EU-MERCI

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

HORIZON 2020 Project Nr. 693845

Technical analysis – Chemical sector (NACE C20)

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

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1 Introduction

NACE C20 Manufacture of chemicals and chemical products includes the transformation of organic and inorganic raw materials by a chemical process and the formation of products. It distinguishes the production of basic chemicals that constitute the first industry group from the production of intermediate and end products produced by further processing of basic chemicals that make up the remaining industry classes. It contains the following sub-catagories:

- 20.1 Manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms: this group includes the manufacture of basic chemical products, fertilisers and associated nitrogen compounds, as well as plastics and synthetic rubber in primary forms.
- 20.2 Manufacture of pesticides and other agrochemical products
- 20.3 Manufacture of paints, varnishes and similar coatings, printing ink and mastics
- 20.4 Manufacture of soap and detergents, cleaning and polishing preparations, perfumes and toilet preparations
- 20.5 Manufacture of other chemical products: this group includes the manufacture of explosives and pyrotechnic products, glues, essential oils and chemical products n.e.c., e.g. photographic chemical material (including film and sensitised paper), composite diagnostic preparations etc.
- 20.6 Manufacture of man-made fibres

The chemicals and pharmaceutical sector contributed to 5% of the EU's GDP (gross domestic product) in 2011 (Eurostat; 2013). Key economic contributions are delivered by 2 key groups: Manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms (NACE C20.1) and Manufacture of pharmaceutical preparations (NACE C21.2), which accounted for 70% of total production value. The pharmaceutical sector is not considered further within this technical paper due to the lack of efficiency measures within the EU-Merci project.

Key economic indicators for the chemicals sector are summarised in next paragraph.

2 Subsector share of energy consumption

The following table provides an estimated overview of the share of energy consumption between subsectors in the manufacture of chemicals and chemical products (NACE C20) in EU28. The petrochemicals and basic inorganic subsectors account for 72% of the energy use in the chemicals sector and reflect the high energy requirements to produce the primary feedstock for the downstream subsectors (polymers, specialty and consumer chemicals).

Table 1: Subsectors energy consumption share in chemical industry.

Subsector Description	**NACE (Group)**	**Category**	**Estimated share of final energy demand**	
Petrochemicals	C20.1	Energy intensive	26,596	47%
Basic inorganic	C20.1; 20.5	Energy intensive	14,147	25%
Polymers	C20.1; 20.6	Non-energy intensive	6,791	12%
Specialty chemicals	C20.2; 20.3	Non-energy intensive	4,527	8%
Consumer chemicals	C20.4	Non-energy intensive	1,132	2%
Pharmaceutical products	C21	Non-energy intensive	3,39566	6%
Total energy demand for chemicals and pharmaceuticals sector for EU28 (2011):			**56,588**	**100%**

3 Key products

The following table shows the main products according to the chemical sectors:

Table 2: key products in chemical sector.

Chemical sector	**Main products**	**Main processes (energy intensive processes)**
Petrochemicals (NACE C20.1)	ethylene, propylene, butadiene (olefins), methanol (alcohols), benzene, toluene and xylenes (aromatics).	“cracking” (either steam or catalytic), which is the process where large hydrocarbon molecules are broken down into smaller ones; and “reforming”, where heat, pressure and/or catalyst are used to restructure hydrocarbons (e.g., converts naphtha to benzene, toluene and xylene).
Description	Product: The petrochemical subsector produces the organic building blocks of the chemical industry, which feed the production of many consumer and industrial products. Because the petrochemical subsector covers numerous products, the manufacturing processes will vary from one product to another. Sometimes the same products will use different raw materials, technological processes, or equipment. Process: As such, energy is used in varying amounts. Nonetheless, the petrochemical subsector is defined by two major energy intensive processes: “cracking” (either steam or catalytic), which is the process where large hydrocarbon molecules are broken down into smaller ones; and “reforming”, where heat, pressure and/or catalyst are used to restructure hydrocarbons (e.g., converts naphtha to benzene, toluene and xylene). There are approximately 55 petrochemical plants in the EU with steam crackers and reformers.	
Basic inorganics (NACE C20.2; C20.5)	chlor-alkalis, sulphuric acid, sulphates; fertilizers (potassium, nitrogen and phosphorus products).	Bosh haber process for semi-product ammonia Electrolysis for semi-product chlorine
Description	Product: The industrial inorganic chemical industry manufactures a variety of products. Many of these products are used as reagents or feedstock in high-tech industries, pharmaceuticals or electronics, as well as in the preparation of inorganic specialties such as catalysts and pigments. Process: The energy consumed to produce different inorganic products can vary significantly; however, a few products dominate energy consumption, such as ammonia and chlorine production. Ammonia is produced in the Haber process where nitrogen and hydrogen, is formed by reacting natural gas and steam at high temperatures, react in the presence of an iron catalyst to form ammonia. There are approximately 42 ammonia plants in the EU. Chlorine (and caustic soda) is produced through electrolysis where an electric current is passed through a brine solution. There are approximately 70 chlorine manufacturing locations in the EU.	

Polymers (NACE C20.1; C20.6)	polyethylene (PE) and polypropylene (PP) (feedstock is ethylene and propylene)	reaction types, polymerisation, polycondensation and polyaddition The primary operations/processes are 1) preparation; 2) reaction; and 3) separation of products.
Description	Process: Polymers are large molecules formed during three basic reaction types, polymerisation, polycondensation and polyaddition. The primary operations/processes are 1) preparation; 2) reaction; and 3) separation of products. Products: Depending on the product, assorted combinations of heat, pressure and catalysts are used during the reaction stage to alter the chemical bonds that hold monomers together, causing them to bond with one another forming chains of monomers. The most widely used feedstock in polymer production is ethylene and propylene which, once reacted, make polyethylene (PE) and polypropylene (PP), respectively.	
Consumer chemicals (NACE C20.4)	soaps, detergents, perfumes	Soap 1) saponification 2) drying; 3) amalgamator 4) rolling mills 5) cutting/pressing Detergents produced through a combination of agglomeration, spray drying, dry mixing steps Perfume 1) Extraction 2) Blending
Description	Progress: The manufacture of soaps, detergents, perfumes involve a broad range of processing and packaging operations. Process: For soaps, the primary process steps are: 1) saponification (hydrolysis of an ester, under basic conditions (e.g., 80oC)); 2) drying; 3) amalgamator (mixer, in which the soap pellets are blended together with fragrance, colorants and all other ingredients; 4) rolling mills (to blend and create a uniform texture); and 5) cutting/pressing (to create final shape). Similar to soap, detergents are produced through a combination of agglomeration, spray drying, dry mixing steps. Perfume production involves two main steps. The first step, extraction, is primary energy consumer and involves the removal of oils from plant substances by steam distillation, solvent extraction, etc. Step two involves blending the collected oils with other	

	substances based on predetermined formulas.	
Specialty chemicals (NACE C20.2; C20.3)	Resin, pigment and additive agents to produce paint Pesticides	Mixing the components to paste Milling Dispersion tank chemical reaction of two or more raw materials (organic or inorganic) in the presence of solvents, catalysts and reagents. Manufacturing can vary from a one-step reaction, followed by packaging the product, or multi-step reaction, followed by fractionation, separation, drying and packaging. Alternately, production can occur through formulation, with no reaction occurring.
Description	Resin, pigment and additive agents are generally major components of paint. There are two main process steps; the first involves mixing the components to form a paste. If the paint is to be for industrial use, it usually is then routed into a milling machine, which is a large cylinder that agitates tiny particles of sand or silica to grind the pigment particles, making them smaller and dispersing them throughout the mixture. In contrast, commercial use paint is processed in a high-speed dispersion tank, which agitates the mixture and blends the pigment into the solvent. Pesticides are manufactured by the chemical reaction of two or more raw materials (organic or inorganic) in the presence of solvents, catalysts and reagents. Manufacturing can vary from a one-step reaction, followed by packaging the product, or multi-step reaction, followed by fractionation, separation, drying and packaging. Alternately, production can occur through formulation, with no reaction occurring. Instead raw materials are mixed, blended, diluted with solvents, inert materials, pigments and packaged.	

