Annex A: General Description of Industry Activities

65. The EHS Guidelines for Petroleum Refining cover processing operations from crude oil to finished liquid products, including liquefied petroleum gas (LPG), Mo-Gas (motor gasoline), kerosene, diesel oil, heating oil, fuel oil, bitumen, asphalt, sulfur and intermediate products for the petrochemical industry (e.g. propane / propylene mixtures, virgin naphtha, middle distillate and vacuum distillate). Finished products are produced from the blending of different intermediate products. These blends are normally referred as gasoline pool, diesel oil pool, LPG pool, among others, and have varying compositions dependent on the configuration of the refinery process.

66. Petroleum refineries are complex systems specifically designed based on the desired products and the properties of the crude oil feedstock. Refineries may range from medium integrated refineries to fully integrated refineries (or total conversion refineries), based on the use of different processing units.

67. The refinery feedstock is crude oil, which is a mixture of hydrocarbon compounds. The hydrocarbons in crude oil are a mixture of three chemical groups including paraffins (normal and isoparaffins), naphthenes, and aromatics. The most common distinction between crude oil types is ‘sweet’ or ‘sour’. Sweet crude oil is normally low in sulfur and lightly paraffinic. Sour crude oil is usually high in sulfur (more than 0.5 wt percent) and heavily naphthenic. Crude oils are also classified into light, medium and heavy, dependent on their content of paraffins, naphthenics, and aromatics.

Process Units

Desalting

68. Desalting is a process to wash the crude oil with fresh water at high temperature and pressure to dissolve, separate and remove the salts and solids. Crude oil and/or reduced crude (commonly referred as oily feedstock) and fresh water are the inputs to the Desalting Unit, and washed crude oil and contaminated water are its outputs.

Primary Distillation Units

69. These units include the Atmospheric Distillation Unit (Topping or CDU) followed by Vacuum Unit (HVU). Desalted crude oil is fed to a distillation tower working at atmospheric pressure where the various fractions composing the crude oil are separated according to their boiling range. The heaviest fractions recovered at CDU bottom (atmospheric residue) do not vaporize under the tower atmospheric pressure, and require further fractionation under vacuum conditions in the vacuum distillation tower.

Bitumen Production Unit

70. The Bitumen Production Unit is fed with vacuum residue. In the Bitumen Blowing Unit (BBU), air is blown into hot bitumen, which causes dehydrogenation and polymerization reactions and yields a harder product with higher viscosity, a higher softening point and reduced penetration. The blown bitumen is removed from the bottom of the oxidation vessel and cooled before being sent to storage.

20 The hydrocarbon mixture may involve different chemical composition and molecular structures with some impurities. Most of these impurities, such as sulfur (largely in the form of organic compounds such as mercaptans and sulfides), nitrogen, vanadium and nickel are chemically bound to the hydrocarbon structures. Others, such as sand/clay, water and water-soluble salts of zinc, chromium and sodium are present as inorganic material.
Bitumen is typically stored in heated, insulated and nitrogen blanketed cone roof tanks fitted with safety valves. The nitrogen discharged into the atmosphere may contain hydrocarbons and sulfur compounds in the form of aerosol-containing liquid droplets.

**Hydrogen Consuming Processes**

71. Hydrotreating and hydro-processing processes are used to remove impurities such as sulfur, nitrogen, oxygen, halides and traces of metal impurities that may deactivate the noble metals catalysts. Hydrotreating also upgrades the quality of the processed fractions by converting olefins and di-olefins into paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing cracks heavy molecules into lighter, more saleable products. Both processes are usually placed upstream of process units, such as the Catalytic Reforming Unit and the Hydrocracking Units, in which sulfur and nitrogen could have adverse effects on catalyst operation. Hydrogen consumption is high and requires the presence of a Hydrogen Plant in the refinery.

72. The C₅ – C₆ isomerization units are based on skeletal isomerization processes (e.g. ‘once-through’ and ‘recycle’ types), used to convert a linear molecule into a branched one with the same raw formula. Typically, low molecular weight normal paraffins (C₄-C₆) are converted into isoparaffins which have a much higher octane index. There are three distinct different types of catalysts currently in use, including chloride promoted catalysts, zeolites, and sulfated zirconium catalysts.

73. The Dienes Hydrogenation and Butylenes Hydroisomerization Unit is placed upstream of the alkylation and based on a highly selective catalytic process. This process hydrogenates acetylenes and dienes into the corresponding mono-olefins without affecting the valuable olefin content of the feedstock, while converting linear butene-1 into linear butenes -2 which in alkylation leads to higher octane gasoline components than those derived from butene-1.

