

EU-MERCI

EU coordinated **ME**thods and procedures based on **Re**al **C**ases for the effective implementation of policies and measures supporting energy efficiency in the **I**ndustry

HORIZON 2020 Project Nr. 693845

Technical analysis – Petroleum refineries sector (NACE C19)

WP4: Picture of efficiency projects implemented by the
Industry sector-by-sector and process-by-process

Table of Contents

1	Introduction	3
1.1	Key Products	3
1.1.1	Coke	3
1.1.2	Refined petroleum products.....	3
1.2	Sector Energy Consumption	3
2	Process Analysis	5
2.1	Desalting.....	7
2.2	Distillation	7
2.2.1	Atmospheric distillation.....	7
2.2.2	Vacuum distillation	8
2.3	Base Oil Production	9
2.4	Bitumen Production	10
2.5	Coking (Delayed & Fluid Coking)	11
2.6	Coking (Flexicoking).....	12
2.7	Catalytic Cracking	13
2.8	Catalytic Reforming	15
2.9	Alkylation	16
2.10	Isomerisation	18
2.11	Polymerisation	19
2.12	Hydrogen Production	20
2.12.1	Steam reforming	20
2.12.2	Gasification of coke.....	20
2.12.3	Gasification of hydrocarbons.....	21
2.12.4	Purification of hydrogen	21
2.13	Etherification	21
2.13.1	MTBE production process.....	22
2.13.2	ETBE production process	22
2.13.3	TAME production process.....	23



2.14	Product Treatment	23
2.15	Gas Separation	24
2.16	Cooling	25
2.17	Natural gas plant	27
3	<i>Energy Intensity of Key Processes.....</i>	29

1 Introduction

The manufacture of coke and refined petroleum products (NACE C19) involves the transformation of raw crude oil and natural gas to different forms of petroleum, such as fuels for vehicles, combustion fuels for the generation of heat and power, saw materials for chemical industries, specialty products such as oils and bitumens, and energy as a by-product of the process. This includes subsectors 19.1 (Manufacture of coke oven products) and 19.2 (Manufacture of refined petroleum products)

1.1 Key Products

1.1.1 Coke

Roughly 90% of the coke consumed in the EU is used in the production of iron from blast oven furnaces. The rest are used in iron foundries, non-ferrous smelters, and the chemical industry. Coke is produced by processing low-ash low sulphur bituminous coal. Pulverised coal is heated in a coke oven, in the absence of oxygen, at high temperatures (1,200-1,300°C), and is the solid material remaining in the oven. The necessary heat is provided by external combustion of fuels and recovered gases. There are approximately 1,900 coke oven installations in the EU.

1.1.2 Refined petroleum products

Refined petroleum products are derived from crude oils through processes such as catalytic cracking and fractional distillation. The type of crude oil a refinery can process depends on the processing units operated as well as the desired product slate. All refineries have crude oil fractional distillation, where crude oil is distilled into a number of fractions; e.g petroleum gases, light and heavy naphtha, asphalts, and residue.

In 2012, there were 83 petroleum refineries in EU-28. Of these, approximately half of Member States have complex refineries, with the remainder considered simple. The level of complexity defines whether a refiner can effectively respond to changes in product supply and demand by shifting its product slate. For example, refineries may produce more gasoline during the spring and summer months when demand is high, than they do during the winter when demand for heating oil is high.

1.2 Sector Energy Consumption

Petroleum processing is one of the most energy intensive industries. In 2012, there were 655 oil refineries in the world with the majority in Asia and 20% in Europe . The top five countries producing

refined oil products in 2015 were the US (868 Mt), China (512 Mt), Russia (273 Mt), India (239 Mt), and Japan (160 Mt).

Since this sector relies almost entirely on raw materials, and since it consumes a large amount of energy and water, refineries produce a large proportion of Greenhouse Gas (GHG) emissions of the industry sector. In 2006, oil and gas accounted for 65% (42% and 23%) of the EU-27 final energy consumption, with an average consumption level of 2.75 GJ/t. In 2015, the total energy consumption for the manufacture of coke and refined petroleum products was 3946 ktoe (DBEIS 2016). The greatest proportion of energy consumption is from internal and external fuels during combustion phases, which can have up to 200 MW of thermal input. However, as there are many stages of thermal combustion within the process (such as catalytic cracking), energy released from combustion can be recovered and used in other processes, therefore reducing the total amount of external energy consumed. Some stages can also be more energy-intensive than others, for example, sulphur removal from products requires high energy for hydrogen production, and atmospheric distillation and vacuum distillation together use 35-40% of the total process consumption.

The main energy sources to run a refinery are heat and electricity. The high heat requirement is provided by fuel combustion directly (via heaters or furnaces) and indirectly (via steam). The fuel required for the production of steam and power or firing the furnaces comes from fuels that are produced by the refinery itself or from external natural gas.

- Refinery fuel gas – This is the fuel that a refinery mainly uses. It is a mixture of methane, ethane, ethylene, and hydrogen. It is produced and collected in the refinery gas system, but has to be used quickly and cannot normally be sold as a product.
- Fuel gas system – This fuel is supplied from the different refinery units with a backup supply from imported natural gas. Normally all units have their own fuel gas knockout drum, in which fuel condensate formed in the fuel gas distribution system is separated.
- Liquid refinery fuel – This is a heavy fuel oil used in the refinery is typically a mixture of the residues from atmospheric and/or vacuum distillation and conversion and cracking processes. Liquid refinery fuels are available in various grades, mainly determined by viscosity.
- Solid fuels – These can be gasified as a fuel gas source for refineries (such as petroleum coke), and are burnt in the coking process and represents a heat production source in the refinery.

2 Process Analysis

Crude oil and natural gas are made up of multiple hydrocarbons and minor amounts of impurities. Therefore, the manufacturing process puts the raw resources through multiple refining facilities (either individually or as a mixture with biofuels) in order to get rid of the impurities and transform the material into a usable medium (Figure 1 and Figure 2). The characteristics of the refinery like the size, configuration, and complexity are influenced by market demand for specific types.

The refining process is split into two main phases:

- Phase 1 – The desalting of the oil and subsequent distillation into various fractions. Further distillation of the lighter components is carried out in every refinery in order to recover methane and ethane for use as refinery fuel, propane and butane, gasoline-blended components, and petrochemical feedstocks.
- Phase 2 – Three types of downstream processes (breaking, combining, and reshaping fractions) in order to change the molecular structure of hydrocarbon molecules. This converts some of the distillation fractions into marketable petroleum products. The volumes of various products are determined by the composition of the crude oil, so if the product doesn't match the market demand, conversion units can be added to restore the balance (Figure 1 and Figure 2).

The processing within these phases are desalting, distillation, base oil production, bitumen production, coking (delayed & fluid coking and flexicoking), catalytic cracking, catalytic reforming, alkylation, isomerisation, polymerisation, hydrogen plant processing, etherification, product treatment, gas separation, refining (cooling and energy systems), and natural gas plant processing.

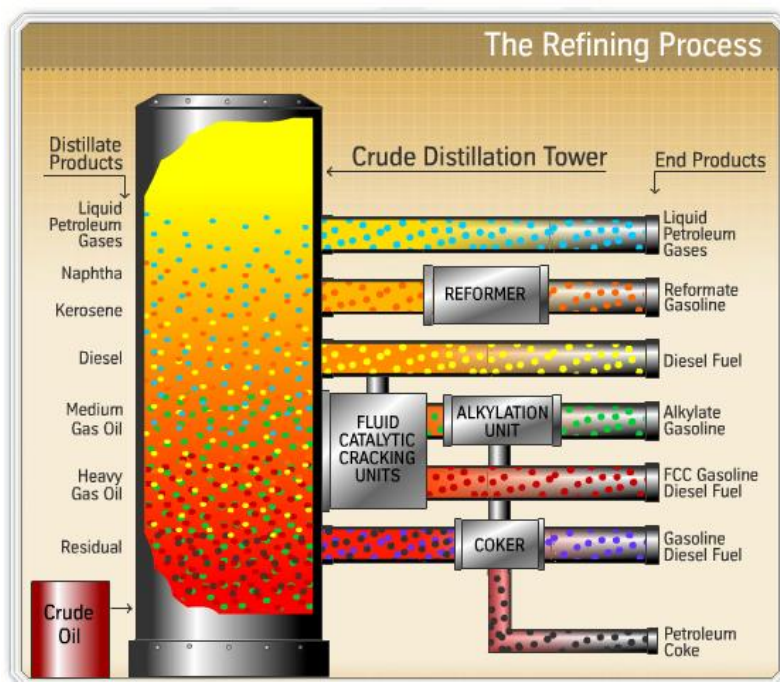


Figure 1: Basic diagram of the production process.

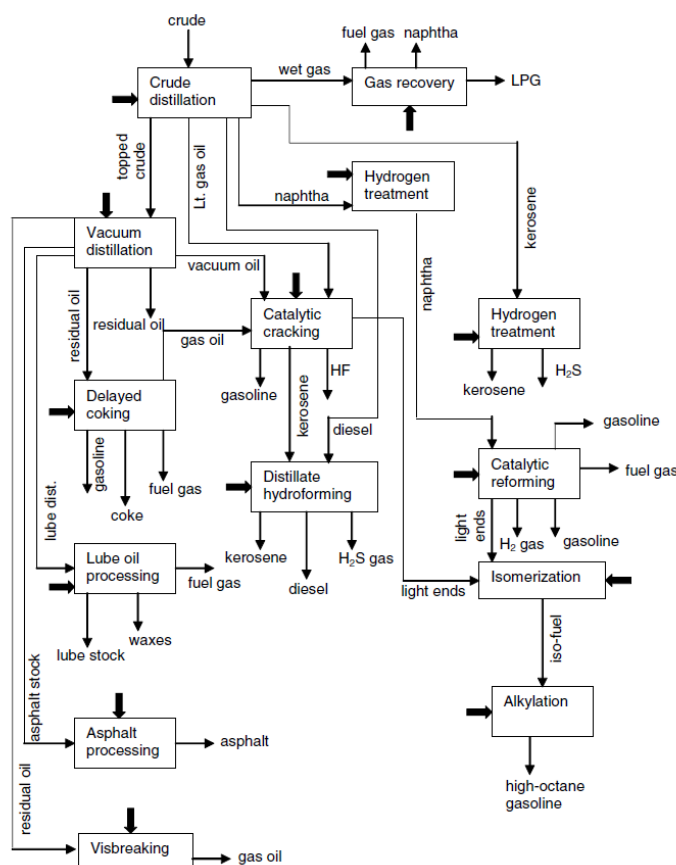


Figure 2: Detailed schematic of the production process.