4 Main processes

The most energy intensive processes are related to the manufacturing of petrochemicals and basic inorganics. The processes are cracking, reforming, Haber-process and electrolysis for chlorine.

Considering that the sector comprises a large number of different products (thus, different processes), for the purpose of this analysis the focus has been on the most energy-intensive processes and technologies.

4.1 Cracking:

Cracking is the process by which saturated hydrocarbons are converted into more sought after unsaturated species. This is a dehydrogenation reaction that can be effected either catalytically or thermally. In Western Europe, the steam cracking process accounts for more than 95% of ethylene and butadiene production and 75% of propylene production. Propylene is also recovered from refining operations, in particular from Fluidised Catalytic Cracker off-gas and through the dehydrogenation of propane.

4.1.1 Catalytic cracking

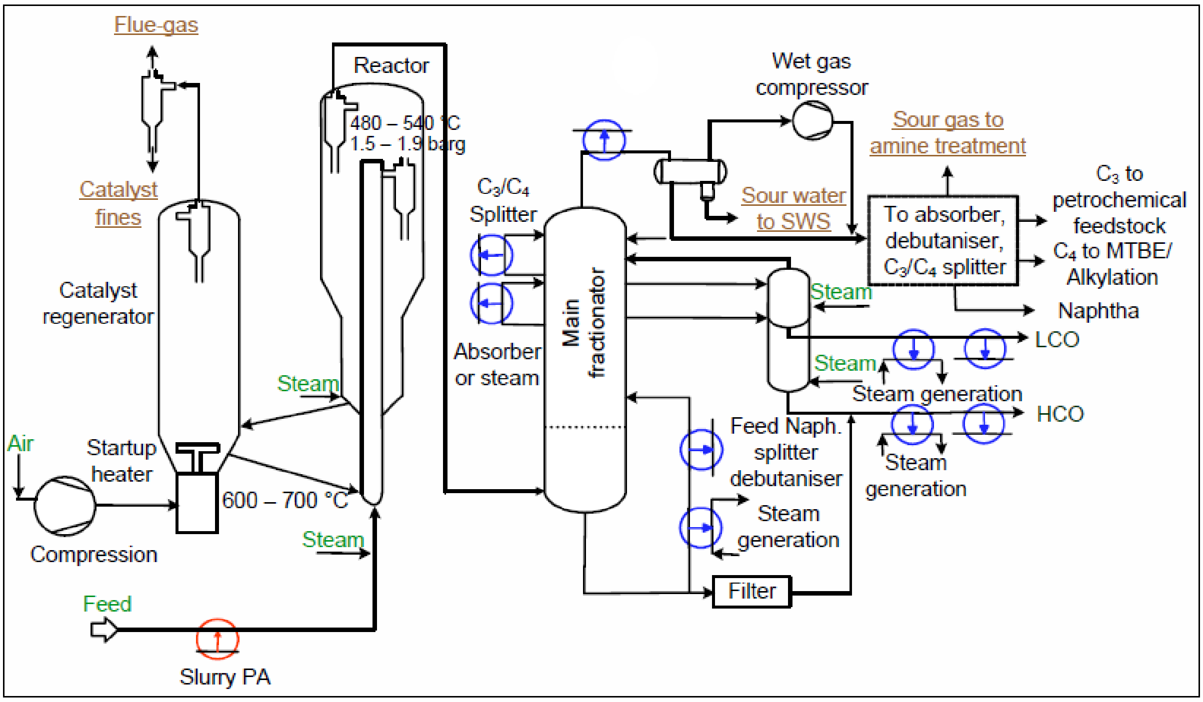

Figure 1: Simplified process flow of catalytic cracker.

Catalytic cracking is the most widely used conversion process for upgrading heavier hydrocarbons into more valuable lower boiling hydrocarbons. In 2008, 56 fluid catalytic cracking (FCC) units were installed in the EU-27. It uses heat and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules.

A number of different catalytic cracking designs are currently in use worldwide, including fixed bed reactors, moving bed reactors, fluidised bed reactors and once-through units. The fluidised and moving bed reactors are by far the most prevalent in world refineries.

Fluid catalytic cracking (FCC) units are by far the most common catalytic cracking units. The FCC unit consists of three distinct sections: the reactor-regenerator section including the air blower and the waste heat boiler, the main fractionator section including the wet gas compressor and the unsaturated gas plant section.

In the FCC process, oil and oil vapour preheated to 250–425 °C come into contact with hot catalyst at about 680–730 °C in the riser reactor. To enhance vaporisation and subsequent cracking, the feed is atomised with steam. 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 catalytic cracking processes produce 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 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. 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.

Various types of equipment are usually used for recovering energy from this process. The hot flue-gases from the regenerator are cooled by means of steam generation in a waste heat boiler or, in case of partial CO combustion, in a CO boiler. Prior to steam generation, electricity can also be produced by expansion of the flue-gases in a turbo-expander. And, in particular for units processing large quantities of residue, additional heat removal from the regenerator can be achieved with catalyst coolers for steam generation.

4.1.2 Steam cracking

Almost the entire world demand for ethylene and butadiene and the majority of propylene, is produced using the steam cracking process. In this process, suitable hydrocarbons are heated to very high temperatures, in the presence of steam, to split or ‘crack’ the molecules into the desired lower olefin products. Most proprietary designs concern the furnace, but there may also be variations in the pressure and temperature of the fractionation columns; refrigeration systems (open versus closed loop); and the use of turbo expanders. Regardless of contractor or feedstock, a cracker can be broken down into three separate sections: pyrolysis; primary fractionation/compression; and product fractionation. The following Figure gives an overview:

