

Mercury in extraction and refining process of crude oil and natural gas



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Abstract

Crude oil and natural gas are predominantly composed by hydrocarbon atoms, water and a wide spectrum of elements at low levels such as arsenic, vanadium and mercury.

The presence of mercury in crude oil and natural gas varies in each stage of extraction and transformation process because it distributes unequally among the vapour, condensate and aqueous phase in function of the pressure and temperature. Mercury causes a wide range of problems for refiners as for example: equipment degradation, toxic waste generation, health impacts and poisoning of catalysts.

In order to remove the contaminant, there are different technologies based on adsorption, chemical oxidation, precipitation or ion exchange treatments. The use of each one depends on the concentration and the physical and chemical state of mercury in crude oil or natural gas.

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Nomenclature

OPEC: Organization of the Petroleum Exporting Countries

LPG: Liquefied Petroleum Gas

TEG: Triethyleneglycol

EOS: Equation Of State

RKS: Redlich-Kwong-Soave

BIP: Binary Interaction Parameters

Chapter 1: Introduction

Over 85% of the world's energy comes from hydrocarbon resources which include: crude oil, natural gas and coal.

Crude oil is a complex mixture of liquid and gaseous hydrocarbons of various molecular weights and other compounds as: nitrogen, sulphur and other metals. The exact composition varies widely in function of the location, the pressure and the temperature, but the proportion of chemical elements moves over fairly narrow limits as follows in the table 1.

Table 1. Percentage range of the components that compose crude oil

Element	Percentage range
Carbon	83 to 87%
Hydrogen	10 to 14%
Nitrogen	0,1 to 2%
Oxygen	0,05 to 1,5%
Sulfur	0,05 to 0,6%
Metals	<0,1%

According to the Organization of the Petroleum Exporting Countries (OPEC), the total amount of crude oil produced by the world is 1.467,012 million barrels and the top 10 producing countries are shown in table 2. [1]

Table 2. Top 10 crude oil producers [1]

	Country	Million barrels/year
1	Venezuela	296,501
2	Saudi Arabia	264,561
3	Iran	151,170
4	Iraq	143,100
5	Kuwait	101,500
6	United Arab Emirates	97,800
7	Russia	79,342
8	Libya	47,097
9	Kazakhstan	39,800
10	Nigeria	37,200

Geographically, crude oil distributes in the world as it appears in figure 1.

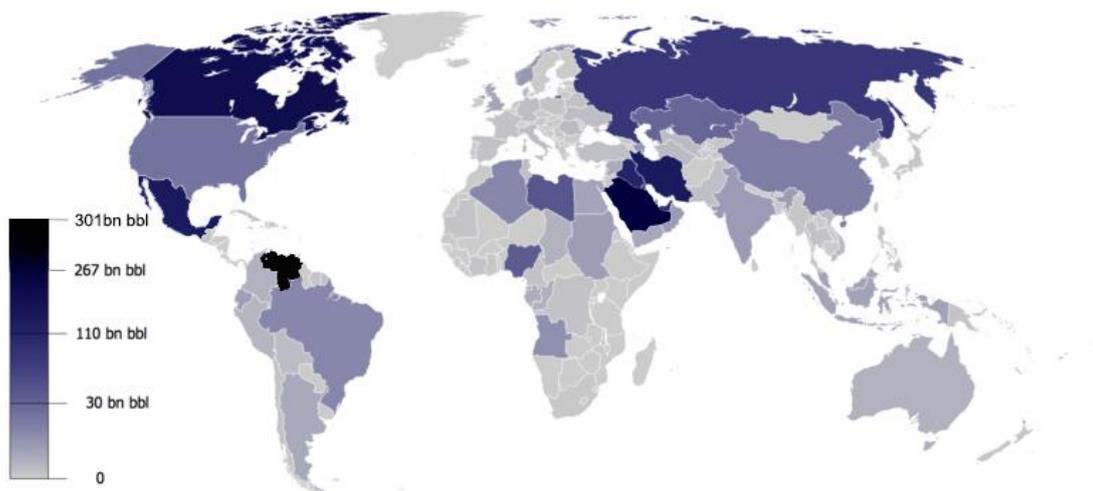


Figure 1. Location of the main crude oil Wells over the world [2]

Natural gas is composed by hydrocarbon molecules that range from one to four carbon atoms. It means that the mixture can contain: methane, ethane, propane and butane.

Table 3. Percentage in volume of the different components of natural gas

% in volume	
Methane (CH₄)	10-98%
Ethane (C₂H₆)	1-10%
Propane (C₃H₈)	Trace to 5%
Butane (C₄H₁₀)	Trace to 2%

Propane and butane burn giving off more heat than methane so, to take advantage of the high calorific power, the propane and butane distilled from natural gas forming Liquefied Petroleum Gas (LPG).

Natural gas also contains gaseous impurities such as water vapour and carbon dioxide, these two components doesn't burn and in consequence the value of the gas decreases.

On the other hand, natural gas is composed by nitrogen, helium and overall, hydrogen sulphide (H₂S). The last one is a very poisonous gas that is lethal in very low concentrations and it also causes corrosion of metal tubing, fittings and valves in the well. [3]

Natural gas receives the name of sweet natural gas if hydrogen sulphide is not detectable and sour natural gas if hydrogen sulphide is detectable. [3]

According to the OPEC, the total volume of natural gas produced by the world is 192,55 billion cubic meters and the top 10 producer countries summarizes in the table 4. [1]

Table 4. Top 10 crude oil producers [1]

	Country	Billion cubic meters/year
1	Russia	46,00
2	Iran	33,09
3	Qatar	25,20
4	Turkmenistan	8,34
5	Saudi Arabia	8,02
6	United States of America	7,08
7	United Arab Emirates	6,09
8	Venezuela	5,53
9	Nigeria	5,11
10	Algeria	4,50

The main natural gas reserves of the world are shown in the figure 2. It is easily to observe that it concentrates in countries of the Middle East, North America and Russia.

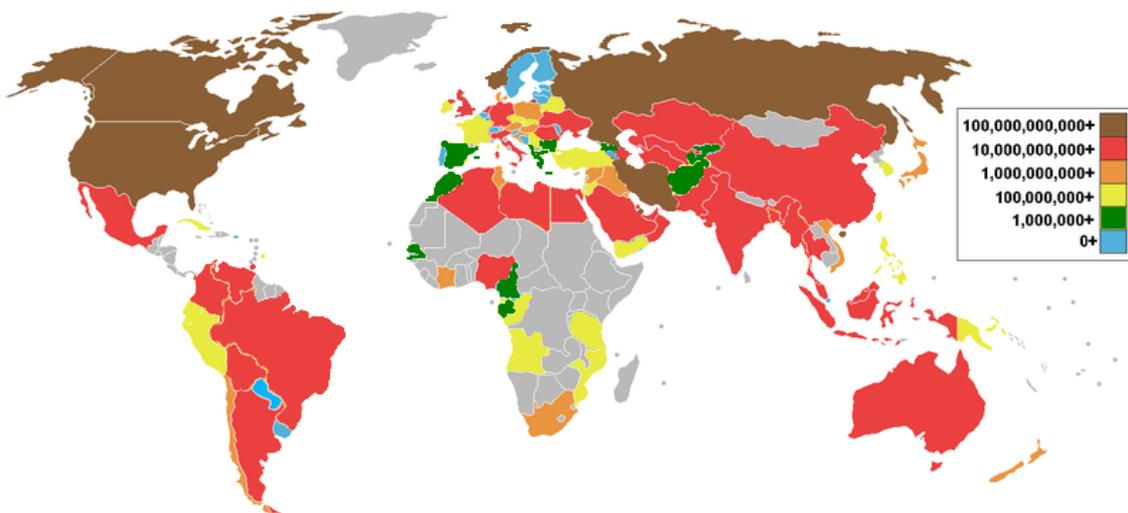


Figure 2. Location of the main natural gas reserves over the world [2]

The difference between crude oil and natural gas is the size of hydrocarbon molecules. While natural gas is a mixture of hydrocarbon molecules that has one, two, three or four carbon atoms. Crude oil is a mixture of more than 100 hydrocarbon molecules that range in size from five to more than sixty carbons in length. [3]

Coal is also an important hydrocarbon resource but it is not going to be analysed although the amount of this combustible is higher than crude oil and natural gas.