2.1 Desalting

As crude oil and heavy residues can contain varying quantities of inorganic compounds (such as salts, sand, and silt), which are detrimental to the activity of many catalysts, it must be desalted before processing. This is done by washing the crude oil or heavy residues with water at high temperature and pressure in order to dissolve, separate, and remove the salts and other water extractable components. The feedstock is first preheated to 115-150°C and mixed with water in a globe valve mixer to dissolve and wash out the salts. The separation efficiency depends on the pH, density, and viscosity of the oil, and the volume of water used per volume of oil (Figure 3).

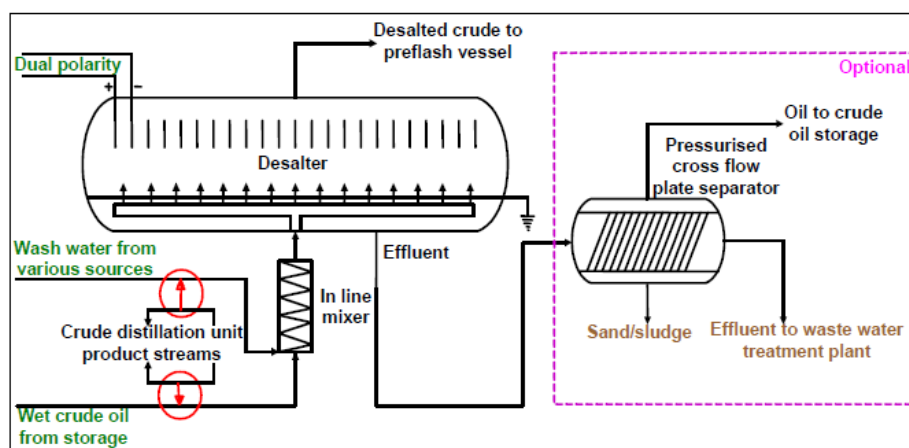


Figure 3: Crude oil desalting process diagram.

2.2 Distillation

Following the desalting of crude oil, the material goes through atmospheric and vacuum distillation.

2.2.1 Atmospheric distillation

The Atmospheric Crude Oil Distillation Unit (CDU) is the first important processing step in a refinery. Crude oil is heated to elevated temperatures and then generally subjected to distillation under atmospheric pressure (or slightly higher), separating the various fractions according to their boiling range. Heavier fractions from the bottom of the CDU, which do not vaporise in this column, can be further separated later by vacuum distillation (Figure 4).

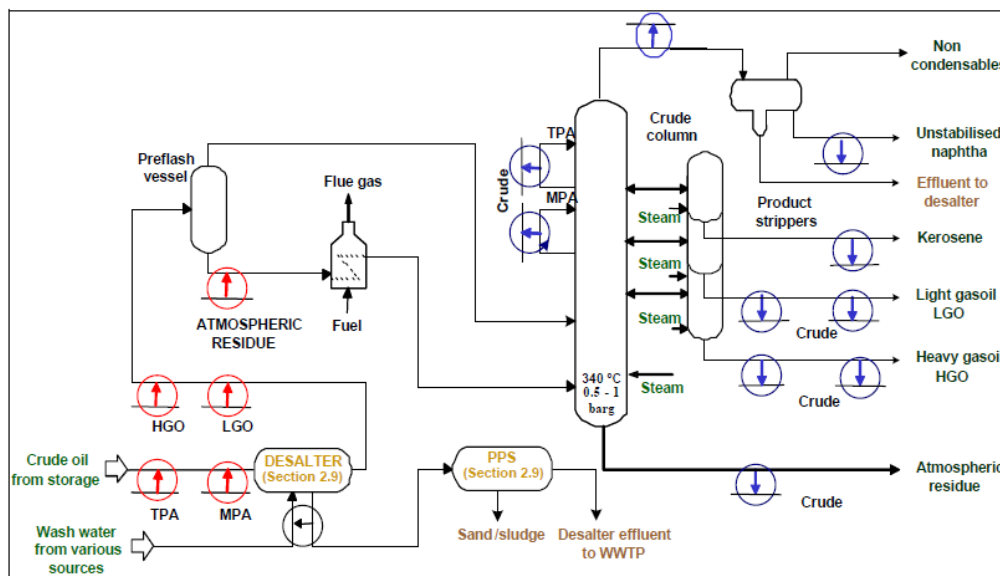


Figure 4: Crude oil atmospheric distillation process diagram.

2.2.2 Vacuum distillation

Atmospheric residue is heated up to 400°C, partially vaporised (30-70 %), and flashed into the base of the vacuum column at a pressure between 40 and 100 mbar (0.04-0.1 kg/cm²). The vacuum inside the fractionator is maintained with steam ejectors, vacuum pumps, barometric condensers, or surface condensers. The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporisation and separation (Figure 5).

The unvaporised part of the feed forms the bottom product and its temperature is controlled at about 355°C to minimise coking. The flashed vapour rising through the column is contacted with wash oil to wash out entrained liquid, coke and metals, then the washed vapour is condensed in two or three main spray sections. In the lower sections of the column, the heavy vacuum distillate and optional medium vacuum gas oil are condensed .

In the upper section of the vacuum column, the light vacuum distillate is condensed. Light (non-condensable) components and steam from the top of the column are condensed and accumulated in an overhead drum for separating the light non-condensables, the heavier condensed gas oil, and the water phase .

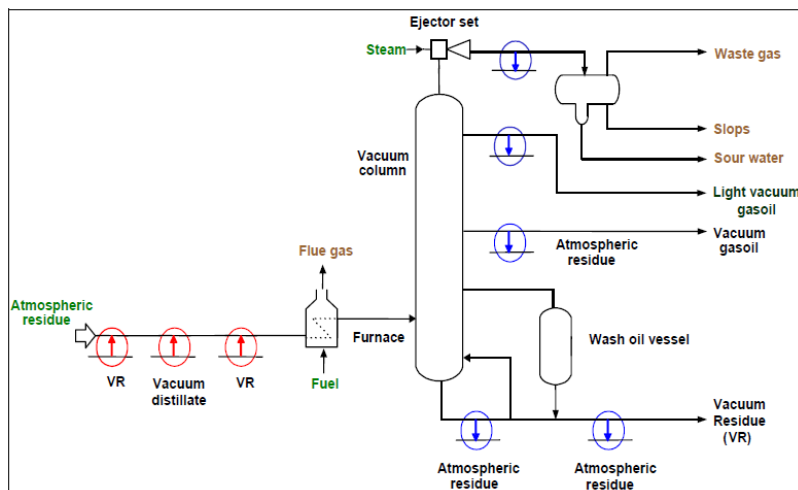


Figure 5: Crude oil vacuum distillation process diagram.

2.3 Base Oil Production

Base oil is only produced in 20% of EU refineries as it is a speciality product and not all crude oil types are suitable. It requires specific characteristics in viscosity, viscosity index, high resistance to oxidation, low pour point, and good dope susceptibility or compatibility. They are also classified by the percentage of saturates, the sulphur content, and the viscosity index into five groups .

The four main process families for improving base oil quality are separation by solvent-based processes, conversion by hydrogenation-based processes, converting to hydrogen-based processes, and gas to liquid . This process goes through solvent deasphalting, solvent-based aromatic extraction, solvent dewaxing, a high-pressure hydrogenation unit, a hydrocracker, catalytic dewaxing, a lube unit, hydrofinishing, clay treatment, and distillation (Figure 6).

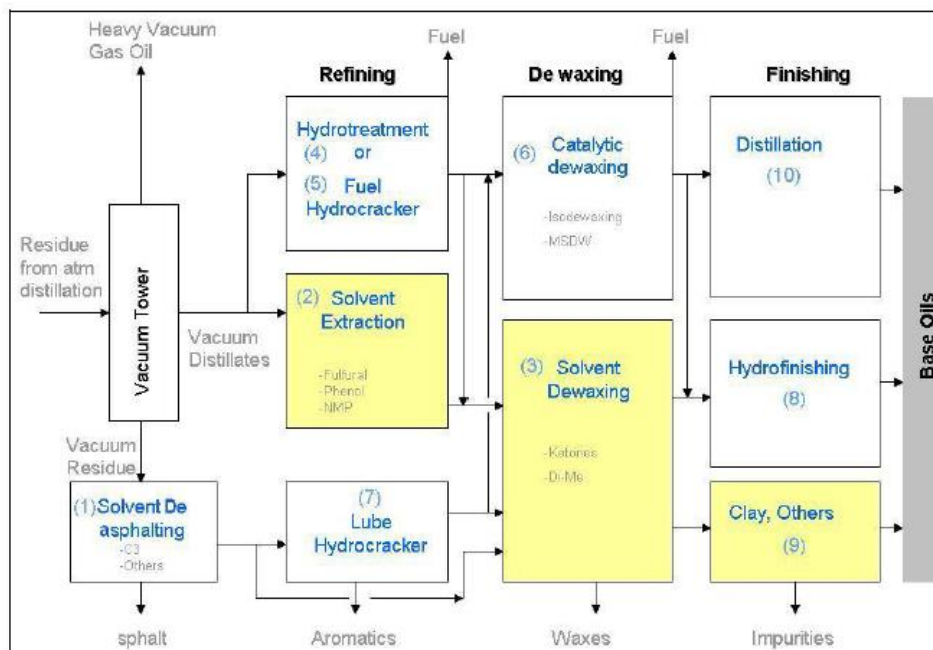


Figure 6: Block scheme of a lubricating oil manufacturing plant with a combination of process options units.

2.4 Bitumen Production

Bitumen is a residue derived from certain crude oils after vacuum distillation has removed waxy distillates. It is typically mixed with other components like gravel to produce asphalt. This process is part of only 45% of EU refineries. The desired properties of bitumen may be achieved either by adjusting distillation conditions or by ‘blowing’. In the latter process, air is blown into hot bitumen causing dehydrogenation and polymerisation reactions and creating a harder product with higher viscosity, higher softening point and a reduced penetration. The properties of the blown bitumen are determined by the residence time in the oxidation vessel, the air rate and the liquid temperature. If any of these parameters are increased, the penetration is reduced and the softening temperature is raised .