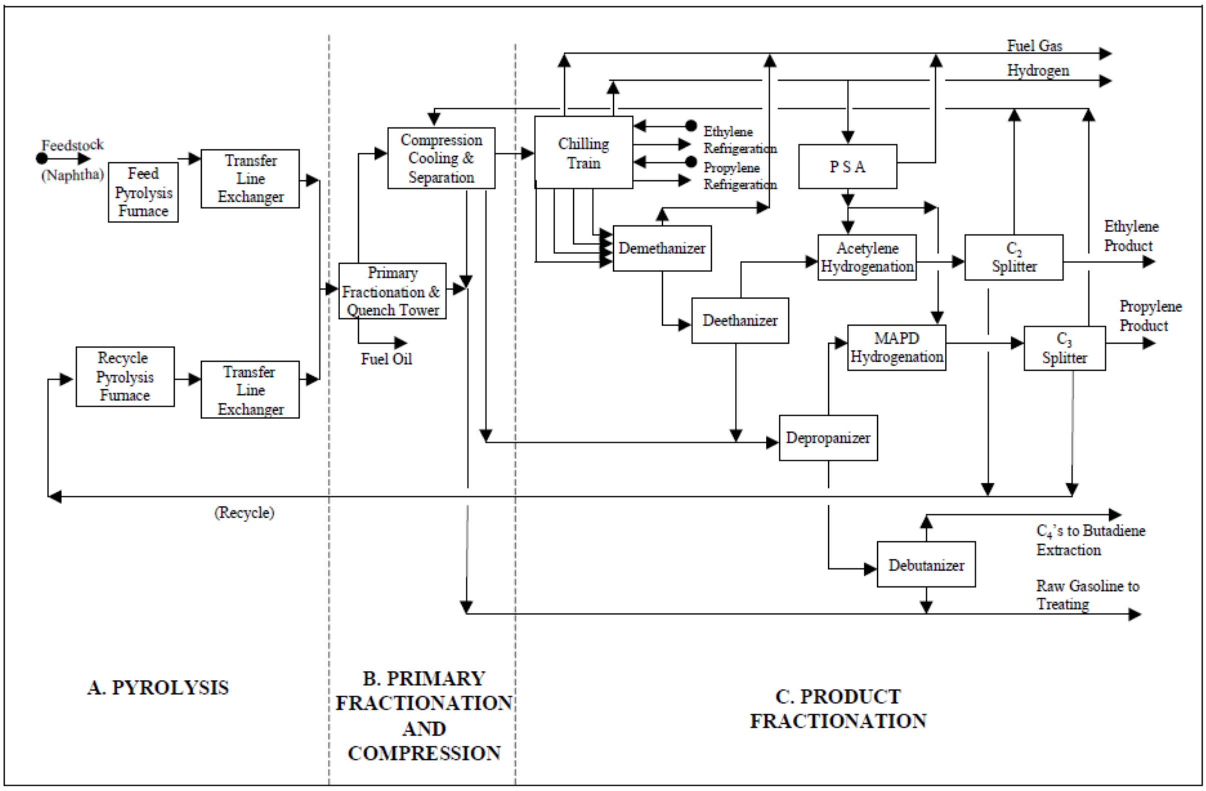

Figure 2: Steam cracking process flowchart.

4.1.2.1 Pyrolysis section

The hydrocarbon feedstock is preheated in heat exchangers and then vaporised with superheated steam before passing into tubes arranged in a cracking furnace. The tubes are externally heated to 750-875 °C by oil or gas fired burners. The conversion of saturated hydrocarbons to unsaturated compounds is highly endothermic and therefore requires a high-energy input. Steam is injected to reduce the partial pressure of the hydrocarbon mixture and also to minimise coke formation. The transfer line exchangers (TLEs) are used to quickly quench the product gases to 550 - 650 ºC (to prevent degradation by secondary reactions) and to generate high-pressure steam for plant re-use. Gas feedstocks usually have secondary TLEs to maximise the heat recovery.

4.1.2.2 Primary fractionation and compression

The primary fractionation and compression section consists of the primary fractionator (naphtha and gas oil feed only), quench tower, gas compressor and gas cleanup facilities. The latter may include an amine unit or caustic unit and drying facilities. The primary fractionator is used to condense out and fractionate fuel oil streams produced from naphtha and gas oil fed crackers. The gases are de-superheated in the quench tower by a circulating oil or water stream. The circulating oil or water stream is used as a medium level heat source for the rest of the plant. Some plants have no quench water tower and use direct cooling of the cracked gas with air coolers and/or cooling water. Tarry bottoms are removed from the system as product, which mostly fuels non-steam cracking furnaces and boilers. Most of the dilution steam is condensed. Dilution steam is generally recovered and recycled back to the front end of the plant. During the start-up of the recovery and fractionation areas gases may be flared whilst the correct operating conditions are established and gas recycles may be used to reduce the need for flaring.

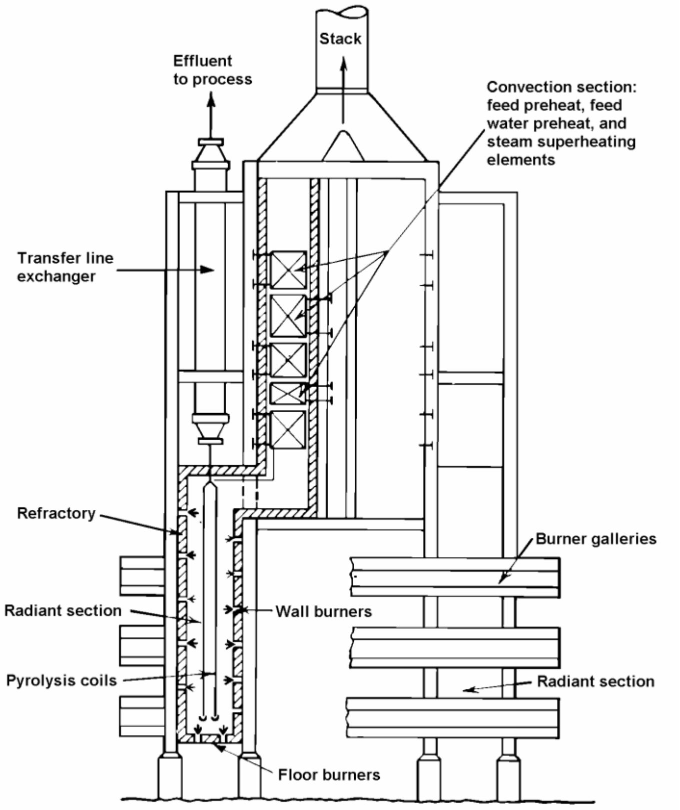

Figure 3: Typical cracking furnace configuration.

Gas compression: Product gases from the quench tower are condensed by four or five stages of gas compression. The gas is cooled after each stage and passed through a liquid knock-out drum. Large centrifugal compressors are used and are usually driven by high-pressure condensing steam turbines, or occasionally by electric motors.

4.1.2.3 Product fractionation

The chilling train usually consists of four or five successive stages of chilling, incorporating ethylene and propylene refrigeration, as well as an elaborate self-refrigeration system. The methane stream from the chilling unit is used as fuel gas, mostly internally in the plant’s furnaces and boilers. The exact process flow sequence varies according to the feedstock and the design arrangement, but various fractionation towers are used to separate the desired products. This may include a sequence of de-methaniser (to further remove methane), followed by a de-ethaniser (to remove ethane, ethylene and a small quantity of acetylene). Bottoms from the de-ethaniser are directed to the de-propaniser and then to a de-butaniser. The lighter the feedstock, the less need for the later separation systems. After separation, the ethylene still contains undesirable acetylene and ethane. Acetylene is either removed by selective catalytic hydrogenation or by extractive distillation. The separation of ethylene and ethane requires a particularly effective column due to the close proximity of their boiling points. The ethane component may be recycled back to the cracker for re-working. Similarly, the C3 fraction still contains methyl acetylene and propadiene after separation. Selective hydrogenation is used to convert this into propylene and propane prior to separation in a C3 splitter.

