitters on the total emission of the significant pollutants. These are usually oxides of sulfur or nitrogen. Small sources can be treated appropriately. The temperatures of waste gases from petroleum works tend to be significantly higher than from combustion processes in some industries, such as power stations or industrial boilers, and so the plume rise due to momentum and buoyancy can be high and has to be taken into account.
- 6.2 There is a dispersion advantage in combining emissions into as few chimneys as is practicable, and in some cases a single common chimney has been built. Much will depend upon the complexity of operations as to how far a works can go along this route. Final chimney heights can only be decided after discussions between managements and the Authority.
- 7.0 General Odour Prevention



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- 7.1 An enormous potential odourous and offensive gaseous and liquid emissions from petroleum works and the utmost care has to be taken in the design, operation, control and training for such works to be acceptable neighbours. The modern industry is aware of these problems and has a high reputation for its efforts to prevent nuisance. In a new refinery, the very latest is expected form high technology control and instrumentation, usually with its own environment division to ensure compliance with regulations and to be the company's own critic.
- 7.2 It is not possible in a note of this kind to cover all aspects of health, safety and the environment for a petroleum works and only the vigilance of the management, cooperation with the Authority and continuing inspection can ensure an acceptable process.
- 7.3 All sources where such odorous air emissions/ offensive vapour emissions can be expected, such as hot wells, vacuum installations, etc., have to be connected to extraction and treatment plant.
- 7.4 The products from petroleum works have to be marketed in small or large containers or in bulk and great care have to be taken to minimize offensive and hazardous emissions from such sources. This is especially true when loading tankers with bulk supplies of volatile organic liquids such as petrol. Vapour return lines and bottom loading are good practices, which should be adopted in well designed systems. Means must be used to deal with spillages.

8.0 Emission Sources

8.1 Miscellaneous Process Vents

Many unit operations at petroleum refineries generate gaseous streams that contain HAP. These streams may be routed to other unit operations for additional processing (i.e., a gas stream from a reactor that is routed to a distillation unit for separation) or they may be sent to a blow down system or vented to the atmosphere. Miscellaneous process vents emit gases to the atmosphere, either directly or after passing through recovery and/or control devices.

8.2 Storage Vessels

Storage vessels contain crude oil, intermediate products, and finished products. Different types of vessels are used to store various types of products. Gases are stored in pressurized vessels that are not vented to the atmosphere during normal operations while liquids are stored in horizontal, fixed roof, or floating roof tanks, depending on properties and volumes to be stored. Liquids with vapour pressures greater than 11 pounds per square inch of air (psia) are typically stored in fixed roof tanks that are vented to a control device. Volatile liquids with vapour pressures up to 11 psia are usually stored in floating roof tanks because such vessels have lower emission rates than fixed roof tanks within this vapour pressure range. Emissions from storage vessels typically occur as working losses. As a storage vessel is filled, HAP-laden vapours inside the tank become displaced and can be emitted to the atmosphere. Also, diurnal temperature changes result in breathing losses of organic HAP-laden vapours from storage vessels.

8.3 Wastewater Streams



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Many refinery process units generate wastewater streams that contain HAP. Significant wastewater sources include the crude desalting unit, process waters, steam stripper blow down, and storage tank draws. Organic HAP compounds in the wastewater can volatilize and be emitted to the atmosphere from wastewater collection and treatment units if these units are open or vented to the atmosphere. Potential sources of HAP emissions associated with wastewater collection and treatment systems include drains, manholes, trenches, surface impoundments, oil/water separators, storage and treatment tanks, junction boxes, sumps, basins, and biological treatment systems.

8.4 Equipment Leaks

Equipment leaks are releases of process fluid or vapour from processing equipment, including pump and compressor seals, process valves, pressure relief devices, open-ended lines, flanges and other connectors, agitators, and instrumentation systems. These releases occur primarily at the interface between connected components of equipment or in sealing mechanisms.

8.5 Gasoline Loading Racks

Loading racks are the collection of equipment, including loading arms, pumps, meters, shutoff valves, relief valves, and other piping and valves used to fill gasoline cargo tanks. Emissions from loading racks may be released when gasoline loaded into cargo tanks displaces vapours inside these containers.