Hydrocarbon resources found in areas composed by sedimentary rock layers formed by particles originated by the breakdown of pre-existing rocks, seashells and salt precipitated from water.

Oil and natural gas comes from the organic matter that is buried and preserved in the ancient sedimentary rock. Whereas oil produced at temperatures near to 65°C and depths around 2130m; natural gas is formed at 150°C and 5500m. [3]

Gas and oil are light in density compared to water so it rises through the fractures of the subsurface rocks to sedimentary rocks that receive the name of reservoir rocks. This contains billions of tiny spaces (pores) where gas and oil flow and moves to a high point in the reservoir rock called trap where the gas and oil is stopped and concentrated and it separates according to its density. [3]

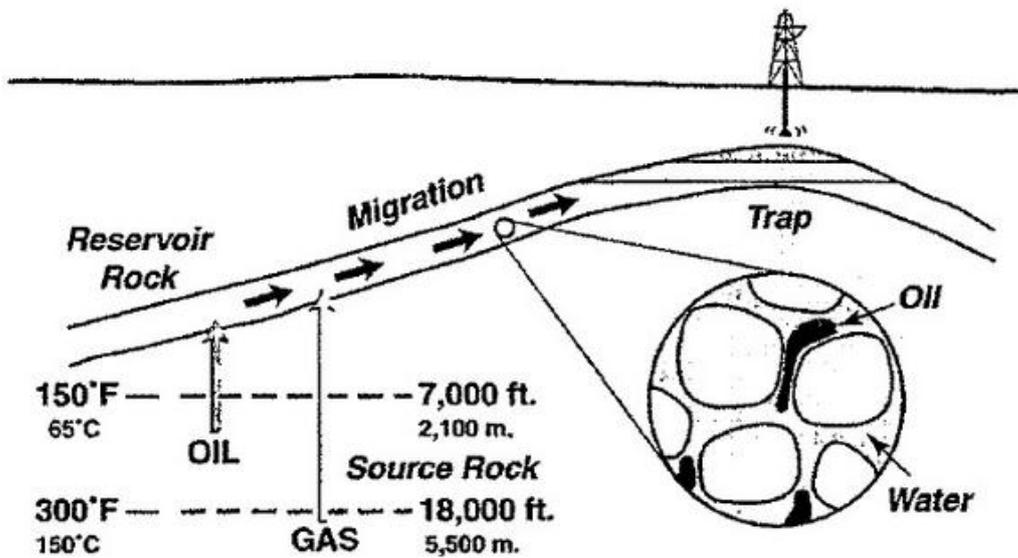


Figure 3. Generation and migration of gas and oil [3].

Although, trap fluids are predominantly composed by hydrocarbons, water and non-hydrocarbon atoms, they also contain a wide spectrum of elements or compounds at low or trace levels such as arsenic, lead, nickel, vanadium and mercury.

This project describes how the mercury distributes in every stage of the crude oil and natural gas and which are the impacts of this contaminant in the whole process.

One of the main parts of the project is focus on the study of the evolution of mercury and their species in the figure 4. In other words, the study is based on how the mercury distributes among the gas, oil and water in function of two parameters: the pressure and the temperature.

According to figure 4, crude oil and natural gas mixed with mercury, extracts from the well and it sends to a top side process where pressure and temperature change and the initial mixture separates in function of its density in: gas, oil and water.

After the separation; gas and oil treat in downstream process whereas water recirculates to the well.

As it studies in the next sections, the mercury that goes to the downstream process causes different problems to the equipment, the workers and the environment. It is for this reason, that in order to avoid these problems, there are different kind of technologies used to remove the mercury from the oil and gas pre-treated.

Objectives

The main objectives of this project are based on known:

- Physical and chemical properties of the mercury, the main stages of the mercury cycle and the different species contained in crude oil and natural gas.
- Thermodynamic partitioning of the mercury on oil, water and gas.
- Data and necessary information to build up a mathematical model able to predict the distribution of the contaminant in the vapour, condensate and aqueous phase.
- Design of a separation system by using *Honeywell Unisim Design R390* and criticize the problems found.
- The distribution of mercury in crude oil and natural gas from its extraction to its refining.
- Processing operation impacts, health impacts and environmental impacts of mercury in crude oil and natural gas treatments.

Technologies used to remove mercury from crude oil and natural gas.

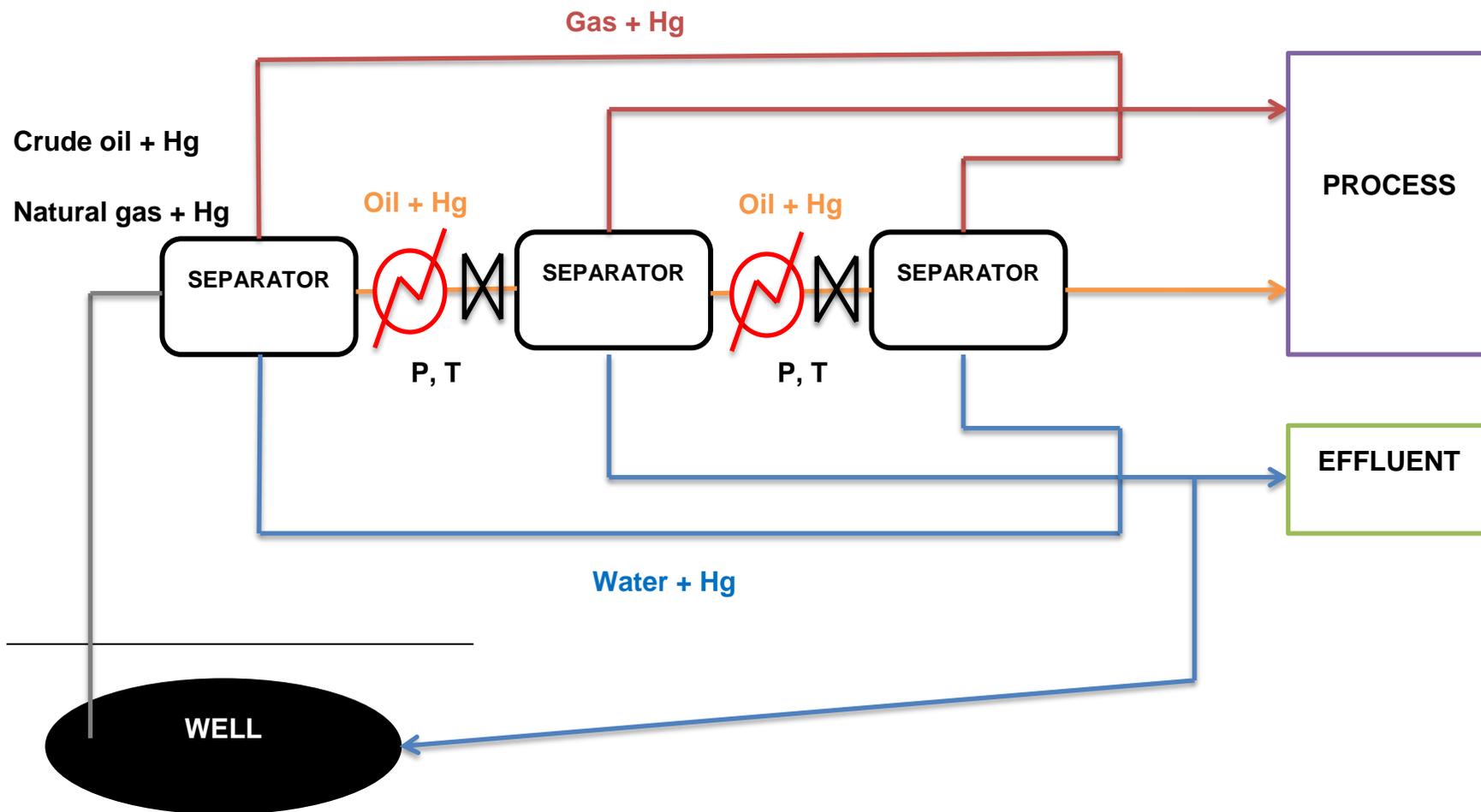


Figure 4. Flowchart of the extraction and topstream process.