4.2 Reforming:

4.2.1 Catalytic reforming

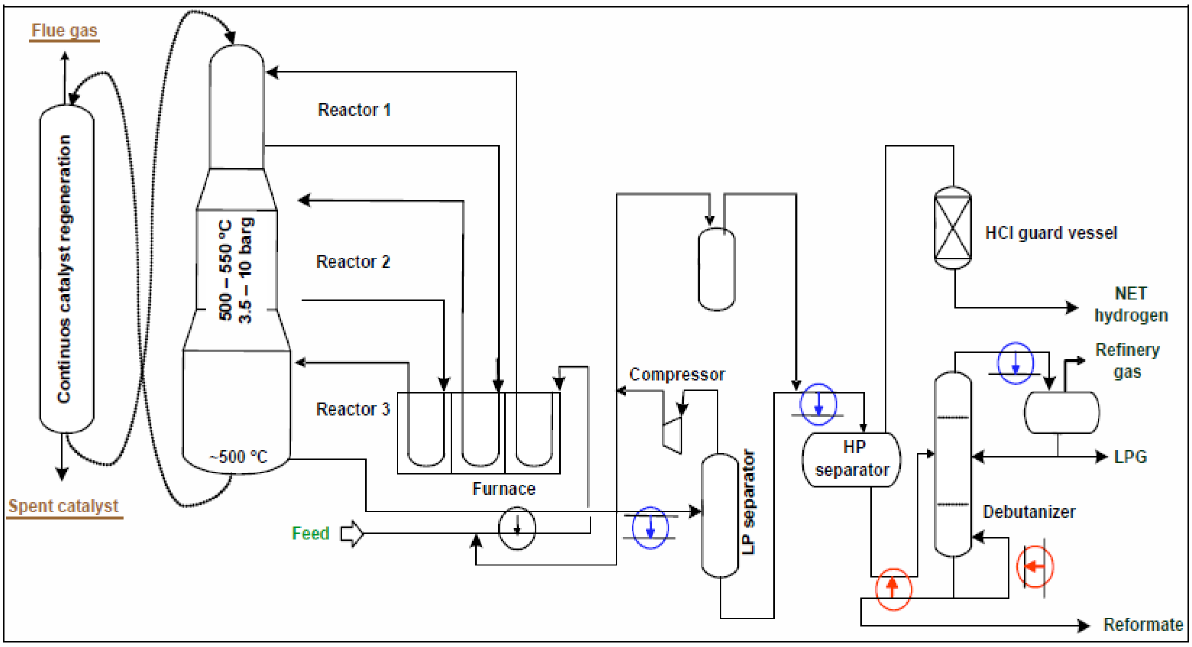

Figure 4: Simplified process flow scheme for a continuous catalytic reformer.

The heavy naphtha leaving the hydrotreating units is a very poor gasoline blend component due to its low octane. The purpose of a catalytic reformer is to upgrade the octane of these streams for use as a gasoline blendstock. The burning characteristics (octane number) of heavy naphtha are improved significantly by catalytic reforming. The most important characteristic of the reformate product is the octane number.

There are several catalytic reforming processes in use today. In general, they can be classified into three categories: continuous, cyclic or semi-regenerative, depending upon the frequency of the catalyst regeneration. The fixed bed or moving bed processes are used in a series of three to six reactors.

4.2.2 Continuous catalytic regeneration (CCR) reforming process

Interheaters are needed between the reactors to provide the heat required for the endothermic dehydrogenation reaction. As the naphtha feed charge proceeds through the reactors, the reaction rates decrease and the reheat needed lessens. Freshly regenerated catalyst is introduced at the top of the first reactor and flows by gravity from top to bottom. From here it is passed on to the next 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 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.

As the CCR process is the latest and most modern type of catalytic reformer process, it has generally a design with a higher heat integration than the semi-regenerative process and leads to a higher energy efficiency. Appropriate revamping of semi-regenerative units can also achieve higher energy efficiency through the same recovery from products, from pump arounds and from integration with the topping and vacuum.

4.3 Haber-Bosch process:

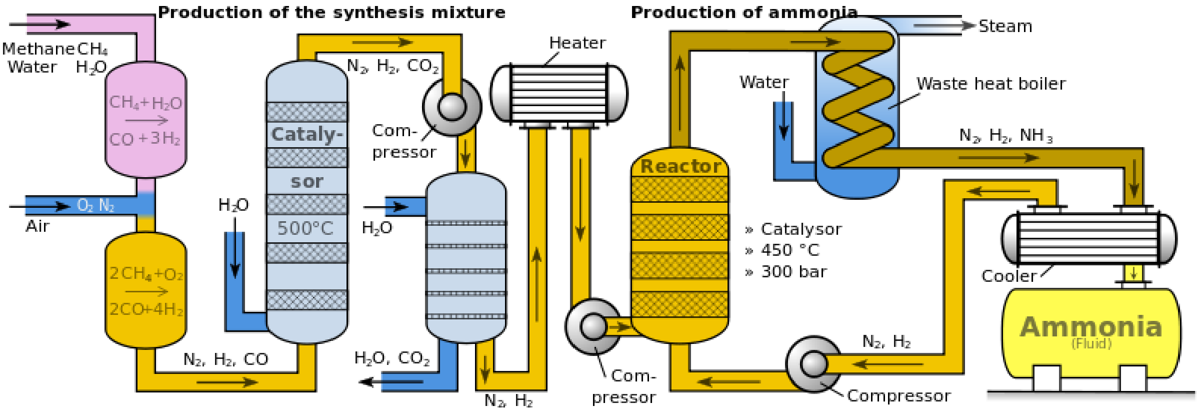

Figure 5: Schematic of the Haber-Bosch process.

Basically, in simple steps:

1) Hydrogen and Nitrogen are extracted and purified with all impurities removed for the process.
2) Both gases are mixed and the mixture is pumped into a compressor. The compressor has extreme conditions, with a pressure of 200 atm. The high pressure causes the particles to gain kinetic energy and makes the temperature rise up to about 300 degrees Celsius. This causes the covalent bonds in the hydrogen and nitrogen molecules to split up.
3) The compressed molecules now enter a converter (reactor). The converter is a tank heated up to a temperature of 400-450 degrees Celsius and is pressurized at 200atm. Inside the compressor, there are shelves of hot iron (Fe^{3+}) to act as the catalyst. Aluminum oxide (Al_2O_3) and potassium oxide (K_2O) are used as promoters to increase the catalyst's efficiency.
4) The gaseous hydrogen and nitrogen reacts on the surface of the hot iron to form gaseous ammonia. However, some of the gases remain unreacted. In addition to the above, the production of ammonia is a reversible reaction and so some of the ammonia formed will decompose back to hydrogen and nitrogen gas. As a result, the final yield is only about 12-15% of its original reactants.
5) The mixture of hydrogen, nitrogen and ammonia is then removed and cooled, where under the right pressure, the ammonia liquifies and is collected.
6) The unreacted hydrogen and nitrogen gases is sent back into the converter and steps 3, 4 and 5 are repeated.

4.4 Chlorine production through electrolysis

Chlorine is produced by passing an electric current through a solution of brine (common salt dissolved in water). This process is called electrolysis. The chemical term for salt is sodium chloride (NaCl).