The BBU will either operate on a continuous basis or in batch mode depending on the quality of the vacuum residue feedstock and the required bitumen product specification. Where the bitumen feed is received from storage, an additional fired heater may be required to preheat the feed to a temperature of about 200-250°C, but it can be up to 550°C (Figure 7).

The residue feed stream is pumped into the top of the oxidation vessel, where the operating pressure in the top of the oxidation vessel is normally around 1 barg and in the bottom around 2 barg, depending on the height of the vessel. As air is sparged into the base of the vessel, oxidation of the residue takes place, resulting in heat between 260°C and 300°C. Different options are applied for adjusting the temperature, which include the addition of colder feed to the oxidation vessel, the

recirculation of cooled bitumen product from the bitumen run down cooler, and in older units direct water quenching. The blown bitumen is removed from the bottom of the oxidation vessel and cooled by rising steam, before being sent to storage .

The overhead vapours are first passed through a vent gas scrubber to remove oil and other oxidation products. In most cases, gas oil is used as once-through scrubbing liquid. The vent gas from the scrubber is subsequently cooled to condense light hydrocarbons and sour water, sometimes in a water spray contact condenser or scrubber. The remaining gas, consisting mainly of light hydrocarbons, N_2 , O_2 , CO_2 and SO_2 , is incinerated at high temperatures ($\sim 800^\circ C$) to ensure complete destruction of minor components such as H_2S , complex aldehydes, and organic acids and phenolic compounds .

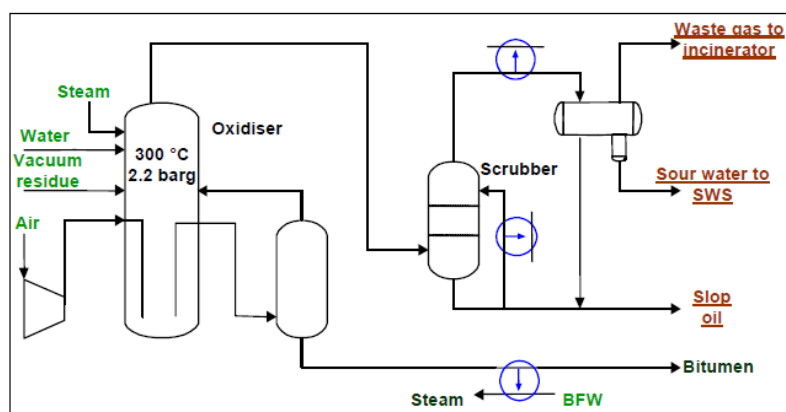


Figure 7: Bitumen blowing unit process diagram.

2.5 Coking (Delayed & Fluid Coking)

Coking is the severe thermal cracking process used to reduce the refinery production of low-value residual fuel oils and transform them into transportation fuels. The process also produces petroleum coke, which is a form of solid carbon with varying impurities. The delayed and fluid coking is the first part of the coking process, which produces the coke material.

The basic process is the same as thermal cracking, except that feed streams are allowed to react for longer without being cooled (Figure 8). The delayed coking feed stream of residual oils is first introduced to a fractionating tower, where residual lighter materials are drawn off and the heavy ends are condensed. The heavy ends are removed, heated in a furnace and fed to an insulated vessel called the coke drum, where the cracking takes place. In the case of fluid coking, a fluidised bed is used. Temperature ($440-450^\circ C$), pressure (1.5-7.0 barg), and recycle ratio are the main process variables which contribute to the quality and yields of delayed coking products. When the coke drum is filled with product, the feed is switched to an empty parallel drum.

When the coke drum is full, steam is injected to remove hydrocarbon vapours. The coke bed is then quenched with water and the cokes are cut out with high pressure water. The cutting water passes to dedicated settlement where coke solids settle out and the clarified water is recycled. The wet green

coke is conveyed to designated open stockpiles, where water drains out and is recycled. Green coke can already be sold and used for energy production. The yield of delayed coking is usually above 80% (25-30% coke, 65-75% light products) conversion of feed to products. The production of petroleum coke is at the ratio of 0.13 tonnes of petroleum coke produced per tonne of feedstock.

Hot vapours from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulphide, and ammonia are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products. Condensed hydrocarbons are reprocessed and collected water is reused for coke drum quenching or cutting. Any remaining vapours commonly pass to the flare system. The heavier products are suitable feedstock for catalytic reforming after proper hydrotreatment. Light oil needs further treatment before being sent to the gas oil blending pool, and the heavy gas oil is preferably sent to a hydrocracker unit for further conversion into light components.

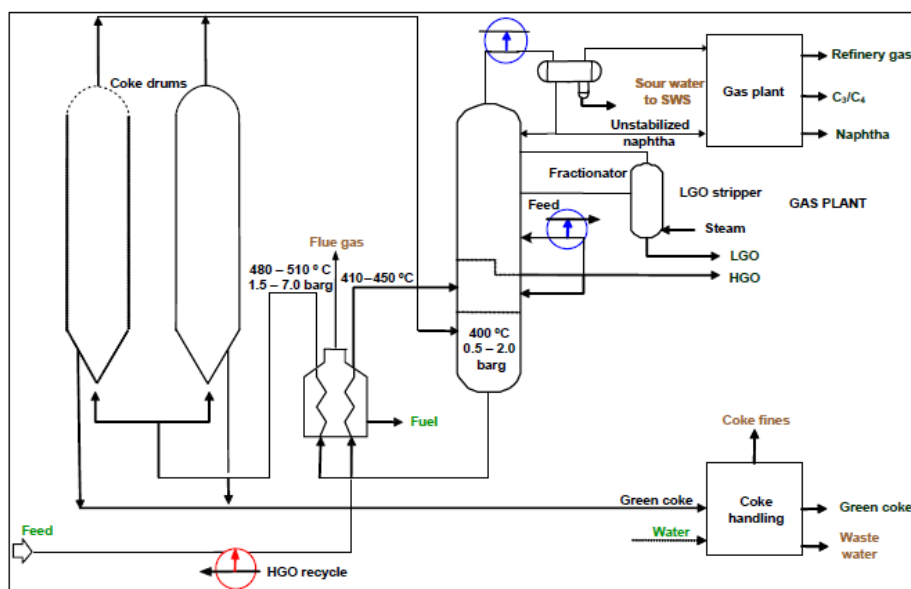


Figure 8: Delayed and fluid coking process diagram.

2.6 Coking (Flexicoking)

Flexicoking is the second part of the coking process, which gasifies the coke produced in a fluid coking process to produce coke gas [Fig. 8]. The flexicoking process typically converts 84-88% of the vacuum residue to gaseous and liquid products, and almost all metals in the feed are concentrated in the solids purged from the process. The flexicoking process uses three major vessels: the reactor, the heater and the gasifier. As auxiliary facilities, the system includes a heater overhead cooling system and a fines removal system, a coke gas sulphur recovery unit, and reactor overhead scrubber. The preheated vacuum residue feed is sprayed into the reactor, where it is thermally cracked, typically at 510-540°C. The freshly formed coke is deposited on the surface of the fluidised recirculated coke particles. In the

gasifier, the coke is reacted at elevated temperatures between 850 and 1,000°C, with air and steam to form coke gas, a mixture of hydrogen, carbon monoxide, and dioxide and nitrogen. Sulphur in the coke is converted in the gasifier primarily to hydrogen sulphide, plus traces of carbonyl sulphide (COS), and nitrogen in the coke is converted to ammonia and nitrogen. Unlike normal gasifiers which are fed with pure oxygen, the flexicoking gasifier is fed with air, resulting in a coke gas with a relatively low calorific value, as it contains a high quantity of inert nitrogen. The cracked hydrocarbon vapour product from the reactor is passed through cyclones to remove coke particles and is subsequently quenched in a scrubber section located at the top of the reactor. Material boiling above 510-520°C is condensed in the scrubber and recycled to the reactor. The lighter material goes overhead to conventional fractionation, gas compression and light ends recovery sections. The treatments and use of the products are very similar to the ones already described in the delayed coker. Pressure relief from the fractionator of the coking processes passes to flare and from the coke drums to the quench tower system.

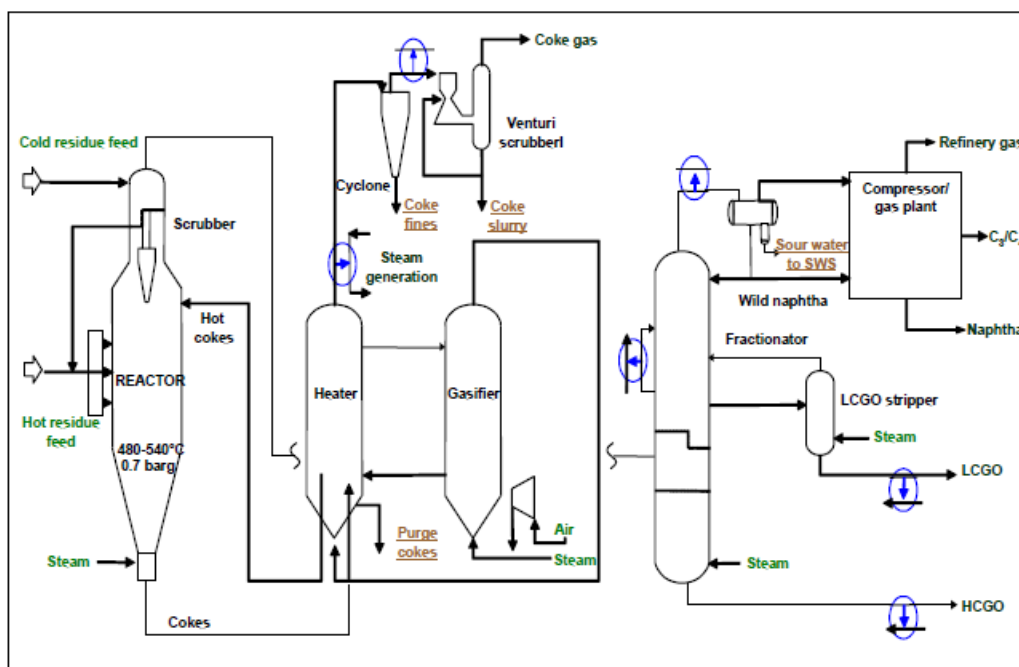


Figure 9: Flexicoker process diagram.