Chapter 2: Mercury

Mercury (Hg) is a chemical element commonly known as quick-silver; its main feature is that it is liquid at standard conditions of pressure and temperature.

This element is extremely rare in the Earth's crust and it is found as native metal or in ores such as cinnabar (mercuric sulfide), corderoite (mercury sulfide chloride) or livingstone (mercury antimony sulfosalt).

Although it is a very rare element in the earth surface, it has much importance in the atmosphere due to the volcanic activity and the fact that elemental mercury readily vaporizes from its liquid state.

In soil and water surfaces the mercury is found as mercuric (Hg^{2+}) and mercurous (Hg^+) states. While mercuric chloride is the predominant form in many surface waters. In following sections, emphasize in the different forms which mercury is found in gas, oil and water.

Mercury cycle

Mercury in the environment is constantly cycled and recycled through a biogeochemical cycle (figure 5). According to [4] the cycle has six major steps:

- 1) Degassing of mercury from rock, soils, and surface waters, or emissions from volcanoes and from human activities. This first stage is favored for the surprisingly degree of volatility of the contaminant.

Table 5 presents the different origins of mercury.

Table 5. Sources of mercury [4]

Natural Occuring	Occupational	Non-occupational
Volcanos	Gold mining	Seafood
Rocks e.g. granite	Metal smelting	Thermometers
Soil & sediment	Cement making	Fluorescent light bulbs
Seawater/freshwater	Petrochemicals	Medicinal products
Cinnabar-HgS	Incineration	Skin care products

- 2) Movement in gaseous form through the atmosphere. Once in the atmosphere, the mercury vapor can circulate for up to a year, and become widely dispersed.
- 3) Deposition of mercury on land and surface waters. The mercury is absorbed by the surface waters and the soil after the elementary mercury vapor suffers a photochemical oxidation to become inorganic mercury that can combine with water vapors and travel back to the Earth's surface as rain.
- 4) Conversion of the element into insoluble mercury sulfide. This transformation takes place inside the water.
- 5) Precipitation or bioconversion into more volatile or soluble forms such as methylmercury. The bioconversion is caused by bacteria that process inorganic divalent mercury into methylmercury.



The reaction depends on the dissolved organic carbon and the pH.

Methylmercury is very toxic and accumulates in the body of the life organisms.

- 6) Reentry into the atmosphere or bioaccumulation in food chains. The methylmercury-processing bacteria may be consumed by the next higher organism up the food chain, or the bacteria may release the methylmercury into the water where it can adsorb to plankton, which can also be consumed by the next higher organism up the food chain.

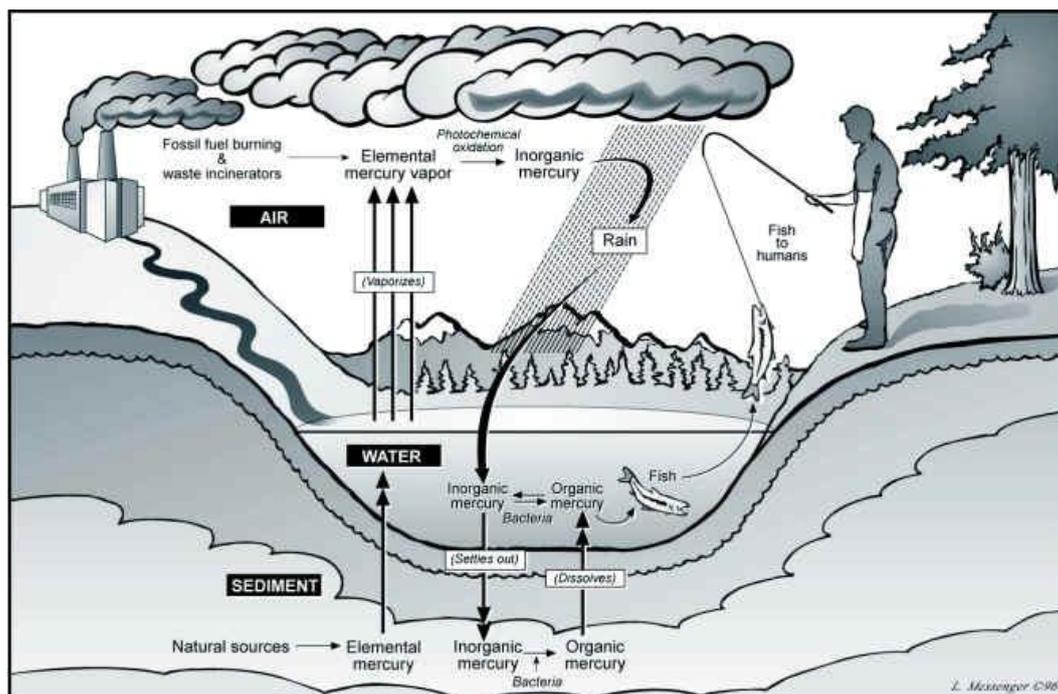


Figure 5. The mercury cycle [4]

Physical properties of mercury

Mercury is a metal silver-colored whose main physical properties are summarized in table 6.

The main physical properties to highlight are: its high density and surface tension, its solubility with some metals like gold and silver giving amalgams and its slightly solubility in water. [5]

Mercury on the other hand, is a poor conductor of heat, but it expands and contract evenly when the temperature changes. It is a fair conductor of electricity. [5]

When the temperature is above 40°C, mercury becomes in intoxic and corrosive vapors heavier than air. It is harmful by ingestion and inhalation. Moreover, it irritates the skin, the eyes and the breath ways. [5]

It is incompatible with nitric acid concentrated, acetylene, ammonia, chlorine and metals.

Table 6. Mercury physical properties [4]

Properties	
Atomic number	80
Atomic weight	200,59 atomic mass units
Boiling point	357°C
Boiling point/rise in pressure	0,0746 °C/torr
Density	13,546 g/cm ³ at 20°C
Diffusivity (in air)	0,112 cm ² /sec
Heat capacity	0,0332 cal/g at 20°C
Henry's law constant	0,0114 atm·m ² /mol
Interfacial tension (Hg/H₂O)	375 dyne/cm at 20°C
Melting point	-38,87°C
Saturation vapour pressure	0,16 N/m ³ (pascal) at 20°C
Surface tension (in air)	436 dyne/cm at 20°C
Vaporization rate (still air)	0,007 mg/cm ² ·hr

Chemical properties

Mercury dissolves in concentrated sulfuric acid and nitric acid and aqua regia to give sulfate, nitrate and chloride salts. It also reacts with solid sulfur flakes so, it uses to absorb mercury vapors. [6]

On the other hand, mercury can react with another metal to form an amalgam. Almost all metals can form amalgams with mercury except iron, zinc, copper, manganese and platinum [6]. It is important to emphasize, that mercury can corrode aluminum so it is not advisable to use this kind of metal for the equipment of the oil plant. Otherwise, can occur accidents as the Skikda plant in Algeria in 1973 when the aluminum of the heat exchangers fails due to the amalgamation with mercury. [4]

Mercury in crude oil and natural gas

The content of mercury in crude oil varies between 0,1 and 20.000 µg/kg whereas in natural gas the amount of mercury oscillates between 0,05 and 5000 µg/Nm³. [7]

The variability in both cases depends on many factors, such as: regional-tectonic position, geologic-structural features of the deposit, the operation conditions and seismic activity.