In industry, elemental chlorine is usually produced by the electrolysis of sodium chloride dissolved in water. This method, the chloralkali process industrialized in 1892, now provides most industrial chlorine gas. The production of chlorine results in the co-products caustic soda (sodium hydroxide, NaOH) and hydrogen gas (H_2). These two products, as well as chlorine itself, are highly reactive. Chlorine can also be produced by the electrolysis of a solution of potassium chloride, in which case the co-products are hydrogen and caustic potash (potassium hydroxide). There are three industrial methods for the extraction of chlorine by electrolysis of chloride solutions:

- the membrane cell process, nowadays most widely used in Europe (64%),

- the mercury cell process, being phased out worldwide because of the toxic character of mercury (use today less than 20%) and
- the diaphragm cell process (used for nearly 14% of installed capacity)

4.4.1 Membrane cell process

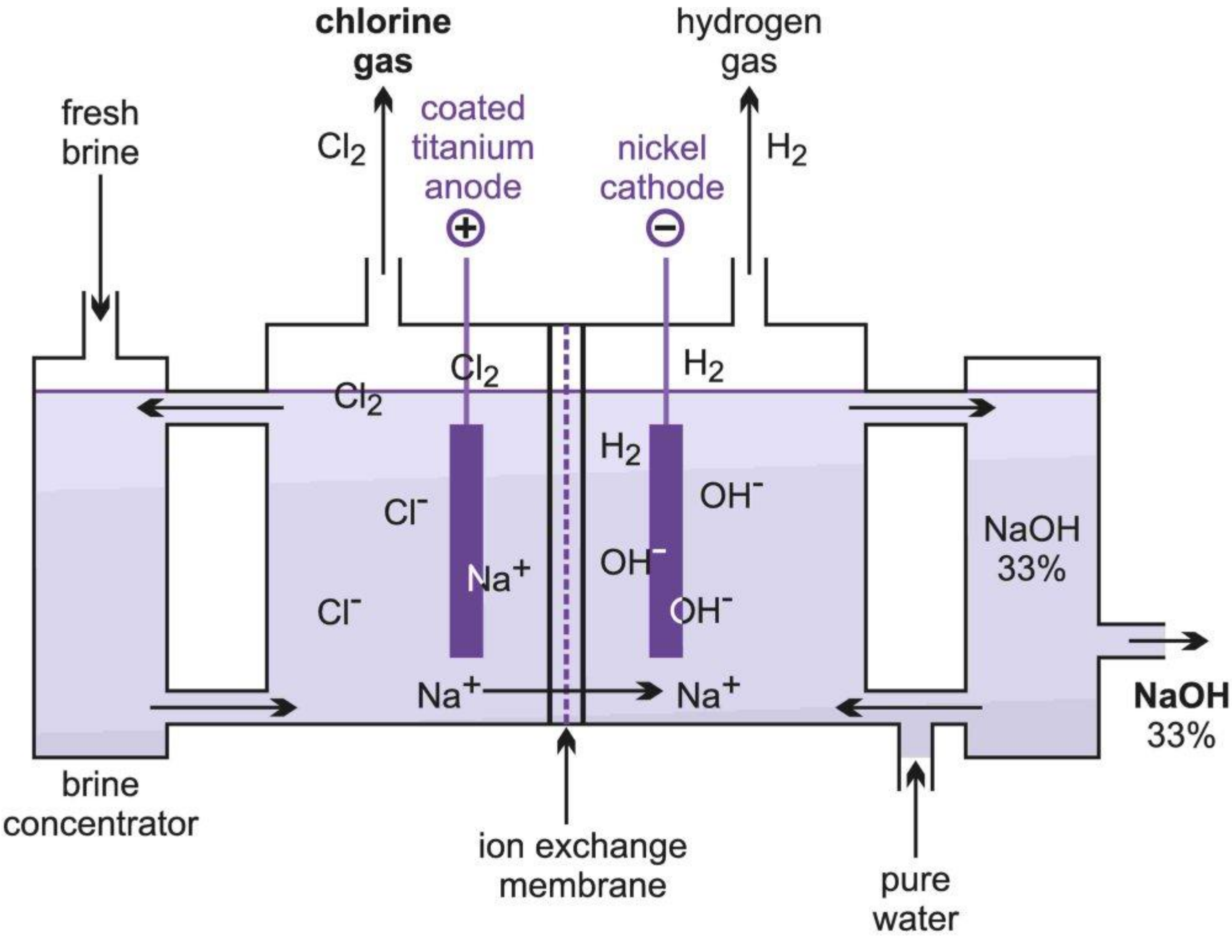

Figure 6: Chlorine production through membrane cell process.

The consumption of electric energy is the lowest of the three processes and the amount of steam needed for concentration of the caustic is relatively small (less than one tonne per tonne of caustic soda). Chlorine producers across Europe are progressively moving towards this method of making their product as the membrane cell process is the most environmentally sound way of manufacturing chlorine. By the end of 2015, membrane cell capacity accounted for 64% of total installed chlorine production capacity in Europe.

4.4.2 Mercury cell process

In the mercury cell process, sodium forms an amalgam (a 'mixture' of two metals) with the mercury at the cathode. The amalgam reacts with the water in a separate reactor called a decomposer where hydrogen gas and caustic soda solution at 50% are produced.

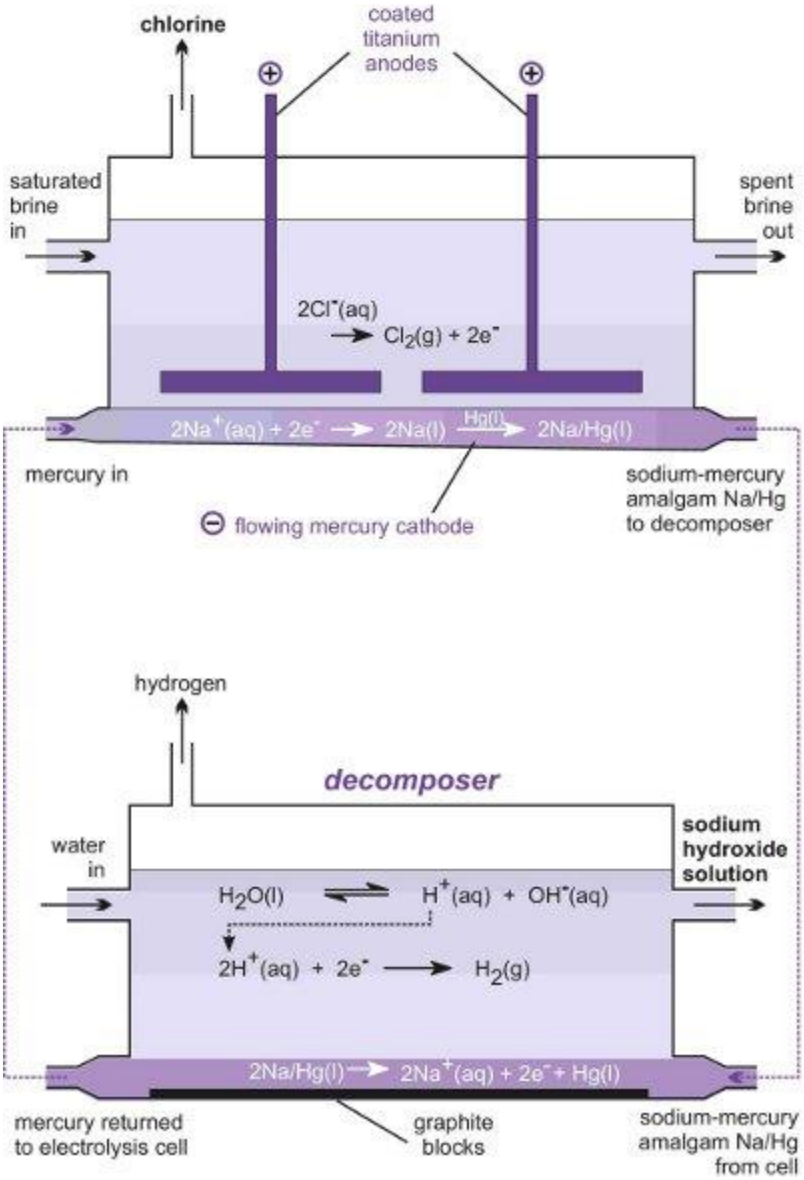

Figure 7: Chlorine production through mercury cell process.