2.7 Catalytic Cracking

Catalytic cracking is the most widely used conversion process for upgrading heavier hydrocarbons into more valuable lower boiling hydrocarbons by using heat and a catalyst to break large the molecules. Compared to other conversion processes, the catalytic cracker process is characterised by a relatively high yield of good quality gasoline and relatively high quantities of C₃ and C₄. Both products are highly olefinic, and therefore are ideal feed streams for the alkylation, etherification, and petrochemical industries.

There are a number of catalytic cracking designs used worldwide, including fixed bed reactors, moving bed reactors, fluidised bed reactors, and once-through units. However, the fluidised and moving bed reactors are the most commonly used.

Fluid catalytic cracking (FCC) consists of three sections: the reactor-regenerator (including the air blower and waste heat boiler), the main fractionator (including the wet gas compressor), and the unsaturated gas plant section (Figure 10). Oil and oil vapour are preheated to 250-425°C and come into contact with a hot catalyst at about 680-730°C in the riser reactor. The cracking process takes place at temperatures between 500 and 540°C and a pressure of 1.5-2.0 barg. The catalyst is in a fine, granular form which mixes intimately with the vaporised feed. The fluidised catalyst and the reacted hydrocarbon vapour are separated mechanically in a (two-stage) cyclone system and any hydrocarbon remaining on the catalyst is removed by steam stripping. The amount of catalyst lost as fines in the reactor and regenerator cyclones is balanced by the addition of fresh catalyst.

The catalytic cracking process produces coke, which collects on the catalyst surface and diminishes its catalytic properties. The catalyst therefore needs to be regenerated continuously essentially by burning the coke off the catalyst at high temperatures.

The catalyst flows into a separate vessel for either single or two-stage regeneration, by burning off the coke deposits. However, in time, the catalyst deactivates gradually and irreversibly due to high-temperature exposure and metal poisoning. The hot regenerated catalyst flows back to the base of the reactor riser, where it is cooled by vaporisation of the feed and by the heat absorption required for cracking reactions.

The cracked hydrocarbon vapours are then fed to a fractionation tower where the various desired fractions are separated and collected. The streams are steam stripped to remove volatile hydrocarbons prior to cooling and sending to storage, and slurry oil is taken from the bottom of the column and cooled by heat exchange with the reactor feed stream and by steam generation, and returned to the column. The recycled slurry oil is used as wash oil and as a quench for the hot reactor overhead vapours to prevent aftercracking. The rest of the slurry oil is filtered or decanted to remove catalyst fines, cooled, and sent to storage. The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate it into three phases: gas, liquid, and sour water streams. The liquid and gas streams are both fed to the gas plant for further separation and the sour water stream is sent to the sour water stripper for purification.

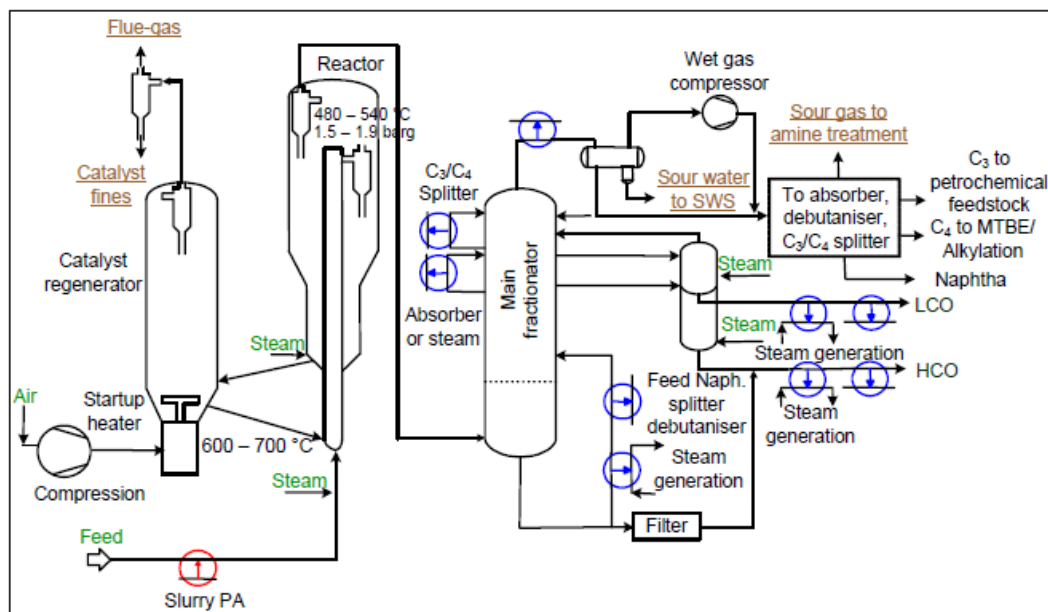


Figure 10: Fluid catalytic cracker process diagram.

In the moving bed process, oil is heated to 400-700°C and passed under pressure through the reactor, where it meets a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated. Some units also use steam to strip the remaining hydrocarbons and oxygen from the catalyst before the catalyst is fed back to the oil stream.

2.8 Catalytic Reforming

This process upgrades the octane of the gasoline blend component leaving the hydrotreating units for use as a gasoline blendstock. The four main reactions that occur during the process are:

- 1) Dehydrogenation of naphthenes to aromatics,
- 2) Dehydrocyclisation of paraffins to aromatics,
- 3) Isomerisation, and
- 4) Hydrocracking

Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulphur, nitrogen, and metallic contaminants. There are several catalytic reforming processes, classified into three categories: continuous, cyclic, and semi-regenerative (depending upon the frequency of the catalyst regeneration).

In the continuous catalytic regeneration (CCR) process (Figure 11), the catalyst can be regenerated continuously and maintained at a high activity rate. The ability to maintain a high catalyst activity and selectivity by continuous catalyst regeneration is the major advantage of this type of unit. As the

naphtha feed charge proceeds through the reactors, the reaction rates decrease and the reheat needed lessens. From here it is passed on to the next reactor. Partially aged catalyst is removed from the bottom of the lowest reactor and sent to an external regenerator, where the carbon is burnt from the catalyst. The catalyst is acidified and reduced before being returned to the lead reactor. The reaction mixture from the last reactor is used to preheat the fresh feed and further cooled down prior to being fed to the low-pressure separator. There the hydrogen-rich gas is separated from the liquid phase. The gas is compressed and partially recycled to the naphtha feed. The remaining vapour is then further compressed, recontacted with the liquid from the low-pressure separator, cooled and fed to the high-pressure separator. The recompression and recontacting is included to maximise recovery of the C₃/C₄ fraction from the hydrogen-rich gas stream. Any excess of this hydrogen-rich gas is routed to the refinery hydrogen system to be used in hydrogen-consuming units like hydrotreaters. The selection of the reformer operating pressure and the hydrogen/feed ratio form a compromise between maximum yields and the coking rate.

The CCR reforming process has a higher energy efficiency per tonne of desired product than the semi-regenerative process, due to better yields and improved heat recovery from the products.

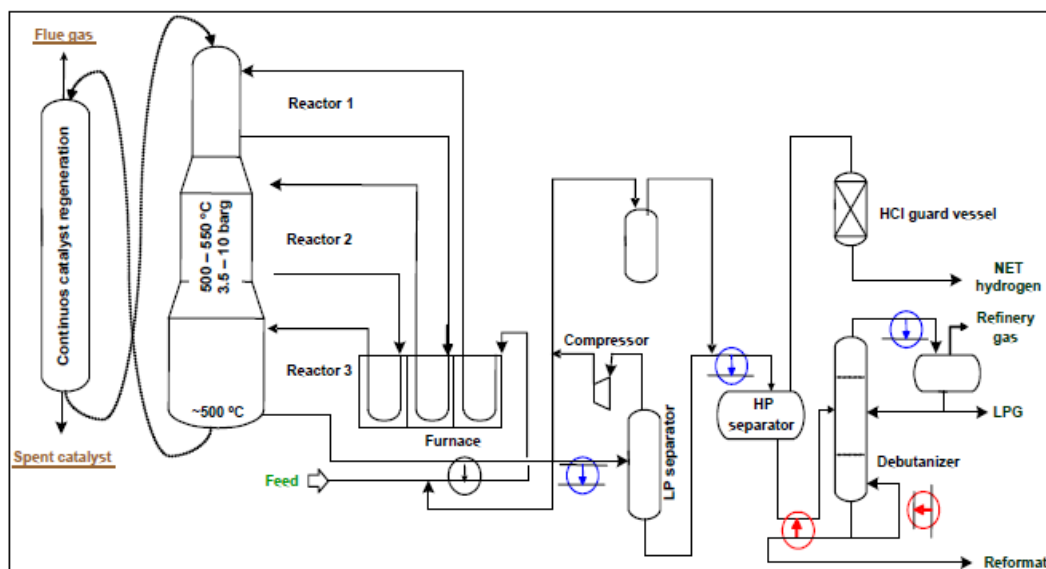


Figure 11: Continuous catalytic reformer process diagram.

2.9 Alkylation

Alkylation involves low temperature reactions with strong acids to yield high-quality motor fuel after blending. Either hydrofluoric acid (HF) or sulphuric acid (H₂SO₄) can be used as catalysts for this process, but H₂SO₄ has been the dominant acid over the last three decades.

In the HF process (Figure 12), the feed enters the reactor and is mixed with the recycled isobutene and HF from the settler. Both the olefin and isobutene feeds are dehydrated at the start in order to

minimise potential corrosion. The reactor, which operates at 25-45°C, is cooled to reduce the heat from the reaction. In the settler, alkylate and excess isobutene are separated from the HF, and the HF is recycled to the reactor, while a slipstream is regenerated by distillation. The organic phase from the settler (the alkylate and unreacted isobutene) flows to the isostripper where the isobutene and other light components are stripped from the alkylate, treated with potassium hydroxide (KOH), and routed to storage as a product. Saturated butanes are normally distilled outside the alkylation unit to produce a concentrated stream of isobutane, which is fed to the alkylation unit with the olefin feed. The isostripper overhead, essentially isobutane, is returned to the reactor. A small overhead slipstream is sent to a depropaniser, where propane is removed. The bottoms of the depropaniser (isobutane) are routed to the isobutane circulation stream, while the depropaniser overhead stream (propane) passes through a HF stripper to remove traces of HF and is sent to storage after final KOH treatment. Normal butanes which come in with the unit feed streams are drawn off as a side-stream from the isostripper, treated with KOH and sent to storage.