8.6 Marine Vessel Loading Operations

Marine vessel loading operations load and unload liquid commodities in bulk, such as crude oil, gasoline and other fuels, and naphtha. The cargo is pumped from the terminal's large, above-ground storage tanks through a network of pipes and into a storage compartment (tank) on the vessel. The HAP emission result from the displaced vapours during the filling operation.

8.7 Cooling Towers

Cooling tower systems include closed loop recirculation systems and once through systems that receive non-contact process water from a heat exchanger for the purposes of cooling the process water prior to returning the water to the heat exchanger or discharging the water to another process unit, waste management unit, or to a receiving water body. Cooling towers typically use force draft air ventilation of the process water to cool the process water. Heat exchangers occasionally develop leaks which result in process fluids entering the cooling tower process water. The HAP and other organics in these process fluids are then emitted to the atmosphere due to stripping in the cooling tower.



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Process Emission Sources Control Technology

| Process Emission Sources | Process Description | Control Technology |
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| Vacuum Distillation | <p>Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high boiling point hydrocarbons. When distilled at atmospheric pressures, the crude oil decomposes and polymerizes and will foul equipment. To separate crude into components, it must be distilled in a vacuum column at a very low pressure and in a steam atmosphere.</p> <p>The major sources of atmospheric emissions from the vacuum distillation column are associated with the steam ejectors or vacuum pumps. A major portion of the vapours withdrawn from the column by the ejectors or pumps is recovered in condensers. Historically, the non-condensable portion of the vapours has been vented to the atmosphere from the condensers.</p> <p>A second source of atmospheric emissions from vacuum distillation columns is combustion products from the process heater. Process heater requirements for the vacuum distillation column are approximately 245 mega joules per cubic meter (MJ/m³) (37,000 British thermal units per barrel [Btu/bbl]) of topped crude processed in the vacuum column.</p> <p>Fugitive hydrocarbon emissions from leaking seals and fittings are also associated with the vacuum distillation unit, but these are minimized by the low operating pressures and low vapour pressures in the unit.</p> | <p>Control technology applicable to the non-condensable emissions vented from the vacuum ejectors or pumps includes venting into blow down systems or fuel gas systems, and incineration in furnaces or waste heat boilers. These control techniques are generally greater than 99 percent efficient in the control of hydrocarbon emissions, but they also contribute to the emission of combustion products.</p> |
| Moving-Bed Catalytic Cracking | <p>In the moving-bed system, typified by the Thermafor Catalytic Cracking (TCC) units, catalyst beads (~0.5 centimeters [cm] [0.2 inches (in.)]) flow into the top of the reactor,</p> | <p>FCC particulate emissions are controlled by cyclones and/or</p> |



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| | <p>where they contact a mixed-phase hydrocarbon feed. Cracking reactions take place as the catalyst and hydrocarbons move concurrently downward through the reactor to a zone where the catalyst is separated from the vapours. The gaseous reaction products flow out of the reactor to the fractionation section of the unit. The catalyst is steam stripped to remove any adsorbed hydrocarbons. It then falls into the regenerator, where coke is burned from the catalyst with air. The regenerated catalyst is separated from the flue gases and recycled to be mixed with fresh hydrocarbon feed. The operating temperatures of the reactor and regenerator in the TCC process are comparable to those in the FCC process..</p> <p>Air emissions from catalytic cracking processes are (1) combustion products from process heaters and (2) flue gas from catalyst regeneration.</p> <p>Emissions from the catalyst regenerator include hydrocarbons, oxides of sulfur, ammonia, aldehydes, oxides of nitrogen, cyanides, carbon monoxide (CO), and particulates.</p> | <p>electrostatic precipitators. Particulate control efficiencies are as high as 80 to 85 percent. Carbon monoxide waste heat boilers reduce the CO and hydrocarbon emissions from FCC units to negligible levels. The particulate emissions from a TCC unit are normally controlled by high-efficiency cyclones. Carbon monoxide and hydrocarbon emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater firebox or smoke plume burner. In some installations, sulfur oxides are removed by passing the regenerator flue gases through a water or caustic scrubber.</p> |
| Coking | <p>Coking is a thermal cracking process used to convert low value residual fuel oil to higher value gas oil and petroleum coke. Vacuum residuals and thermal tars are cracked in the coking process at high temperature and low pressure. Products are petroleum coke, gas oils, and lighter petroleum stocks. Delayed coking is the most widely used process today, but fluid coking is expected to become an important process in the future.</p> <p>Air emissions from thermal cracking processes include coke dust from decoking operations, combustion gases from the visbreaking and coking process heaters, and fugitive emissions. Fugitive emissions from miscellaneous leaks are significant because</p> | <p>Particulate emission control is accomplished in the decoking operation by wetting down the coke. Generally, there is no control of hydrocarbon emissions from delayed coking. However, some facilities are now collecting coke drum emissions in an enclosed system and routing them to a refinery flare.</p> |