Of the three processes, the mercury process uses the most electricity, but no steam is required to concentrate the caustic solution. The use of mercury demands measures to prevent environmental contamination. Also, mercury must be removed from the hydrogen gas and caustic soda solution.

Mercury losses have been considerably reduced over the years. Increasingly, chlorine producers are moving towards membrane technology, which has much less impact on the environment.

In 2015, emissions for all mercury cells across Western Europe reached 0.68 grammes per tonne of chlorine capacity, slightly higher than the all-time low of 0.74 grammes per tonne of chlorine capacity in 2014.

Today, twenty-three mercury-based chlorine plants remain to be phased out or converted to non-mercury technology at a cost of more than 3,000 million €. These plants account for an ever decreasing part (less than 20% in 2015) of European chlorine capacity.

4.4.3 Diaphragm cell process

In the diaphragm cell process the anode area is separated from the cathode area by a permeable diaphragm. The brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment.

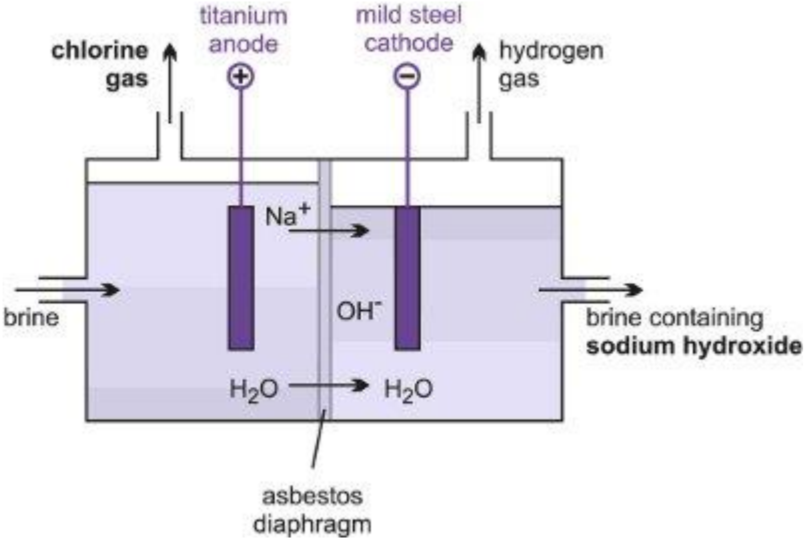

Figure 8: Chlorine production through diaphgram cell process.

In 2015, the diaphragm process accounted for less than 14% of total installed European chlorine production capacity.

5 Energy intensity of key processes

The chemicals subsector is characterised by the considerable use of fossil fuels and biomass for energy and feedstock. The bulk of energy and feedstock use occurs in a few key production processes. Steam cracking; ammonia production; and chlorine production, which occur in the petrochemicals and basic inorganics upstream manufacturing subsectors, are estimated to account for over 30% of energy use in the chemicals and pharmaceutical sector. The following table presents a summary of the energy intensities associated with each manufacturing subsector.

Product	**EU**		
	NACE (group)	**Energy use** [MJ/€ sales]	**Energy use** [GJ/tonne]
Petrochemicals	C20.1	12.5	15
Basic inorganic	C20.1; 20.5	12	-
Polymers	C20.1; 20.6	3.25	3
Specialty chemicals	C20.2; 20.3	2	-
Consumer chemicals	C20.4	0.75	-

As expected, petrochemicals and basic inorganics have the highest energy intensity within the chemicals subsector. Unlike downstream manufacturing, which requires energy to support reactions and mechanical processes (e.g., drying, mixing, rolling), upstream production requires significant quantities of energy (heat) to break and transform organic and inorganic molecules. For example, polymer production is approximately 5 times less energy intensive per unit of production than petrochemical.

Based on the sector energy demand energy presented and production values, the overall sector energy intensity is estimated to be 0.08 ktoe/€ (million) in 2011.

6 EU final energy consumption for chemical and pharmaceutical production

The following Figure presents the average fuel mix for EU chemical and pharmaceutical plants in 2012.

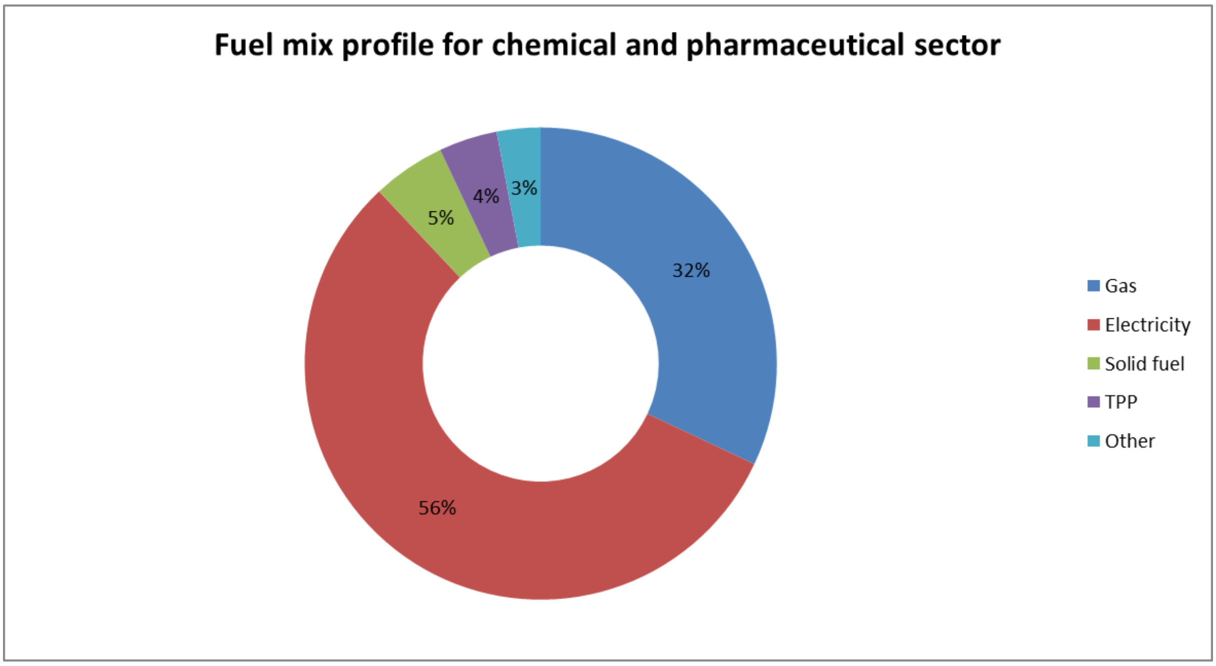

Figure 9: Fuel mix profile for EU chemical and pharmaceutical sector.