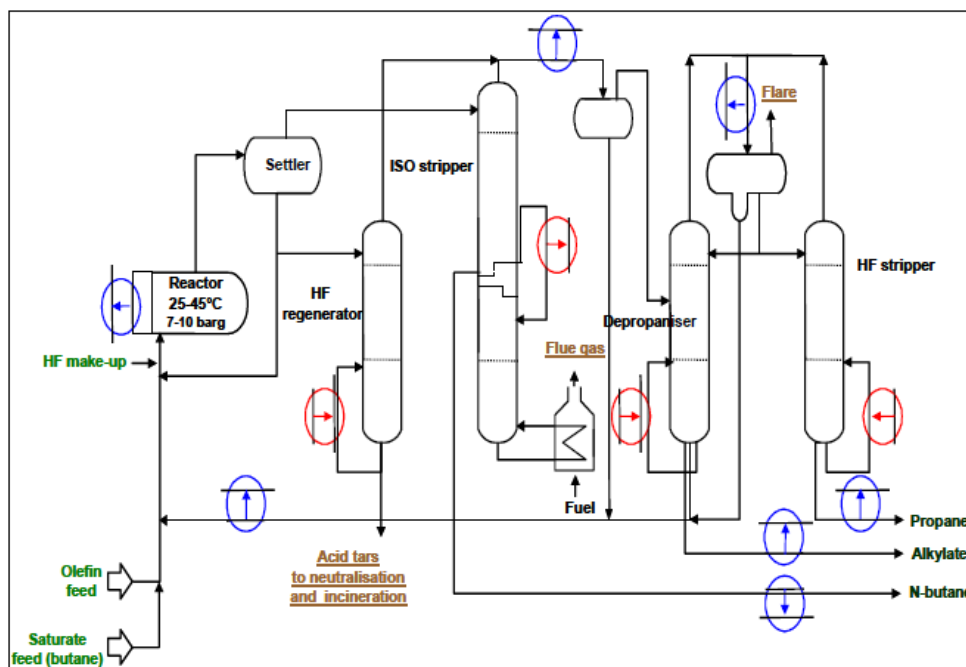


Figure 12: HF alkylation unit process diagram.

In the H_2SO_4 process [Fig. 11b], olefin and butylene feeds are combined in the presence of H_2SO_4 , which comes to contact with the recycle stream of H_2SO_4 in the reactor. The reactor circulation stream enhances a large interface area at low temperatures (4-15 °C). Reaction products are first separated in a flash drum and then through a debutaniser.

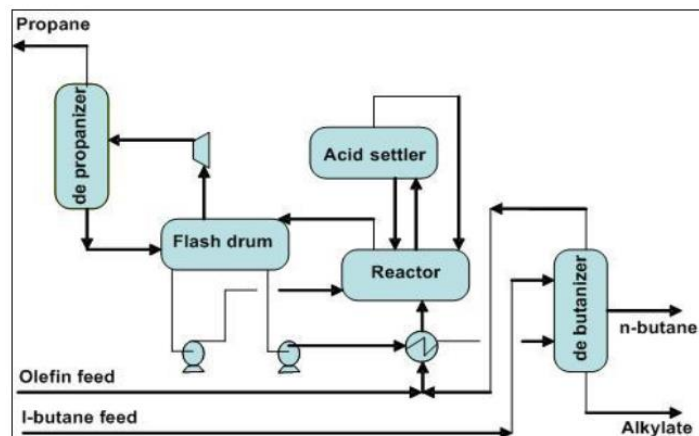


Figure 13: H_2SO_4 alkylation process diagram.

2.10 Isomerisation

This stage is used to rearrange the molecules of the feedstock (butane, pentane, or hexane-rich feed stream) without adding or removing from the original molecule. Typically, low-molecular-weight paraffins ($\text{C}_4\text{-C}_6$) are converted to isoparaffins with a much higher octane index. The isomerisation of olefins is also included in this section. The isomerisation reactions occur in the presence of hydrogen and catalyst. The atmosphere of hydrogen is used to minimise carbon deposits on the catalyst, but with a low hydrogen consumption. The reactions normally take place in two reactors in a series. An advantage of the two-reactor scheme is that the first reactor may operate at higher temperatures to kinetically drive the reactions, while the tail reactor may be operated at lower temperatures to push the desired products closer to equilibrium conversion (Figure 14).

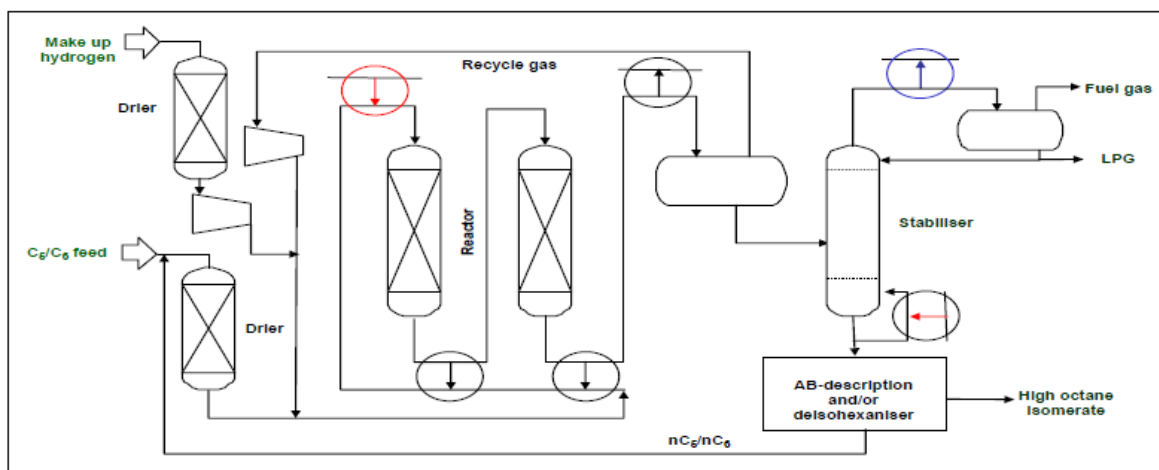


Figure 14: Isomerisation unit process diagram.

There are several isomerisation process designs based on three isomerisation catalyst technologies that can be further designed to operate with or without hydrogen recycle and with or without

hydrocarbon recycle. In general, they can be classified into two categories: hydrocarbon once-through (where only fresh feed is processed) or hydrocarbon recycled (where the unconverted, lower octane paraffins are recycled for further conversion). After isomerisation, the light ends are fractionated from the product stream leaving the reactor and are then sent to refinery fuel gas or to the light ends recovery unit.

2.11 Polymerisation

Polymerisation is occasionally used to convert propene and butene to high-octane gasoline blending components. 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 and extruded in pellets or in small cylinder forms. All reactions are exothermic, and therefore the process requires temperature control. The feed must be free of: sulphur, which poisons the catalyst; basic materials, which neutralise the catalyst and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans, then with an amine solution to remove hydrogen sulphide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer (Figure 15).

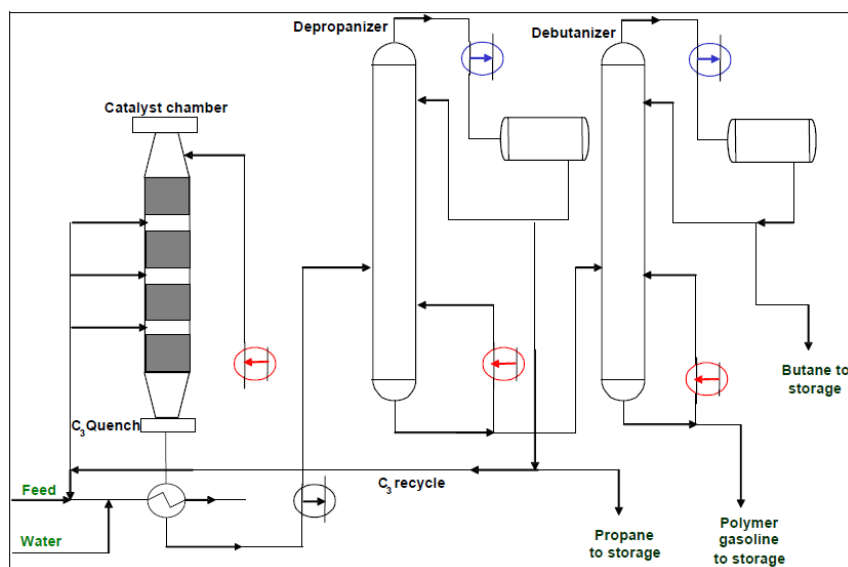


Figure 15: Polymerisation unit process diagram.

2.12 Hydrogen Production

A hydrogen plant is used to produce hydrogen for use in hydrocracking and other hydrogen-consuming refinery process units from natural gas to heavy residue oils and coke, and can be provided via three processes:

- 1) Reforming operations for hydrotreating (refineries with the simplest configuration can produce sufficient quantities);
- 2) Steam reforming of light ends or natural gas;
- 3) Partial oxidation (gasification) of heavy oil fractions to produce syngas where hydrogen can be separated.

2.12.1 Steam reforming

In steam reforming (the most common method), only light hydrocarbons are reacted with steam to form hydrogen. However, all products of a refinery could be used for hydrogen production by partial oxidation. The most interesting option from the economic point of view is to use products with a low market value. In some refineries, heavy oil residues are transformed to petroleum coke and subsequently gasified to produce syngas. The steam methane reforming process for pure hydrogen production consists of four stages: a desulphurisation unit, a steam methane reformer, shift reactor(s), and finally pressure swing adsorption (Figure 16). The reaction is typically carried out at 750–1,000 °C and a pressure of 20–40 barg over a fixed catalyst bed, which is very sensitive to poisoning. Desulphurisation of the feedstock is required in order to protect the catalyst in the reformer furnace against deactivation.