The mercury content varies widely as a function of location as shown in table 7.

Table 7. Crude oil mercury content in function of the location [7]

Country	Mercury Concentration (µg/kg)
Africa	2,7
Asia	220,1
Europe	8,7
Middle East	0,8
South America	5,3
North America	3,2

The total amount of mercury inside the crude oil that it processes in United Kingdom in 2009 is around 750 kg per each 50,7 million tons of crude oil processed. [7]

In natural gas the amount of mercury also varies in function of the location according to the table 8.

Table 8. Natural gas mercury content in function of the location [7]

Country	Mercury Concentration ($\mu\text{g}/\text{Nm}^3$)
Algeria	50-80
Eastern Europe	$1,2 \times 10^3$
Germany (northern)	15-450
Germany (southern)	<0,1-0,3
Middle East	1-9
South America	69-119
North America	0,005-40

United Kingdom process in 2009 40.3 billion of natural gas m^3 and it generates between 1380 and 1720 kg of mercury. [7]

However, according to [8], the amount of mercury in natural gas has revealed a short-term time variability of the mercury concentration. The fluctuations have regular periods from few minutes to several hours and can be represented as a set of harmonics with different spectral intensity and stability in time.

Nature of mercury compounds

The complex variety of species in oil can be separated into three categories: volatile mercury (including elemental mercury and dialkylmercury), insoluble mercury (of uncertain chemical identity) and dissolved forms (including elemental mercury oil, dialkylmercury, mono-alkylmercury and loosely complexed ionic mercury). [7]

According to [9] crude oil and natural gas can be found in the following chemical forms, which differ in their chemical and physical properties:

- 1) Dissolved elemental mercury: Elemental mercury occur naturally in geologic compounds. It is soluble in liquid aliphatic hydrocarbons, is highly adsorptive on metallic surfaces and it is for this reason that reacts with iron oxide corrosion products on pipe and equipment walls. The

degree of volatility of the contaminant is very high and predominantly distributes among the LPG and naphtha product streams during the distillation of crude.

- 2) Dissolved organic mercury (RHgR and RHgX , where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$, etc. and $\text{X} = \text{Cl}^-$ or other inorganic anion): Dissolved organic mercury compounds are highly soluble in crude oil and gas condensate, the adsorptive tendencies are similar to elemental mercury but differ in their boiling points and solubility. This category includes dialkylmercury and monomethylmercury halides.
- 3) Inorganic (ionic) mercury salts (Hg^{2+}X or Hg^{2+}X_2 , where X is an inorganic ion): Mercury salts are soluble in oil and gas condensate and they partition to the water phase in primary separations. Mercuric chlorides have a high solubility in organic liquids.
- 4) Complexed mercury (HgK or HgK_2): Mercury can exist in hydrocarbons as a complex, where K could be an organic acid, organic sulphide, thiophene, mercaptan or thiol.
- 5) Suspended mercury compounds: The most common examples are mercuric sulphide (HgS) and selenide (HgSe), which are insoluble in water and oil but may be present as suspended solid particles of very small particle size.
- 6) Suspended adsorbed mercury: Organic mercury that is not dissolved but it is adsorbed on inert particles such as sand or wax. This kind of mercury can be separated by filtration or centrifugation.

Chapter 3: Petroleum and natural gas process

Wide varieties of processing schemes exist for refining crude oil and for natural gas separation but the majority of gas and oil processing facilities are similar in their basic designs and configurations. [9]

In general, the processing of oil is directed to maximize gasoline manufacture while gas processing is directed to separate methane (sales gas) from other gas components. However, there are differences in processing steps depending on two facts: the composition of the hydrocarbon chain and the market objectives. [9]

Petroleum refining

The petroleum refining divides in two different processes: upstream processes and downstream processes. In the first group the impurities of the raw material are removed whereas in the second set of operations, crude oil is transformed in other valuable products of different density such as LPG, gasoline, kerosene, fuel or asphalt among others.

Upstream process

The upstream process includes two different processes to improve the conditions of the oil and to extract the impurities of it, as for example: water, dissolution solids or gas. All these processes are described following the references of [10].

- 1) Desalinization: The main species removed in this stage are $MgCl_2$ and $NaCl$. Two different technologies are followed:
 - a. Decantation with chemical products: The crude is washed by fatty acids modified, NH_3 , ethylic alcohol and soda caustic. Then, the mixture stores in a temperature between 120 and 150°C. Finally the two phases (desalinated crude and salt water) are separated by decantation.
 - b. Decantation with electrical method: It uses electrodes that discharge a 17.000-33.000 V. The efficiency of this method it's around the 90%.

- 2) Stabilization: This process is based on the separation of the highest volatility gases dissolved inside the crude. It uses two distillation columns which work at 140°C and a pressure that ranges between 3-15 bar. C1, C2, C3 and C4 are obtained.
- 3) Transport: The oil and natural gas transport to the refinery plant by two different ways:
 - a. Boat
 - b. Piper

Downstream process

The descriptions of the downstream processes come from [10].

- 4) Topping: The crude separates in different fractions in function of the market needs.

Topping is based in two different steps:

- a) Atmospheric or primary distillation: Crude introduces to the bottom of the fractional column and it submits at temperatures between 350 and 370°C and to atmospheric pressure. Then the crude separates inside the column according to the boiling point of different sealable products (figure 6).

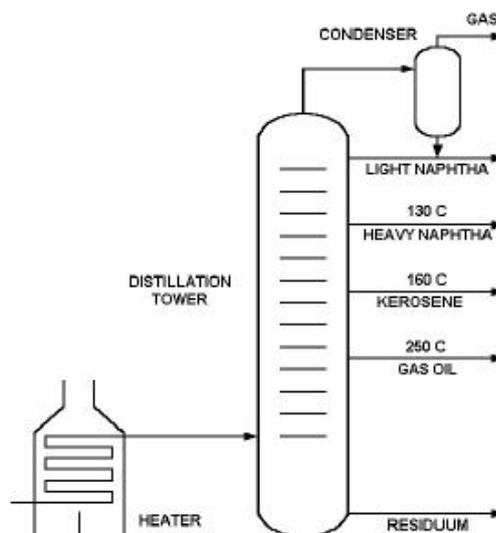


Figure 6. Atmospheric distillation [9]

b) Vacuum distillation: The atmospheric distillation waste submits at temperatures near to 400°C and pressures of 35mmHg. These conditions allows to extract lighter products without modify the molecular structure of the crude.

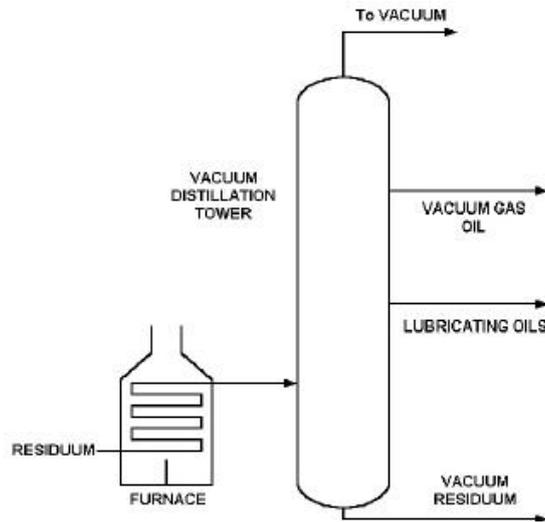


Figure 7. Vacuum distillation [9]

The products of the atmospheric distillation are lighter; they are compressed between 1 and 18 carbon atoms such as: gases, LPG, light gasoline, kerosene, gasoil and waste. Whereas in the vacuum distillation the products are heavier (up than 18 carbon atoms) like for example: gasoil, fuel-oil, lubricants, asphalts, wax and other wastes.