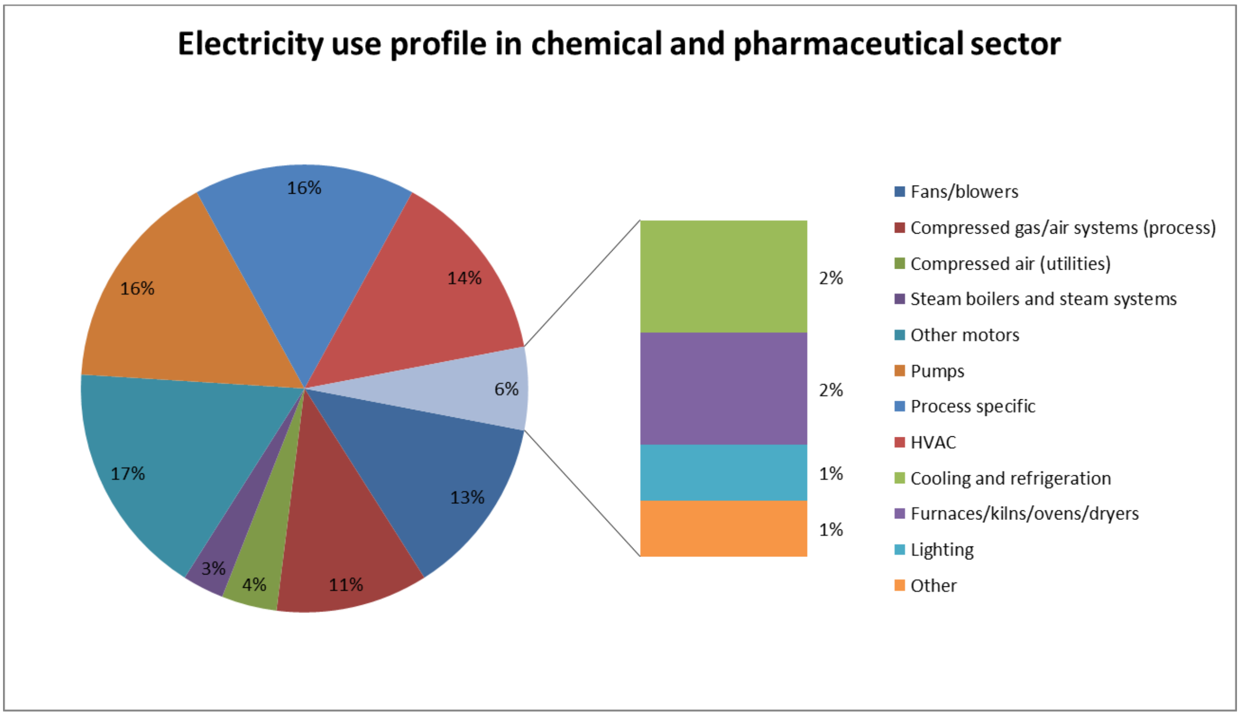

Figure 10: Electricity use profile in chemical and pharmaceutical sector.

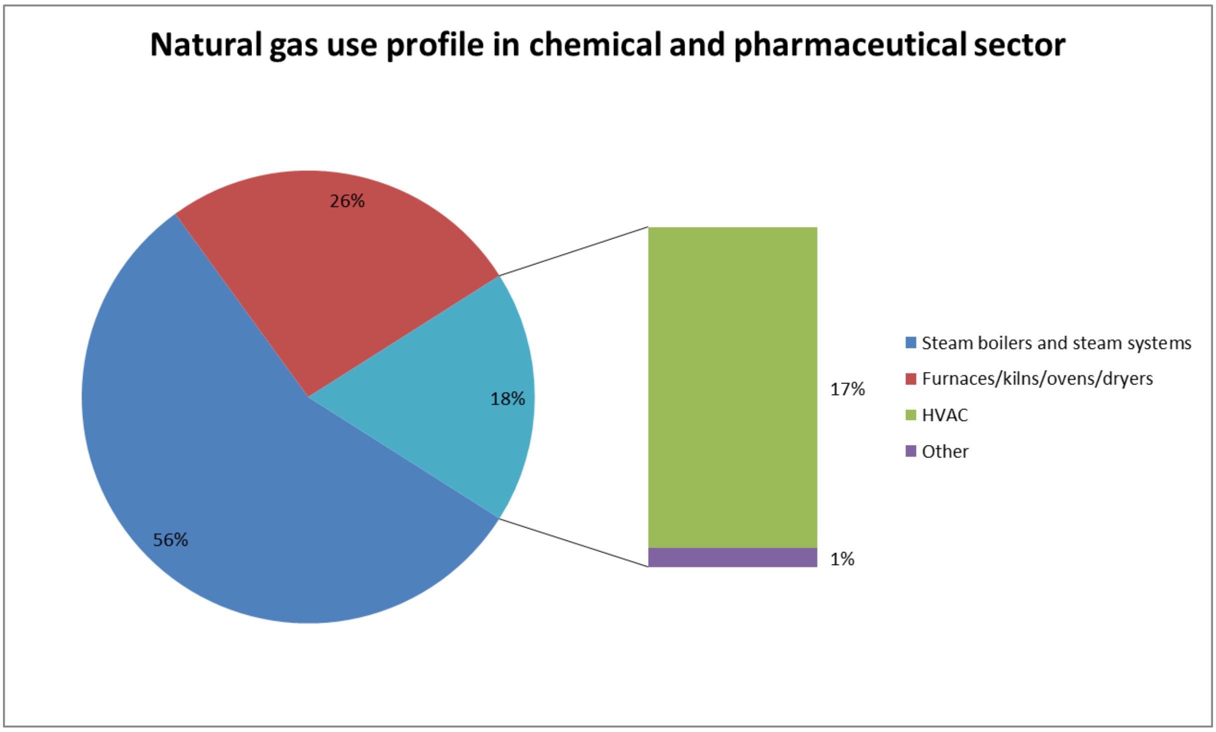

Figure 11: Natural gas use profile in chemical and pharmaceutical sector.

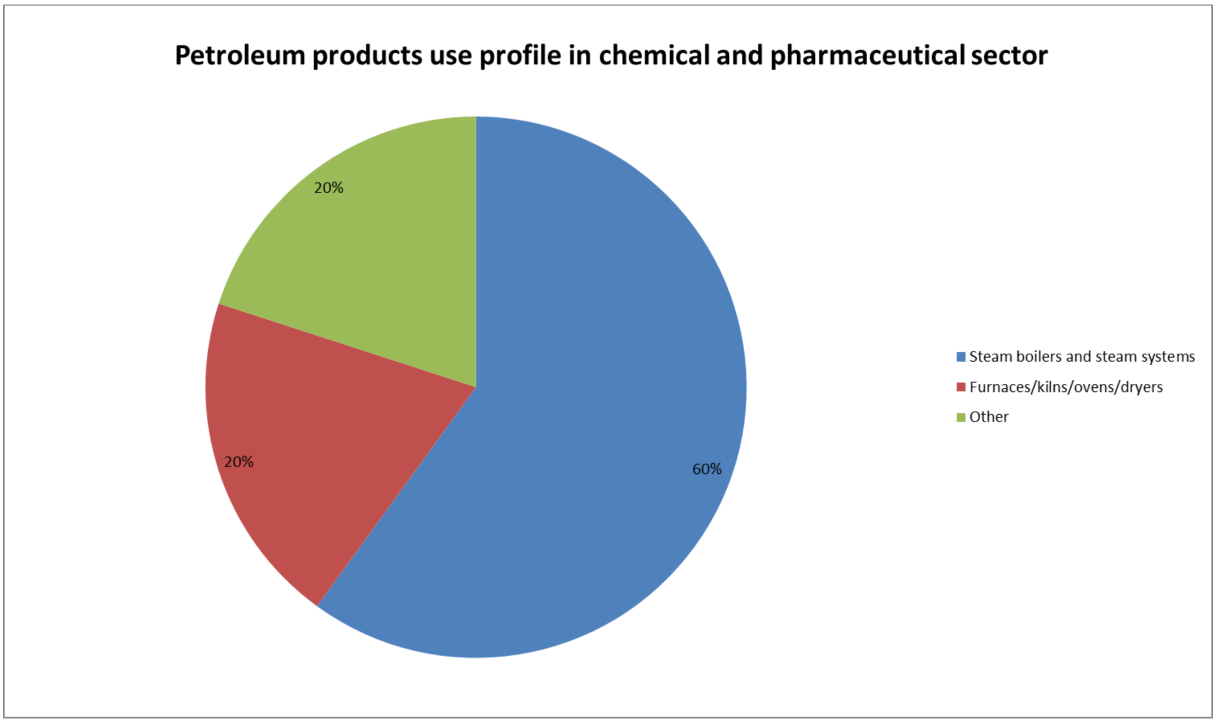

Figure 12: Petroleum products use profile in chemical and pharmaceutical sector.