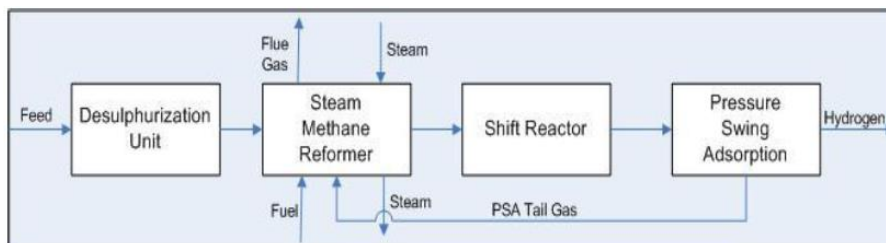


Figure 16: Diagram of the four steps of hydrogen production by steam methane reforming.

2.12.2 Gasification of coke

The processes used for the gasification of petroleum coke are the same as those used in the gasification of coal and they are integrated in the Flexicoke. In an oxygen-blown operating mode of a gasifier, the gas produced can be processed to recover hydrogen or synthesis gas, or can be used as a medium-calorific value fuel. The gasifier product gas (syngas, CO, H₂, CO₂, CH₄, and H₂O), after it has passed the cyclones, contains hydrogen sulphide (H₂S) and carbonyl sulphide (COS). With a sulphur adsorbent in the gasifier, the sulphur content of the gas can be drastically reduced. If no sorbent is

used, the sulphur content of the gas will be in proportion to the sulphur in the feed. The particulates in product gas are removed in the barrier filter. Volatile metals and alkali tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burnt and the calcium sulphide is oxidised to sulphate. In this hot gas clean up system, there is no aqueous condensate produced, although some may be produced in subsequent processing of the gas.

2.12.3 Gasification of hydrocarbons

In partial oxidation, hydrocarbon feed reacts with oxygen at high temperatures to produce a mixture of hydrogen and carbon monoxide. Since the high temperature takes the place of a catalyst, partial oxidation is not limited to the light, clean feedstocks required for steam reforming. Hydrogen processing in this system depends on how much of the gas is to be recovered as hydrogen, and how much is to be used as fuel. Where hydrogen production is a relatively small part of the total gas stream, a membrane is normally used to withdraw a hydrogen-rich stream. That stream is then refined in a purification unit.

2.12.4 Purification of hydrogen

A wide variety of processes are used to purify hydrogen streams. Since the streams are available at a wide variety of compositions, flows, and pressures, the method of purification will vary. They include wet scrubbing, membrane systems, cryogenic separation and pressure swing adsorption (PSA). This last technique is the most commonly used. In the PSA plant, most impurities can be removed to any desired level. Several layers of adsorbents (molecular sieves) remove carbon dioxide, water, carbon monoxide, methane, and nitrogen from the out-stream. Nitrogen is the most difficult to remove of the common impurities, and removing it completely requires additional adsorbent. Since nitrogen acts mainly as a diluent, it is usually left in the product if the hydrogen is not going to be used in a very high-pressure system such as a hydrocracker or a common network. Hydrogen purity is 99.9-99.999% after the PSA unit. The residual constituent of the product gas is usually less than 10ppm CO. Several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is used as fuel at a convenient location .

2.13 Etherification

This process is the addition of different ethers to the gasoline in order to meet both oxygen requirements and vapour pressure limits for improved performance and environmental requirements. The most common ethers used as additives are methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME).

2.13.1 MTBE production process

The feed stream is cooled prior to entering the top of the primary reactor. The resin catalyst in the primary reactor is a fixed bed of small beads. The reactants flow down through the catalyst bed and exit the bottom of the reactor. Effluent from the primary reactor contains ether, methanol and unreacted iso-olefin and usually some paraffins from the feed. A significant amount of the effluent is cooled and recycled to control the reactor temperature. The net effluent feeds to a fractionator with a section containing catalyst or to a second reactor. Ether is withdrawn as the bottom product, and unreacted alcohol vapour and iso-olefin vapour flow up into the catalyst reaction to be converted to ether. The process usually produces an ether stream and a relatively small stream of unreacted hydrocarbons and methanol. The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling. The excess methanol and unreacted hydrocarbons are withdrawn as net overhead product, and fed to a methanol recovery tower. In this tower, the excess methanol is extracted by contact with water. The resultant methanol-water mixture is distilled to recover the methanol, which is then recycled to the primary reaction (Figure 17).

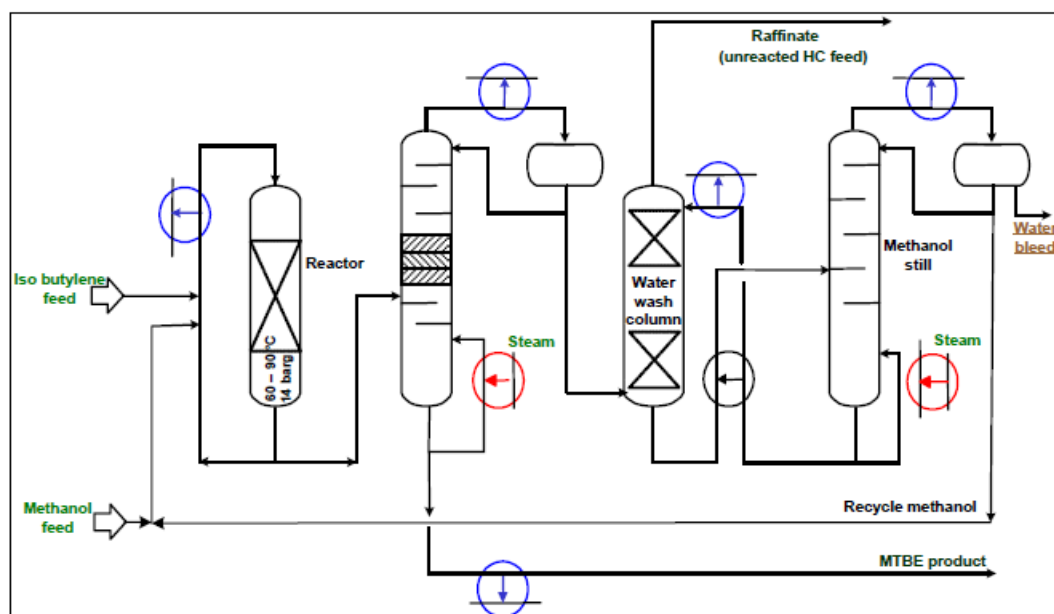


Figure 17: MTBE production process diagram.

2.13.2 ETBE production process

The MTBE unit is able to produce ETBE with minor modifications and elimination of bottlenecking (increase capacity of the column and cooler, increase bottom temperature in catalytic column, change top and bottom temperature in ethanol/water column) .

2.13.3 TAME production process

In this process, C₅ isoamylenes are separated from the light catcracked spirit stream (LCCS) from the FCC unit and catalytically reacted with methanol in the presence of hydrogen to produce TAME. The main stages for TAME production are pentane removal, scavenging, reaction, and purification (Figure 18).

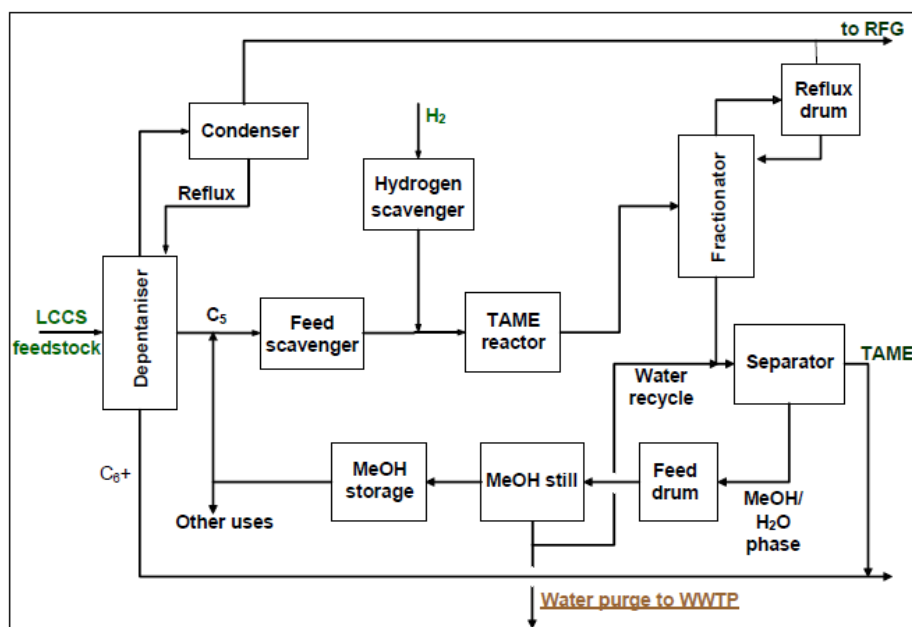


Figure 18: TAME production process diagram.

2.14 Product Treatment

In order to achieve certain specifications, two processes are used to treat the products to remove undesired properties associated with sulphur, nitrogen, or oxygen contaminants:

- 1) The first set of processes extracts the component from the stream to be treated;
- 2) The second set is composed of the systems where the chemical to be treated is not removed from the stream to be treated.

Mercaptans are removed from light hydrocarbon streams by a concentrated alkaline wash in an extraction column under elevated pressure (5 barg). If H₂S or acids are present, a caustic prewash is required. The treated and odour-free hydrocarbon stream leaves the reactor as an overhead stream (Figure 19).

The aqueous bottom phase is heated to 50°C, mixed with air, and fed to the oxidation reactor. The dissolved NaSR is now converted into disulphides (which are insoluble in caustic soda water solution) at 4.5 barg. By using an excess of air and adding catalyst, a high rate of reaction is maintained. In this

way, the alkaline solution is regenerated. The liquid from the reactor is routed to a vessel where spent air, the disulphide fraction insoluble in the caustic solution and the caustic solution are separated. The spent air is routed to an incinerator or process furnace, the disulphides are usually recycled to the crude, and the regenerated caustic is circulated to the extraction column.

Another oxidation process is also a mercaptan oxidation process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic are injected into the hydrocarbon stream and the caustic cannot regenerate. As the hydrocarbon passes through the mercaptan oxidation catalyst bed, sulphur mercaptans are oxidised to disulphide.