5) Cracking: The heaviest and the largest hydrocarbon molecules broke to more light and volatile molecules. There are different manners to broke the hydrocarbon chain:

a) Thermal cracking: The heaviest and largest hydrocarbon molecules submits at 500-600°C and 30-40 atm and the resulting product is gasoline and olefins.

Since the 1940's this method has been replaced by catalytic cracking because the efficiency is higher. Despite of this fact, this method is keeping used to treat the wastes.

- b) Catalytic cracking: The breaking reaction is affected by an acid catalyst based on a mixture of silica (85%) and alumina (15%) it breaks the bounds of the chain and avoids the secondary reactions. There are three different industrial processes in function of the situation of the catalyst: fix bed, mobile bed and fluidized bed. This operation is one of the most important in the refinery because it covers the gasoline demand of the market.

 - c) Hydrocracking: Is based on the addition of hydrogen in the catalytic cracking process. At high pressures (200-400 atm) and high temperatures (400°C), the catalysts hydrogenate the unsaturated hydrocarbons. This method avoids the coking of the catalyst (the relationship between Hydrogen and Carbon increase) whereas the percentage of sulfur decreases.
- 6) Improvement of the properties: The properties of certain fractions change to increase its quality. The purposes of these modifications are based on the improvement of the amount of octanes or the carburant quality.
- 7) Refine: It is based on the removal of the undesirable components of the oil. There are two types of depuration processes:
- a. Physical
 - b. Chemical

Gas processing

In gas processing, there aren't any transformations to produce salable products. The treatments are designed to remove unwanted constituents such as CO₂, H₂S or H₂O and trace contaminants (metals). The separations are cryogenic utilizing a selective condensation of fractions (C₂, C₃ and C₄) by removal of heat. [9]

On one hand, the water removal is one of the main operations in gas processing. It consists in putting in contact gas with triethyleneglycol (TEG).

TEG absorbs water and it is regenerated by continuous process that boils off the water. [9]

On the other hand, the removal of H₂S and CO₂ is also very important to avoid corrosion problems. They separate by mixing the gas with amine solutions and carbonate solutions that selectively absorb the pollutants. [9]

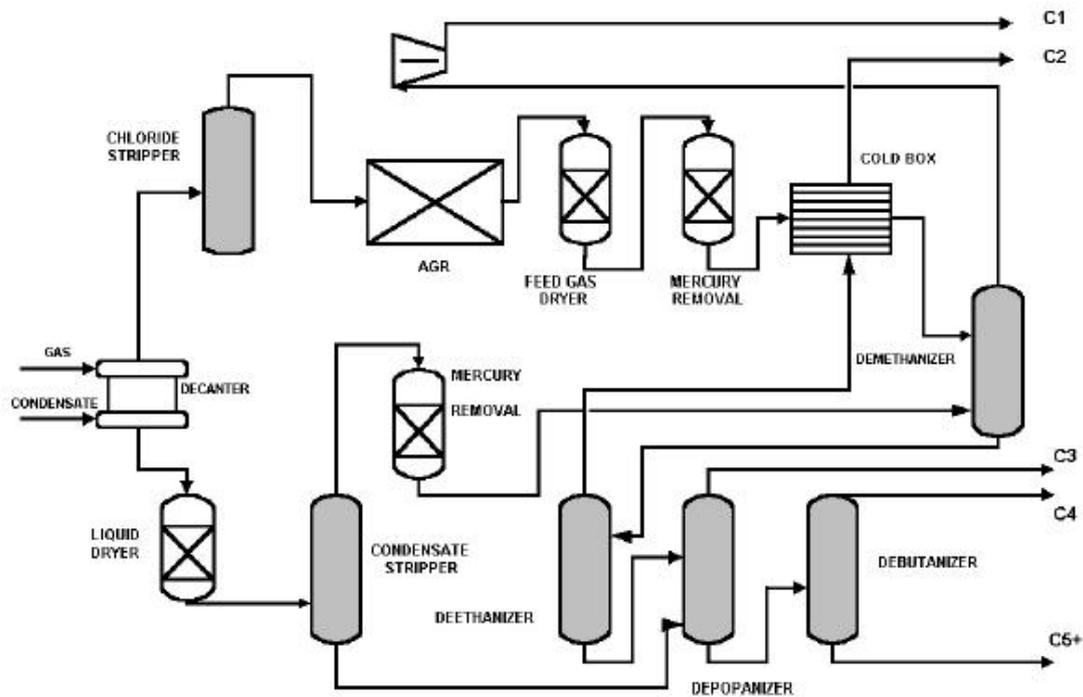


Figure 8. Gas plant liquid processing [9]

According to figure 8, the gas separation process involves cooling gas to liquefy C₂-C₅. The cryogenic heat exchanger is called cold box and is typically manufactured from aluminum. As it describes in following sections, mercury removal units based on adsorbent technologies are applied upstream of the cold box to prevent condensation of mercury and damage of the equipment. [9]

The use of mercury removal units in gas processing depends on different factors: the amount of mercury in feeds, whether aluminum heat exchangers are utilized or whether downstream customers of gas products have specifications for mercury [9].

Chapter 4: Thermodynamic partitioning of mercury in gas, oil and water

Crude oil contains trace levels of mercury. This contaminant has different impacts in the oil plant processing, the operators and the environment. It is for this reason, that in the last years, the distribution of mercury among the gas, oil and water has become on an interest issue for processing engineers.

The advance of the computer simulation software has been contributed in the definition of mathematical models able to predict the distribution of mercury in the different phases of the fluid in function of its different variables such as temperature or pressure.

Mathematical methods have become a powerful tool to know the mobility of the mercury and to anticipate to possible future impacts. However, it is important to be aware of its limitations.

This section tries to explain how mercury distributes through the mixture of oil, water and natural gas (figure 9).

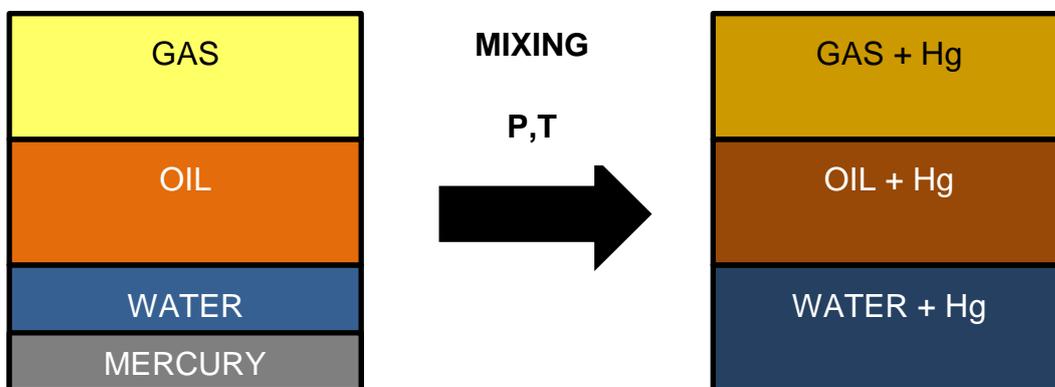


Figure 9. Distribution of mercury in gas, oil and water in function of the pressure and the temperature

In order to know the distribution of that metal in the different phases of crude oil, an analysis of experimental data based on [11] has been done. After that and using that evidences, an examination of the model considered by [12] have been discussed.

In the following section, a simulation with *Honeywell Unisim Design R390* has been done. However, during the simulation processing, some problems and limitations found so the reliability of the results have been affected.

Finally, a comparison between the results obtained in [12] and the results of *Honeywell Unisim Design R390* have been discussed.

Analysis of experimental data

The study made by [11] presents the data of the amount of mercury contained in mercury crude oil.