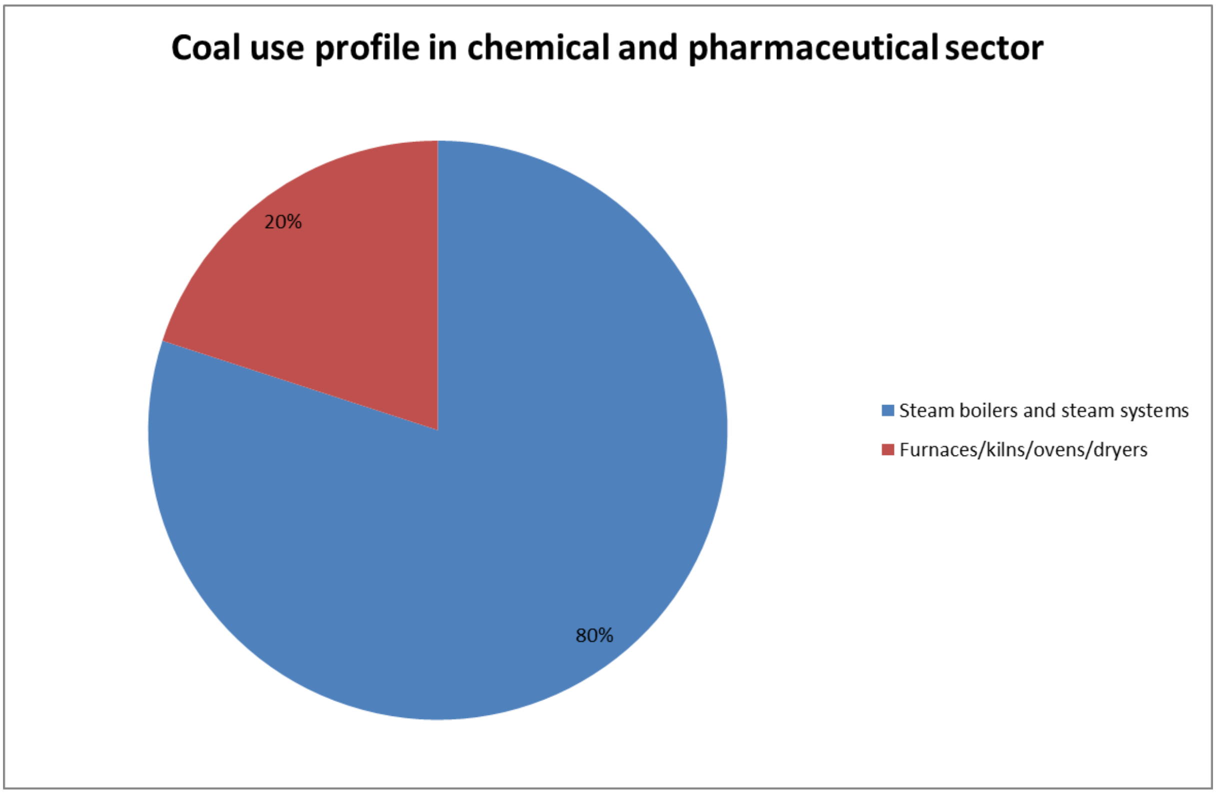

Figure 13: Coal use profile in chemical and pharmaceutical sector.

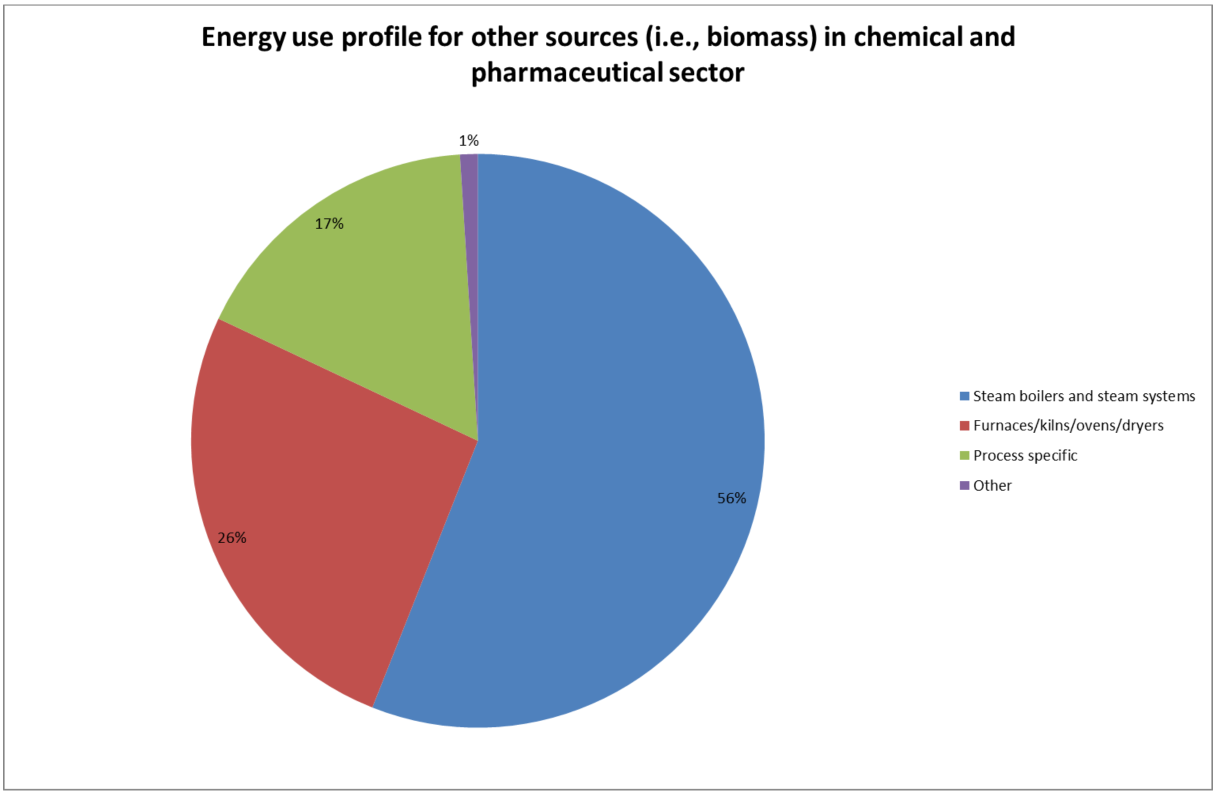

Figure 14: Energy use profile for other sources (i.e., biomass) in chemical and pharmaceutical sector.