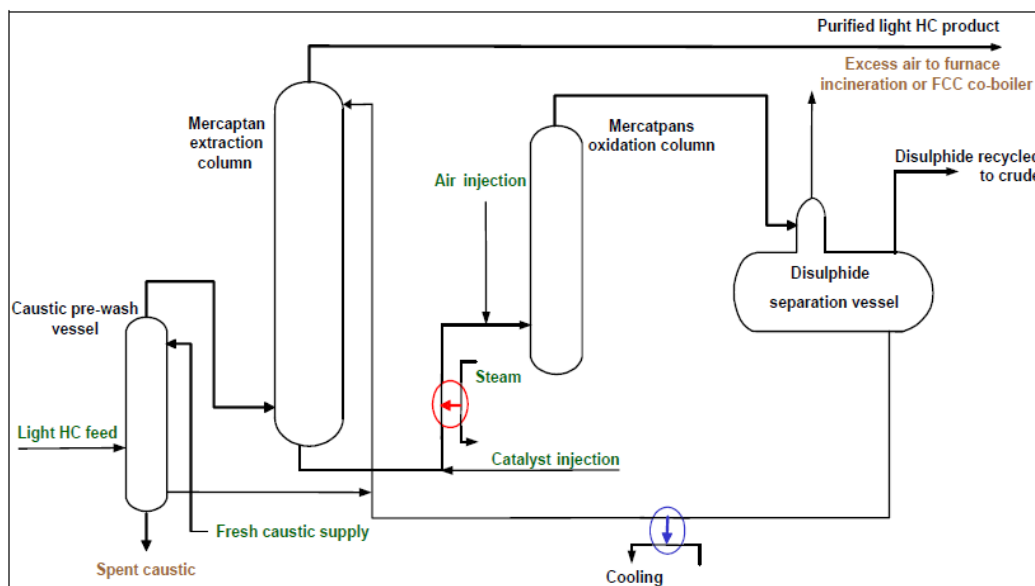


Figure 19: Mercaptan oxidation extraction process diagram.

2.15 Gas Separation

This process is meant to recover and separate C_1 - C_5 and higher compounds from various refinery off-gases via distillation. In mineral oil refineries, a gas plant (single or multiple) is used to handle different gas streams from different processes (e.g. catalytic reformers, catalytic crackers, and distillation units). This unit consists of two column: an absorber/stripper (de-ethaniser) and a de-propaniser (Figure 20)

The absorber strips all light C_2 -minus components to maximise recovery of C_3 -plus components from the feed streams. The feed stream to the gas plant is cooled and chilled, the residual vapour phase from this being routed to a refrigerated absorber, meeting chilled recycled light gasoline absorbent. The absorber overhead is the C_1 , C_2 fraction. The bottoms are combined with the liquid stream from chilling, and pass to the first fractionator or de-ethaniser. The first fractionator overheads are combined with the absorber overheads while the bottoms pass to the second fractionator to produce a C_3/C_4 overheads stream and debutanised gasoline bottoms. A recontacting section, where vapours from various units are compressed and recontacted with the de-ethaniser overhead, can be installed to

maximise the C_3/C_4 recovery. The bottoms of the de-ethaniser column, mainly C_3/C_4 compounds, are fed to the depropaniser column. This overheads stream is routed to a third fractionator to split the C_3 and C_4 streams as overheads (propane) and bottoms (butane), respectively. Products pass to pressurised storage via any final sweetening by selective molecular sieve adsorption. Subsequent loading of transport containers is carried out by means such as closed-loop systems or by venting and release to the refinery fuel gas system.

The gasoline bottom stream passes to a fourth fractionator to produce a depentanised fraction for use as chilled, recycled gasoline on the absorber. The net output is blended to form the gasoline product. A vessel containing a bed of caustic pellets can be installed in the butane system as an additional guard, although water and H_2S should have been removed in the top of the de-ethaniser and de-propaniser column. If no (or insufficient) upstream treatment has taken place, this can also be done in the unit itself.

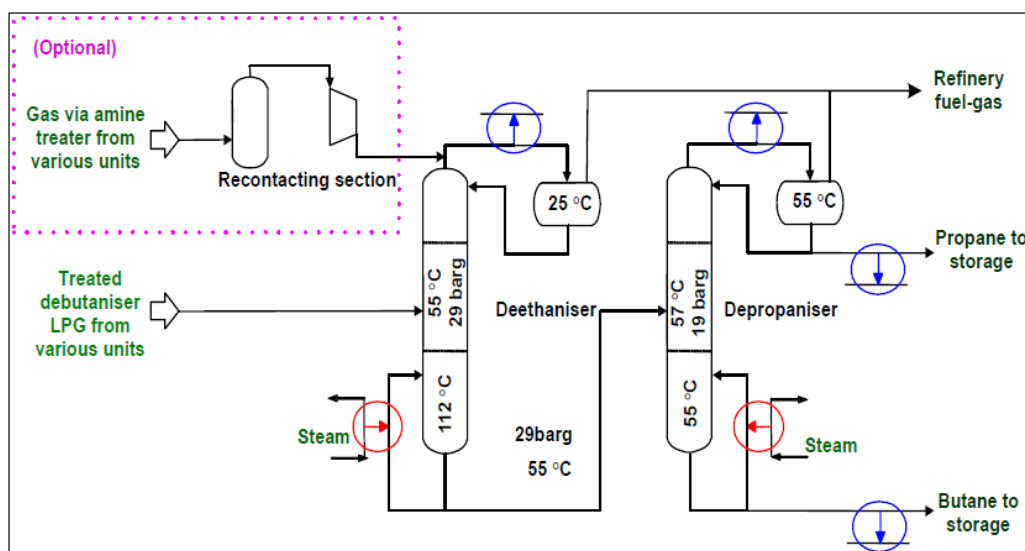


Figure 20: Gas plant process diagram.

2.16 Cooling

In a refinery, the cooling of feed and product streams is required to allow refinery process operations to take place at the right temperatures and to bring products to their appropriate storage temperature. Even though heat integration of process systems ensures that significant cooling can be achieved by exchanging heat between streams to be cooled and streams to be heated, additional cooling is still required. This additional cooling should be provided by an external cooling medium: water and/or air.

A wide range of techniques is used for cooling purposes in oil refineries. Most refineries use a combination of the techniques available. The selection of a cooling system depends on the required cooling temperature, the cooling capacity, contamination risk and local circumstances (Figure 21).

- Air cooling – Where the process stream in the tubes is cooled by fan-delivered air (Figure 21).
- Direct water cooling – Only used in cokers, gasifiers, and some sludge incinerators due to the high level of contamination generated (Figure 21).
- Once-through system – Water is extracted from a surface body of water, filtered, and passed around the refinery to enable cooling through heat exchangers. The water is passed through a process unit once and is then either treated or discharged without treatment (Figure 21).
- Circulation system – Cooling water is repeatedly recycled through cooling towers using ambient air (Figure 21).
- Wet closed system – Tempered water is used when process streams to be cooled should not be exposed to the low cooling water temperatures (Figure 21).
- Hybrid systems – Both air and water are used to maximise the use of air cooling and the rest is done by water cooling (Figure 21).
- Refrigeration systems – Used in specific cases for safety reasons in order to cool the process streams below ambient temperatures (Figure 21).

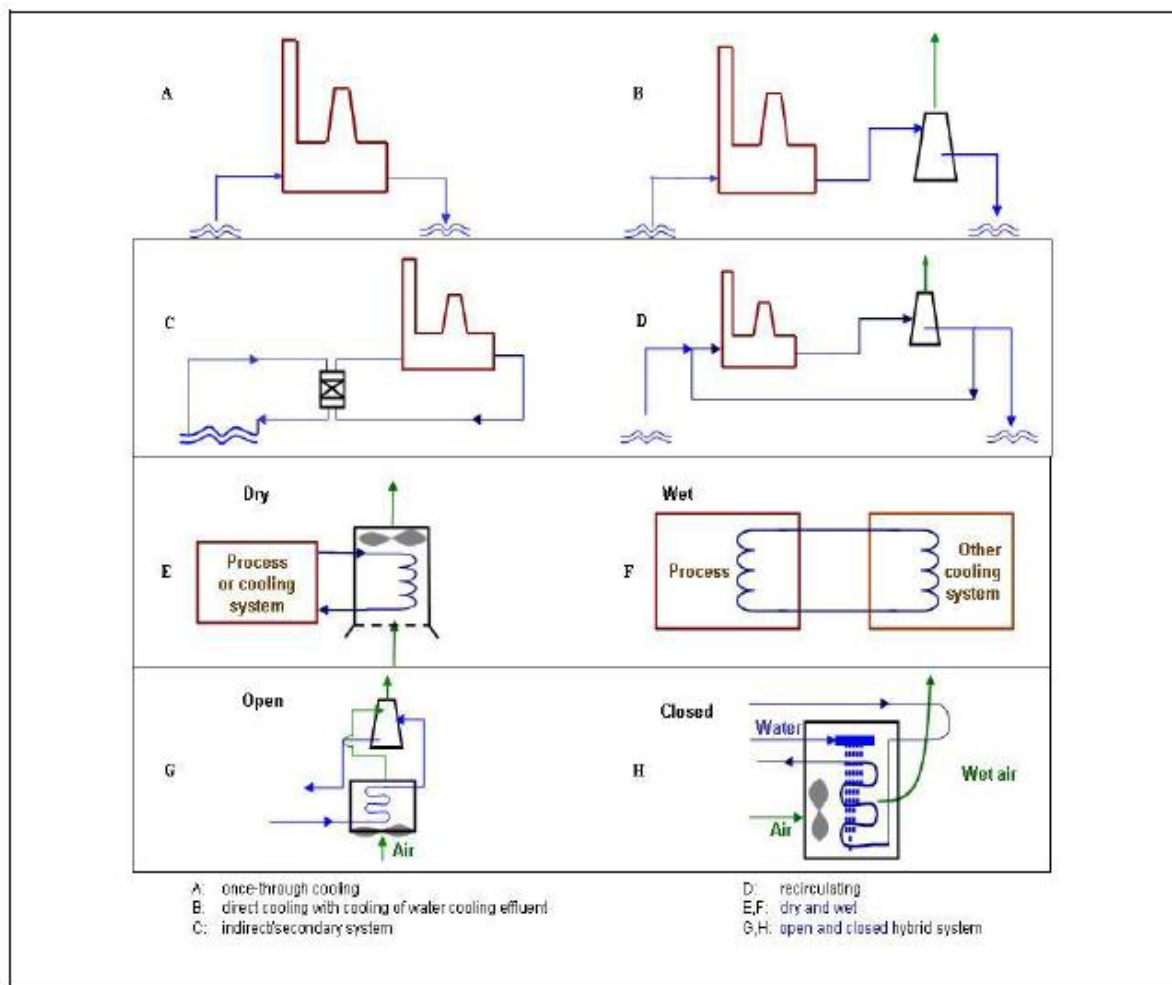


Figure 21: Diagram of the different cooling systems used throughout the petroleum refining process.