As it shows figure 10, total mercury in crude oil oscillates between 0,5 and 5000 ng/g. The diagram shows the mercury content in different crude oils and the number inside each bar indicates the number of samples for each kind of crude.

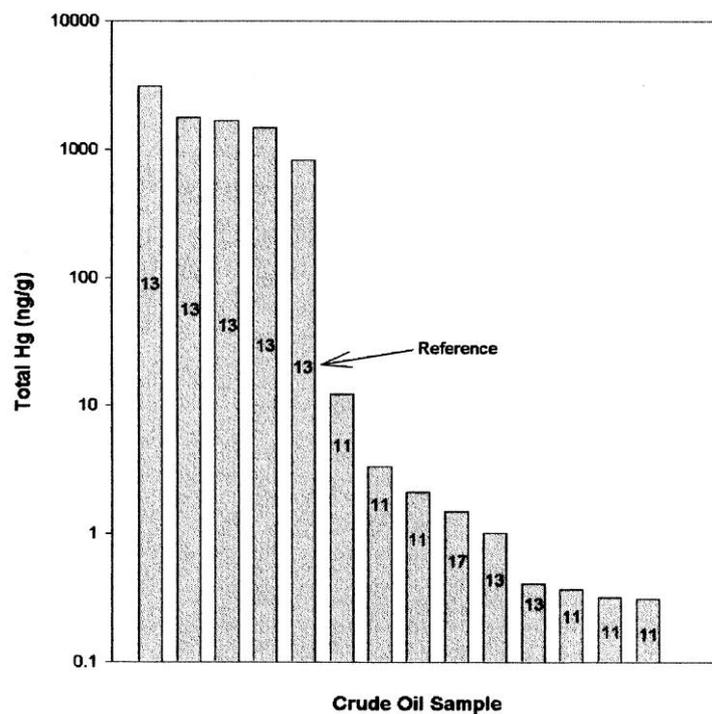


Figure 10. Total mercury in crude oil [11]

According to [11] (figure 11) natural gas is composed from 8 to 9000 ng/g. As well as in the last figure, the number inside the bar indicates the number of samples.

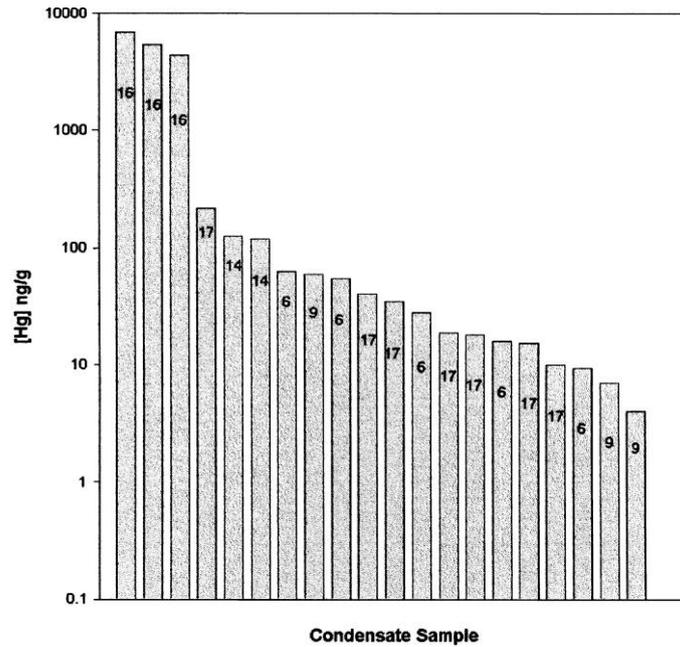


Figure 11. Total mercury in natural gas [11]

As it describes in the last section, after the downstream processes, crude oil and natural gas separate in different valuable fractions by a primary distillation.

Two studies have been done and they check that the total amount of mercury varies in function of the temperature according to the figure 12.

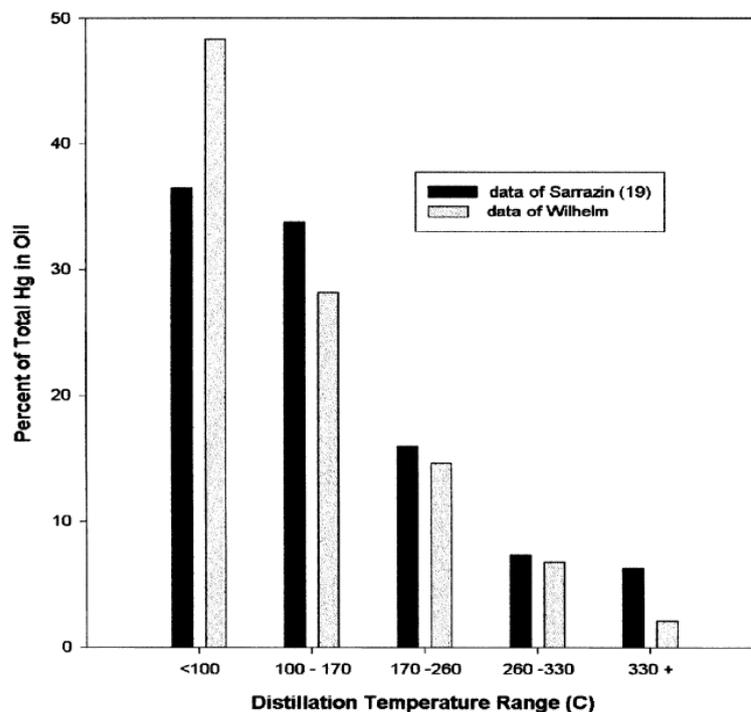


Figure 12. Distribution of mercury compounds in distillation cuts [11]

In both cases, the low percentage of mercury concentrates in the higher temperature fractions (residuum) whereas the high percentage of mercury is in the more volatile fractions such as LPG or light naphtas.

Once known the partitioning of mercury in the primary distillation cuts, it is interesting to be aware of the distribution of the distinct species of the contaminant.

Studies developed by Tao indicate that ionic mercury was the dominant species in the condensates examined. Hg^0 did not exceed 25% of the total in any of the condensate samples; the dialkyl species was detected >10% in some condensates whereas the monoalkyl species was detected but a very low concentrations. In naphtas, the dominant species are $RHgR$ while Hg^0 appear in the lighter gas fraction. [11]

Figure 13 summarizes how the different mercury species distributes in crude oil, naphtas and condensates.

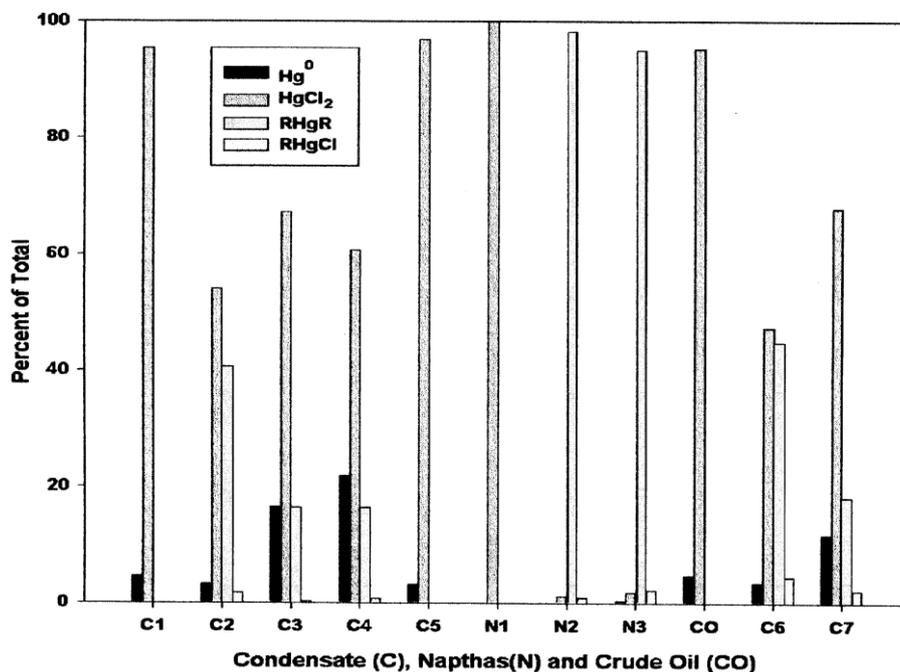


Figure 13. Distribution of mercury compounds in liquid hydrocarbons [11].