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| | <p>of the high temperatures involved, and are dependent upon equipment type and configuration, operating conditions, and general maintenance practices. Particulate emissions from delayed coking operations are potentially very significant. These emissions are associated with removing the coke from the coke drum and subsequent handling and storage operations. Hydrocarbon emissions are also associated with cooling and venting the coke drum before coke removal.</p> | |
| Blow Down System | <p>The blow down system provides for the safe disposal of hydrocarbons (vapour and liquid) discharged from pressure relief devices. Most refining processing units and equipment subject to planned or unplanned hydrocarbon discharges are manifolded into a collection unit, called blow down system. By using a series of flash drums and condensers arranged in decreasing pressure, blow down material is separated into vapour and liquid cuts. The separated liquid is recycled into the refinery. The gaseous cuts can either be smokelessly flared or recycled.</p> | <p>Emissions from the blow down system can be effectively controlled by combustion of the non condensables in a flare. To obtain complete combustion or smokeless burning, steam is injected in the combustion zone of the flare to provide turbulence and air. Steam injection also reduces emissions of nitrogen oxides by lowering the flame temperature.</p> |
| Compressor Engines | <p>Many older refineries run high-pressure compressors with reciprocating and gas turbine engines fired with natural gas. Natural gas has usually been a cheap, abundant source of energy. Examples of refining units operating at high pressure include hydrodesulphurization, isomerization, reforming, and hydrocracking. Internal combustion engines are less reliable and harder to maintain than are steam engines or electric motors. For this reason, and because of increasing natural gas costs, very few such units have been installed in the last few years. The major source of emissions from compressor engines is combustion products in the exhaust gas. These emissions include CO, hydrocarbons, nitrogen oxides, aldehydes, and ammonia. Sulfur oxides may also be present, depending on the sulfur content of the natural gas. All these</p> | <p>The major emission control technique applied to compressor engines is carburetion adjustment similar to that applied on automobiles. Catalyst systems similar to those of automobiles may also be effective in reducing emissions.</p> |



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| | emissions are significantly higher in exhaust from reciprocating engines than from turbine engines. | |
| Asphalt Blowing | <p>The asphalt blowing process polymerizes asphaltic residual oils by oxidation, increasing their melting temperature and hardness to achieve an increased resistance to weathering. The oils, containing a large quantity of polycyclic aromatic compounds (asphaltic oils), are oxidized by blowing heated air through a heated batch mixture. The reaction is exothermic, and quench steam is sometimes needed for temperature control. In some cases, ferric chloride or phosphorus pentoxide is used as a catalyst to increase the reaction rate and to impart special characteristics to the asphalt. Air emissions from asphalt blowing are primarily hydrocarbon vapours vented with the blowing air. The quantities of emissions are small because of the prior removal of volatile hydrocarbons in the distillation units, but the emissions may contain hazardous polynuclear organics.</p> | Emissions from asphalt blowing can be controlled to negligible levels by vapour scrubbing, incineration, or both. |
| Cooling Towers | <p>Cooling towers are used extensively in refinery cooling water systems to transfer waste heat from the cooling water to the atmosphere. The only refineries not employing cooling towers are those with once-through cooling. The increasing scarcity of a large water supply required for once-through cooling is contributing to the disappearance of that form of refinery cooling. In the cooling tower, warm cooling water returning from refinery processes is contacted with air by cascading through packing. Atmospheric emissions from the cooling tower consist of fugitive VOCs and gases stripped from the cooling water as the air and water come into contact. These contaminants enter the cooling water system from leaking heat exchangers and condensers. Although the predominant contaminants in cooling water are VOCs, dissolved gases such as H₂S and ammonia may also be found.</p> | Control of cooling tower emissions is accomplished by reducing contamination of cooling water through the proper maintenance of heat exchangers and condensers. The effectiveness of cooling tower controls is highly variable, depending on refinery configuration and existing maintenance practices. |