**Pretreating and Catalytic Reformer Unit**

74. The typical feedstocks are heavy virgin naphtha (HVN) from the crude distillation unit and, when applicable, the hydrotreated heavy naphtha from the hydrocracker unit. Naphtha feed, mixed with a hydrogen-rich gas stream, is heated and vaporized and then fed into the hydrotreater reactor (pretreating), which contains a fixed bed of cobalt / nickel / molybdenum catalyst. The C₅-minus hydrocarbons contained in the product, after the separation of hydrogen, are removed in a stripping tower. The heavy naphtha, free from nitrogen and sulfur compounds, leaving the hydrotreating section, enters the Catalytic Reformer Section to be upgraded for use as high octane gasoline blend-stock.

75. There are four major types of reactions which occur during the reforming process: (1) dehydrogenation of naphthenes to aromatics; (2) dehydrocyclization of paraffins to aromatics; (3) isomerization; and (4) hydrocracking. There are several catalytic reforming

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21 The hydrotreating process can be divided into a number of reaction categories: naphtha hydrotreating (or pretreating, where upstream of reforming), hydrodesulfurization (HDS, including Middle Distillate Hydrodesulfurization Unit, Selective Catalytic Hydrodesulfurization, and Diesel Oil Deep Hydrodesulfurization), selective hydrocracking (or dewaxing), hydrodenitification, saturation of olefins and saturation of aromatics, residue hydrotreating.

22 The Hydrocracking Unit is one of the most versatile of all refining processes, capable of converting any fraction, from atmospheric gas oils to residual (de-asphalted) oil, into products with a molecular weight lower than that of the feed. The Hydrocracking reactions occur under high hydrogen partial pressure in catalytic reactors at a substantially high pressure (35 to 200 bar) and at temperatures between 280 and 475°C. The catalyst (CoNi/Mo based) has a two-fold function: hydrogenation and cracking. The most common types of reactor technologies applied are Fixed Bed and Ebullated Bed. The selection of the type of technology is predominantly determined by the metal content in the feed.
processes in use and they can be classified into three categories including ‘continuous’, which makes use of moving bed reactors, as well as ‘cyclic’ and ‘semi-regenerative’, both making use of fixed bed reactors.

**Catalytic Cracking Units (Catcrackers)**

76. Catalytic Cracking is by far the most widely used conversion process to upgrade heavy hydrocarbons into more valuable lower boiling hydrocarbons. It makes use of both heat and catalyst to break the large hydrocarbon molecules into smaller, lighter molecules. Unlike the hydrotreater unit, no hydrogen is used and, consequently, limited desulfurization takes place during the process. Catalytic cracking designs include moving-bed reactors, fluidized-bed reactors (e.g. Fluid Catalytic Cracking Unit [FCCU], Residue Catalytic Cracking Unit [RCCU]), and once-through units. FCCU feed stream is the desulfurized heavy vacuum gasoil coming from hydrocracking. RCCU treats heavier feedstocks, such as the atmospheric distillation residue.

77. In both processes, oil and vapor are contacted with hot catalyst in the ‘Riser Reactor’. The cracking process takes place in presence of a zeolite type catalyst. The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in a cyclone system and any oil remaining on the catalyst is removed by feeding steam in the stripping section of the reactor. The catalytic cracking processes produce coke. This is deposited on the catalyst surface, thereby reducing activity and selectivity. Catalysts should be continuously regenerated, essentially by burning off the coke from the catalyst at high temperature in the regenerator. Products are separated by means of a fractionation train.

**Gas Plant Units**

78. Low boiling hydrocarbons are usually treated in a common separation plant operating at elevated pressure. Gas plants allow recovery and separation by distillation of C1 - C5 hydrocarbons and higher compounds from the various refinery off-gases. The Gas Plant consists of a fractionation train where the following streams are separated: C1-C2 fraction; C3 fraction (propane); C4 fraction (butane); and debutanized gasoline. Amine Treating Units remove hydrogen sulfide and carbonyl sulfide from all product streams. Before being sent to the relevant storages, liquid products pass through to Sweetening Units based on selective adsorption on molecular sieves.