In natural gas plants, the distribution of mercury among the distinct gases that compose the feeding depends on the existence of mercury removal systems (figure 14).

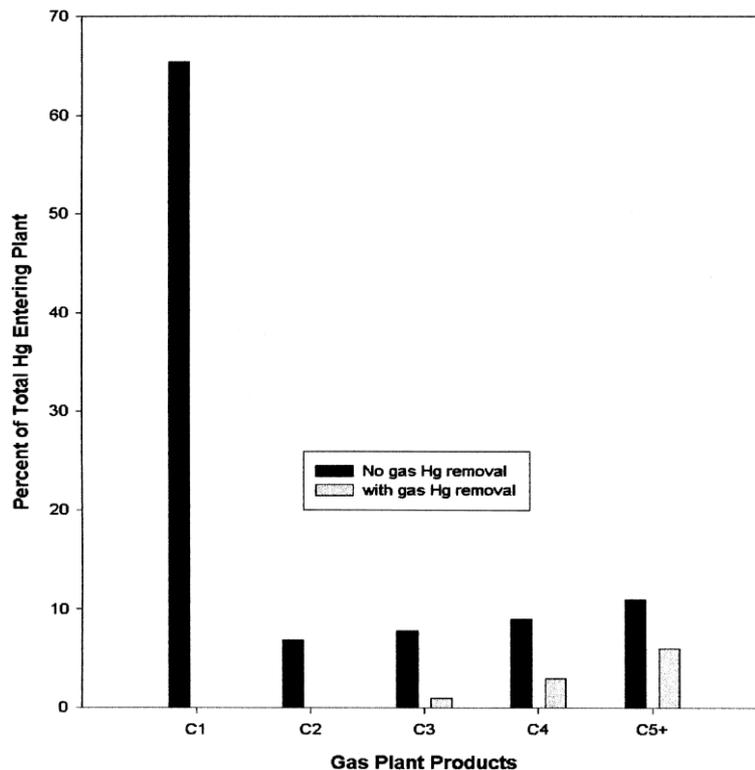


Figure 14. Distribution of mercury compounds in gas plant products [11].

Mercury partitioning by a mathematical model

According to [12], experimental data described in the last section, helps to estimate the partitioning of mercury in gas, oil and water by using an equation of state (EOS) compiled by a multiphase flash calculation program.

The modelling of mercury partitioning has been doing by an equation of state based on Redlich-Kwong-Soave (RKS).

The equation and their parameters describes in the following lines:

$$p = \frac{R \cdot T}{V_m - b} - \frac{a_m}{V_m \cdot (V_m + b_m)}$$

$$a_i = \frac{0,427 \cdot R^2 \cdot T_{c_i}^2}{P_{c_i}} \cdot \left[\sqrt{1 + (1 - T_{r_i}^{0,5}) \cdot (0,374 + 1,542 \cdot \omega_i - 0,270 \cdot \omega_i^2)} \right]$$

$$a_j = \frac{0,427 \cdot R^2 \cdot T_{c_j}^2}{P_{C_j}} \cdot \left[\sqrt{1 + (1 - T_{r_j}^{0,5}) \cdot (0,374 + 1,542 \cdot \omega_j - 0,270 \cdot \omega_j^2)} \right]$$

$$b_i = \frac{0,08664 \cdot R \cdot T_{C_i}}{P_{C_i}}$$

$$a_m = \sum_{i=1}^n \sum_{j=1}^n x_i \cdot x_j \cdot \sqrt{a_i \cdot a_j} \cdot (1 - k_{ij})$$

$$b_m = \sum_{i=1}^n x_i \cdot b_i$$

$$\omega_i = -\log(p_r^{sat_i}) - 1 \quad \omega_j = -\log(p_r^{sat_j}) - 1$$

$$p_r^{sat_i} = \frac{p_{sat_i}}{P_{C_i}} \quad p_r^{sat_j} = \frac{p_{sat_j}}{P_{C_j}}$$

$$V_m = \frac{V}{n}$$

Where:

T = Absolute temperature

T_C = Absolute temperature at the critical point

V_C = Molar volume at the critical point

p = Pressure absolute

P_C = Pressure at the critical point

V_m = Molar volume

n = Number of mixture components

x_i = molar fraction *i* component

k_{ij} = binary interaction parameter

In order to incorporate mercury and its compounds into a predictive EOS, some basic physical property data for the pure components are required [12]:

- Solubility of mercury species as a function of temperature and pressure
- Vapour pressures
- Binary interaction parameters

Solubility of mercury species

Elemental mercury (Hg^0) is soluble in liquid aliphatic hydrocarbons to a few 1-3 ppm whereas the solubility in water is 0,05 ppm. [11]

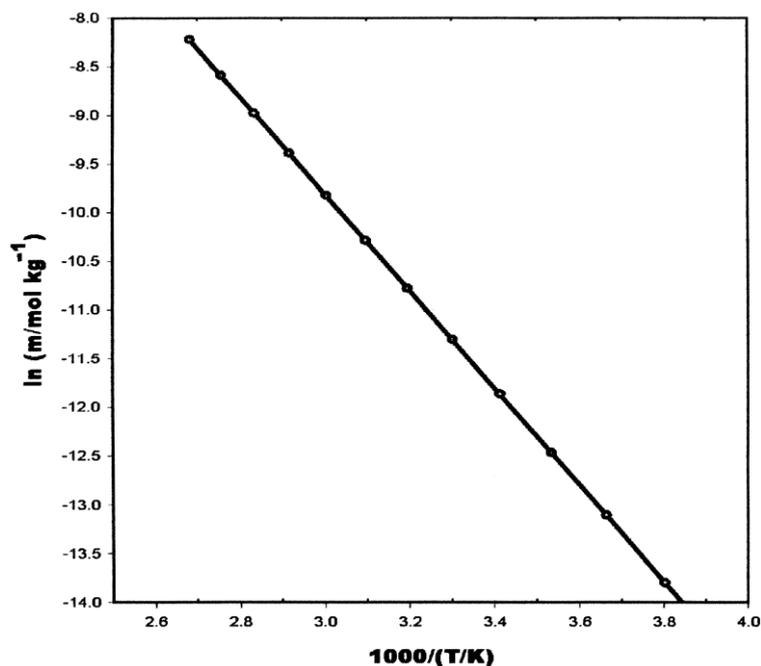


Figure 15. Solubility of elemental mercury in normal alkanes as a function of temperature [11]

Organic mercury compounds (R-Hg-R and R-Hg-Cl) are highly soluble in crude oil and gas condensate. Dialkylmercury compounds partition to hydrocarbon liquids according to their boiling points (table 9). Monomethylmercury halides partition preferentially to water.

Table 9. Boiling point of organic mercury compounds and elemental mercury [11]

Hg compound	Boiling point (°C)
Hg ⁰	357
(CH ₃) ₂ Hg	96
(C ₂ H ₅) ₂ Hg	170
(C ₃ H ₇) ₂ Hg	190
(C ₄ H ₉) ₂ Hg	206

Mercuric halides (HgCl) are about ten times more soluble than Hg⁰ in gas, condensate and oil. The degree to which HgCl distributes between water and the liquid hydrocarbon in primary separations depends on the salinity and pH.