2.17 Natural gas plant

This stage of the refinery is to remove the treatment chemicals and to remove any contaminants from the well-head stream in order to produce a methane-rich gas, which satisfies statutory and contractual specifications. The contaminants that are removed are solids (sands, clay, carbonates, metals, and mercury), liquids (water, hydrocarbons, and chemicals), and gases (acidic gases, CO_2 , nitrogen, and hydrogen).

The purification plant consists of an acid gas treatment (sweetening plant) where acid gases such as CO_2 , H_2S , SO_2 are separated. Natural gas is considered 'sour' when it contains significantly greater amounts of hydrogen sulphide than those required to comply with the pipeline quality specifications or when it contains such amounts of SO_2 or CO_2 to make it impractical to use without purification. The H_2S must be removed before the gas can be utilised. If H_2S is present, the gas is usually sweetened by absorption of the H_2S in an amine solution (Figure 22).

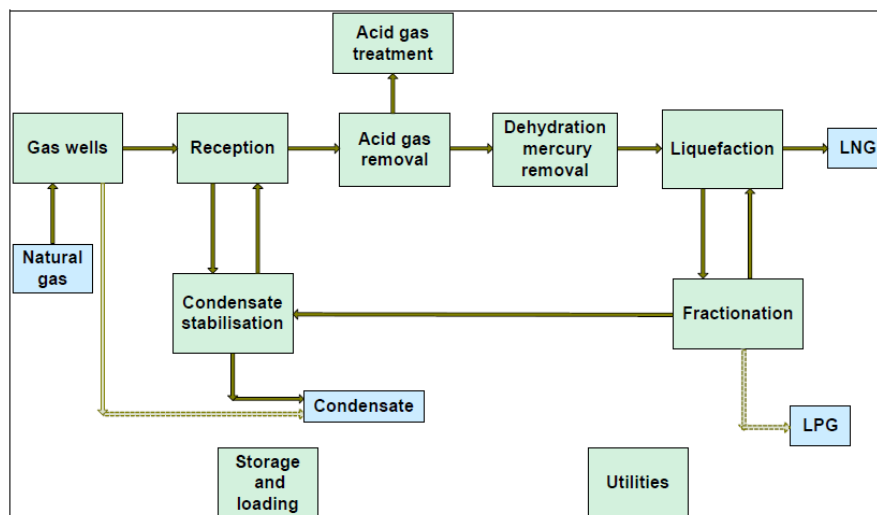


Figure 22: Natural gas plant process diagram.

3 Energy Intensity of Key Processes

Some stages of petroleum production require more energy than others. The most energy intensive stages are the processing of gasoline (using mainly fuel and electricity), lube stocks (using mainly steam), kerosene (using mainly electricity), and diesel (using mainly electricity) (Table 1). As these levels of production are very energy intensive, they could generate considerable emissions, so caution should be taken for these. Energy allocation at the refining process level, accounting for process-dependant gasoline production, 61.3% of process fuels, 53.5% of electricity and 27.6% of steam are allocated to gasoline. After gasoline (at 50.1%), the fuel use in the sector is dominated by catalyst coke (25.7%), natural gas (17.3%) and fuel oil (6.9%) (based on UK refineries).

Table 1: Process energy allocation for Petroleum refineries.

Process	Fuel [%]	Steam [%]	Electricity [%]	Energy Intensity [toe/t]
Crude distillation unit	26.2	26.2	8.5	0.015
Vacuum distillation unit	7.9	13.5	1.9	0.006
Thermal cracking	8.5	-1.1	10.1	0.003
Fluid catalytic cracking	7.5	0.1	15.3	0.004
Hydrocracking	4.7	3.9	12.8	0.004
Reforming	14.4	10.9	7.4	0.008
Hydrotreating	17.6	28.9	34.4	0.016
Deasphalting	1.1	0	0.5	0
Alkylation	0.9	12.9	6.1	0.004
Aromatics	0.8	0.4	0.6	0
Asphalt	4.1	0	1.6	0.001
Isomerisation	6.2	4.3	0.8	0.003
Total	100	100	100	0.063
% usage	49.7	34.1	16.2	

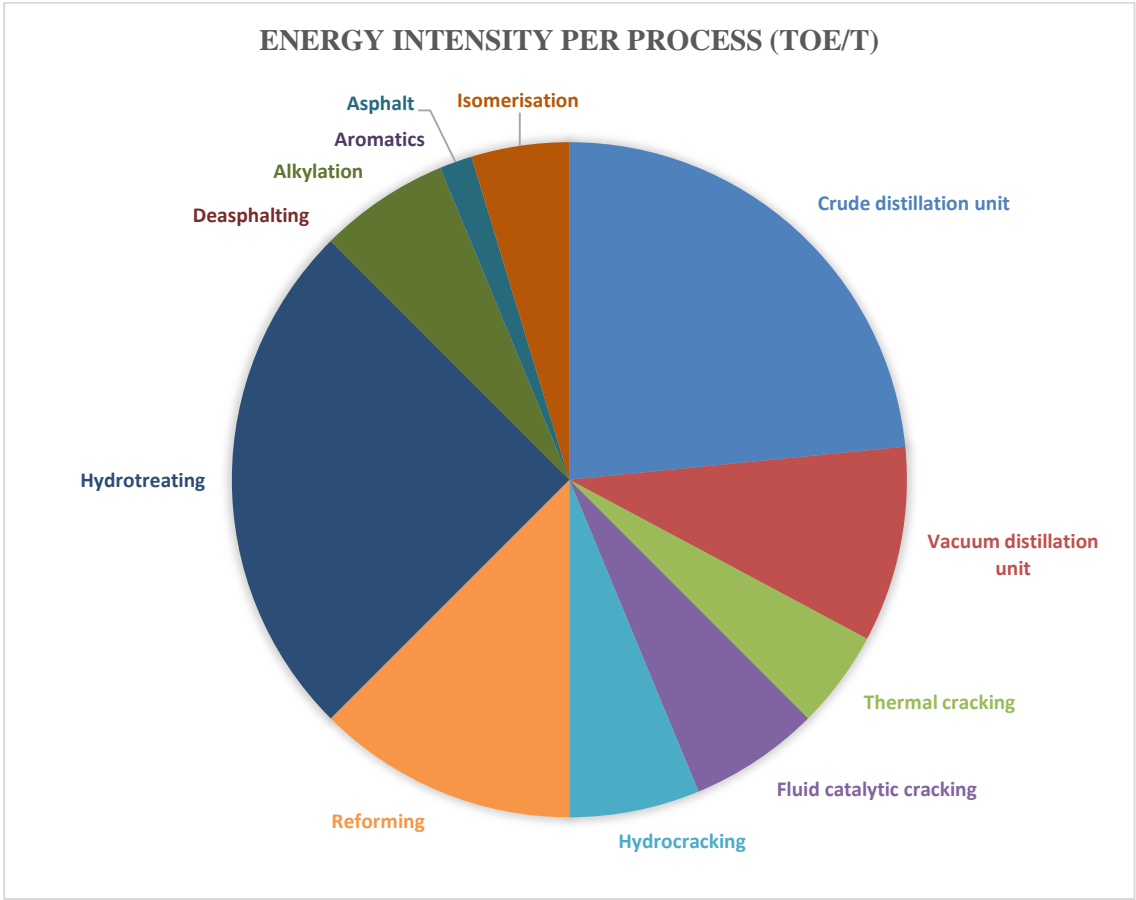


Figure 23: Process energy allocation of final product per 1 kg of crude feed.

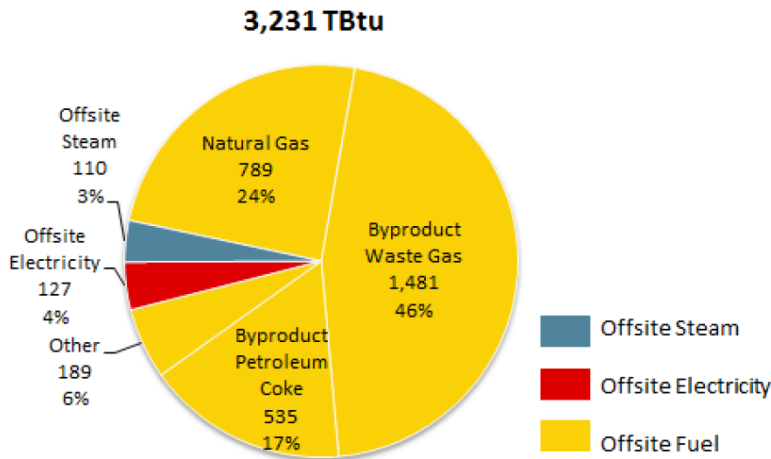


Figure 24: Offsite energy supply in the petroleum refining sector.

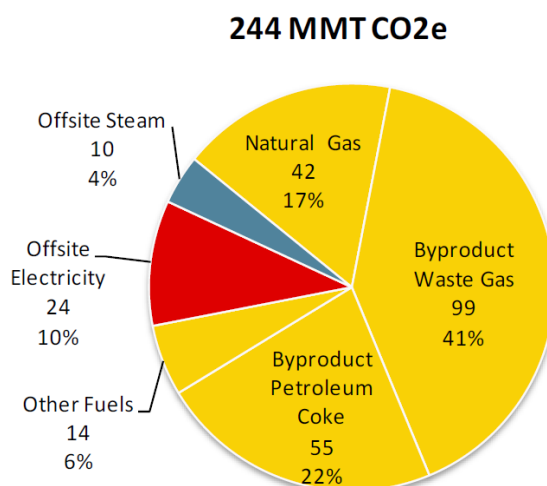


Figure 25: Total GHG combustion emissions in the petroleum refining sector (by energy supply type).

Table 2: Subsector share of energy consumption in 2011.

Description	NACE (Group)	Category	Estimated share of final energy demand	
			[ktoe]	[%]
Manufacture of coke oven products	C19.1	Energy intensive	4081	8
Manufacture of refined petroleum products	C19.2	Energy intensive	47,948	92
Total			52,028	100