**Etherification Units**

79. The feedstocks of MTBE/ETBE units are the C4 hydrocarbons stream coming from the FCCU, and methanol or ethanol. Isobutylene reacts with methanol or ethanol to yield directly MTBE (methyl-tert-butyl-ether) or ETBE (ethyl-tert-butyl-ether), respectively. The reactors can be of adiabatic or tubular type or combined with a fractionation tower (this type of reactor is normally referred as Catalytic Distillation Reactor or Reactor Column). The catalyst is a sulfonic resin. The feedstock of TAME units is LCN, (composed of C5 hydrocarbons, both paraffins and olefins). However, only the reactive isoamylene (2-methyl-butene-1 and 2-methyl-butene-2) react with methanol to directly yield TAME (tert-amyl-methyl-ether). Adiabatic type reactors are used, and the catalyst is the same as for the MTBE / ETBE Units.

**Alkylation Units**

80. The purpose of the alkylation unit is to produce a high-quality gasoline blending component called alkylate. Alkylation is the reaction of C3 and C4 olefins with isobutane to form higher molecular-weight isoparaffins with high octane number (preferably iso-octane).
The process involves low-temperature reaction conditions conducted in the presence of very strong acids (hydrofluoric acid or non fuming sulfuric acid). The reaction in hydrofluoric acid alkylation produces acid soluble oil (normally referred as ASO) which, after neutralization, is burned in a furnace by means of a dedicated burner. The reaction in sulfuric acid alkylation produces acid sludges (spent acid), which are burned to recover sulfuric acid (sulfuric acid regeneration).

81. The acid sludges are fed into a decomposition furnace together with fuel gas, where, at 1,050°C, the decomposition of the sulfuric acid into sulfur dioxide takes place. The gas leaving the furnace is cooled down to 350°C in a waste heat boiler, and then further cooled and filtered. The gas and condensed water are fed to the gas treatment system.

**Polymerization Unit**

82. In polymerization process unit, the C3 and C4 olefins are dimerized and oligomerized to produce the so called polymeric gasoline as high octane blending component. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst adsorbed onto natural silica.

**Coking Units**

83. Coking is a severe thermal cracking process used primarily to reduce refinery production of low-value residual fuel oils and transform them into transportation fuels, such as gasoline and light and heavy gas oils. As a part of the process, coking also produces petroleum coke, which is essentially solid carbon, with varying amounts of impurities and containing 5–6 percent hydrocarbons. Two types of coking processes exist: the delayed coking and the fluid coking processes. The flexi-coking process is similar to fluid coking, but has fully integrated gasification suitable to gasify the fluidized coke in order to produce coke gas.

84. The hot vapors from the coke drums contain cracked lighter hydrocarbon products, hydrogen sulfide and ammonia, and are fed back to the fractionator where these lighter hydrocarbon products can be treated in a sour gas treatment system. The condensed hydrocarbons are reprocessed, whereas water is re-used for coke drum quenching or cutting.

85. The sulfur contained in the coke is converted in flexicoking gasifiers, primarily into hydrogen sulfide, and into traces of carbonyl sulfide. The nitrogen contained in the coke is converted into ammonia.

**Visbreaking Unit**

86. The Visbreaking Unit is a well-established non catalytic thermal cracking process that converts atmospheric or vacuum residues to gas, naphtha, distillates and tar. It uses heat and pressure to break large hydrocarbon molecules into smaller lighter molecules.

87. The most important factor in controlling the cracking severity should always be the stability and the viscosity of the so called visbroken residue, which is fed to the fuel oil pool. In general, an increase in the temperature in or residence time results in an increase in cracking severity. Increased severity increases gasoline yield and, at the same time, produces cracked residue (fuel oil) of lower viscosity. Excessive cracking, however, leads to an unstable fuel oil, resulting in sludge and sediment formation during storage.
There are two types of visbreaker operations: coil or furnace cracking and soaker cracking. The gas produced is fed to an amine treating unit, to remove hydrogen sulfide.

Lube Oil Production Units

A base oil complex typically consists of a vacuum distillation tower, a deasphalting unit, an aromatic extraction unit, a dewaxing unit, an optional high pressure hydrogenation unit and a hydrofinishing unit to improve color and stability, to meet product specifications and to remove impurities. A conventional base oil complex is very labor intensive, mainly due to its batch operation, the many grades of base oil normally produced and the associated intensive product handling operations.

Gas Treatment and Sulfur Recovery Units

Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the SO\textsubscript{x} emission limits and to recover saleable elemental sulfur. Process off-gas streams, or sour gas, from the coker unit, FCCU, hydrotreating units and hydroprocessing units, contain high concentrations of hydrogen sulfide and carbonyl sulfide mixed with light refinery fuel gases. Before elemental sulfur is recovered, the fuel gases (primarily methane and ethane) need to be separated from hydrogen sulfide and carbonyl sulfides. This is typically accomplished by dissolving hydrogen sulfide and carbonyl sulfides in a chemical solvent. The solvents most commonly used are amines, such as diethanolamine (DEA). Dry adsorbent, such as molecular sieves, activated carbon and iron sponge are also used.

In the amine solvent processes conducted in the amine gas treating units, DEA solution, or another amine solvent, is pumped to an absorption tower where the gases are contacted and hydrogen sulfide and carbonyl sulfide are dissolved in the solution. The fuel gases, free from hydrogen sulfide and carbonyl sulfide, are removed and sent to refinery fuel gas network. The amine-hydrogen sulfide and carbonyl sulfide solution is regenerated by heating and steam stripping to remove the hydrogen sulfide gas before recycling back to the absorber. Hydrogen sulfide and carbonyl sulfide are sent to the Claus Unit for sulfur recovery. Air emissions from sulfur recovery units will consist of hydrogen sulfide, SO\textsubscript{x} and NO\textsubscript{x} in the process tail gas, as well as fugitive emissions.

The Claus process consists of the partial combustion of the hydrogen sulfide and carbonyl sulfide-rich gas stream and then of reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur. Claus units remove only 90 percent of hydrogen sulfide and carbonyl sulfide, and are followed by other processes to complete sulfur removal (up to 99.5 percent).

Sour Water Stripper Unit (SWSU)

Many process units generate sulfides and ammonia-contaminated water, normally referred as sour water. Sour Water Stripper Unit (SWSU) permits reusing sour water by removing sulfides and ammonia. The process operation is complicated by the presence of other chemicals, such as phenol, and cyanides.
Hydrogen Plant

94. Normally the feedstock the hydrogen plant is the methane obtained by the refinery process units, LPG, or refinery external natural gas, if available. This unit normally consists of a reformer and produces a hydrogen – carbon monoxide mixture, referred as synthetic gas (syngas). After passing through a heat recovery section, cold syngas enters the shift conversion reactor where, under an iron or copper based catalyst, carbon monoxide is reacted with water to yield more hydrogen and carbon dioxide. The latter is separated in an amine absorption – regeneration unit. A closed drain system collects and recovers any amine drains and spills, thereby preventing them from being purged into the WWTU.

Chemical Treatment Units

95. Chemical treatments are used to achieve certain product specifications. The Extraction Sweetening Units are designed to reduce the mercaptans content of hydrocarbon streams to mitigate odor nuisance and to reduce corrosivity. These treatments are accomplished by either extraction or oxidation or both, depending on the treated process stream. The extraction process removes the mercaptans by caustic extraction, resulting in a lower sulfur content. The sweetening process causes the mercaptans to be converted into less odorous and less corrosive disulfides which remain in the product. As a result, no reduction in the total sulfur content takes place during sweetening and, consequently, it is only applied to those streams where sulfur content is not a problem.

96. The spent caustic scrubbing liquor (spent caustic) coming from the Extraction Unit is one of the most problematic waste streams generated in refineries. This is primarily due to the very high sulfides concentration which make it non suitable for direct discharge into the WWTU. High levels of sulfides can also create odor and safety problems when released as gas.

97. In the Caustic Oxidation Unit, the reactive sulfides contained in the spent caustic liquor are oxidized into soluble thiosulfates, sulfites and sulfates. The treated stream is then suitable for bio-treatment in the WWTU.

Gasification Units

98. The gasification units include Coke Gasification, Hydrocarbons Gasification (Partial Oxidation), and Hydrogen Purification (i.e., Wet Scrubbing, Membrane Systems, Cryogenic Separation and Pressure-Swing Adsorption). The synthetic gas produced by coke gasification contains hydrogen sulfide and carbonyl sulfide, and the gas is treated in an Amine Treating Unit.

Blending Facilities

99. Blending is the final operation in petroleum refining. It consists of mixing the products in various proportions to meet commercial specifications. Blending can be carried out in-line or in batch blending tanks.

100. Air emissions from blending include fugitive VOC from blending tanks, valves, pumps and mixing operations.

Auxiliary Facilities

101. Auxiliary facilities at petroleum refineries typically consist of waste water treatment units, blow down and flare systems, vapor recovery units (e.g. thermal oxidation, absorption, adsorption, membrane separation and cryogenic condensation), and energy/electricity systems (e.g. boilers, furnaces, gas turbines).