Table 10. Solubility of some mercury compounds in hexane [11]

Species	Solubility (ppb)	Temperature (°C)
Hg ⁰	1,200	27,5
HgCl ₂	11,500	27,5
CH ₃ HgCl	>1,000,000	20
(CH ₃) ₂ Hg	∞	

There are other species like suspended mercury compounds and particularly HgS that is insoluble in water and oil.

Solubility of mercury in gases are very limited and often don't cover the ambient temperature range [12].

Vapor pressure of mercury compounds

In base of [11], figure 16 shows distinct data studies of vapor pressure of elemental mercury and organic mercury compounds as function of temperature.

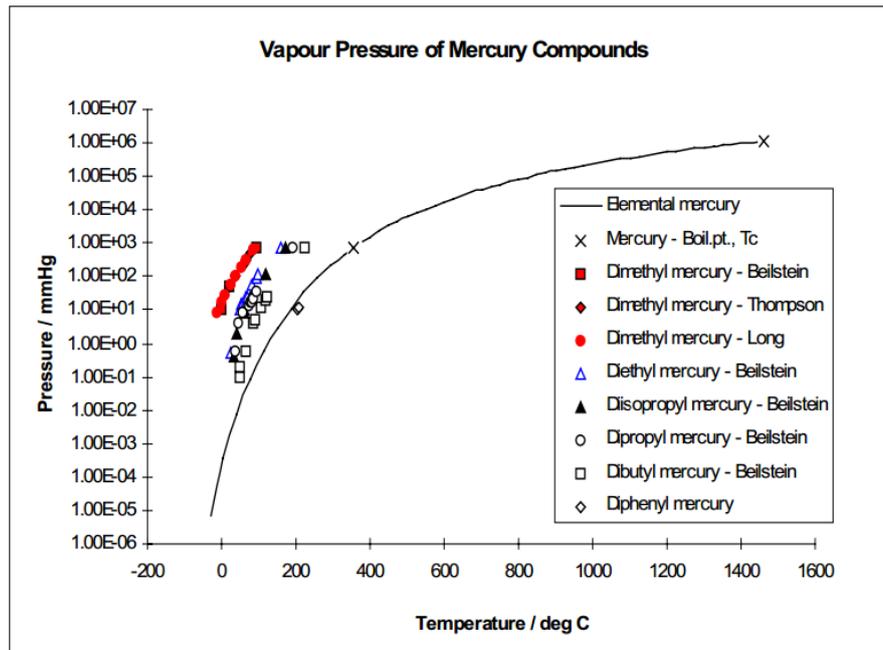


Figure 16. Vapour pressure of elemental and organic mercury compounds in function of the temperature [12]

Binary interaction parameters (k_{ij})

Binary interaction parameters are empirical factors used in EOS to calibrate the extent of non-ideality in a binary mixture. With this data, the prediction of the multicomponent phase equilibrium is more reliable.

Data for the solubility provide the suitable framework for fitting binary interaction parameters. According to [12] the BIP for RKSA of the mixture between mercury and alkanes appears in the figure 17.

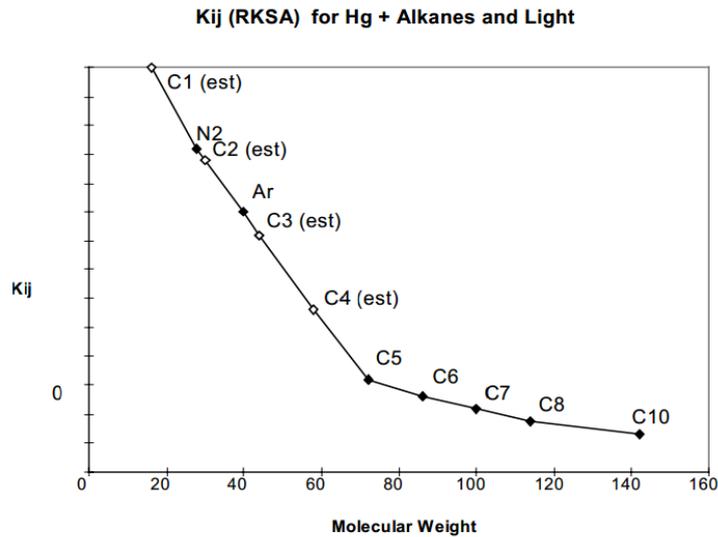


Figure 17. Binary interaction parameters for the mixture between mercury and alkanes as a function of molecular weight [12]

Figure 17 is extracted from [12] and in that source, the scale of binary interaction parameters doesn't appear.

It is important to observe that the solubility in any liquid hydrocarbons lighter than n-pentane have been estimated.

Results

According to [12] data described above is enough to build a model able to describe the mercury distribution in gas, oil and water.

In order to analyse the veracity of the results of the model, it is important to compare this results with the experimental data from the bibliography.

The following graphics shows the partitioning of mercury in three different situations:

- Partitioning between gas and condensate phases

Firstly, it is important to notice that for high mercury condensates without H₂S, there are two points with K values set arbitrarily to 10. These values are for cases where no mercury is detectable in the condensate so the true values could be much higher.

In condensates with a high proportion of H₂S, the K values are low because the gas phase mercury content is reduced by chemical reactions.

In general, the tendency followed by experimental data and the mathematical model is that K values increase as pressure falls. However, the experimental data that shows the opposite trend, being too low at low pressures. Despite this fact, predictions from the model appear reasonable when compared with the scattered experimental data. [12]

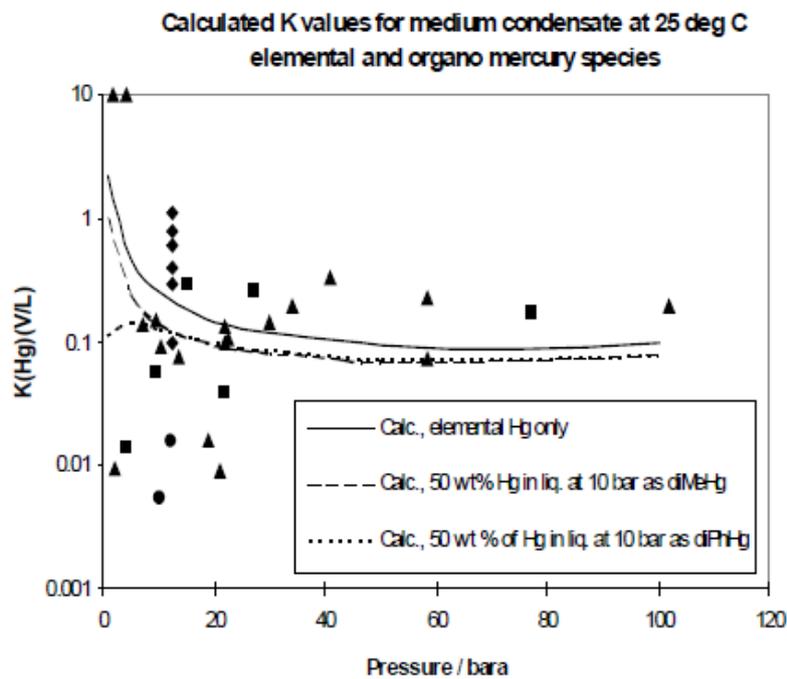


Figure 18. Vapor-liquid K values against pressure [12].

- Partitioning between gas phase and aqueous phase

Figure 19 shows the relationship between the vapour and aqueous phase. The calculations were performed for: elemental mercury, dimethylmercury, diphenylmercury, 50% elemental mercury + 50% diphenylmercury and 50% of elemental mercury + 50% of diphenylmercury.

The model represents the solubility of mercury and organomercury compounds in an aqueous phase.

It is observable, that the majority of curves are similar, except for the 50% elemental mercury + 50% diphenylmercury where the K values are lower. This behaviour is due to the insolubility of this mixture in the gas phase.

On the other hand, almost all the literature data fall below the predicted curves this probably indicates that other species are present in the water, such as suspended particles of mercury sulphide.

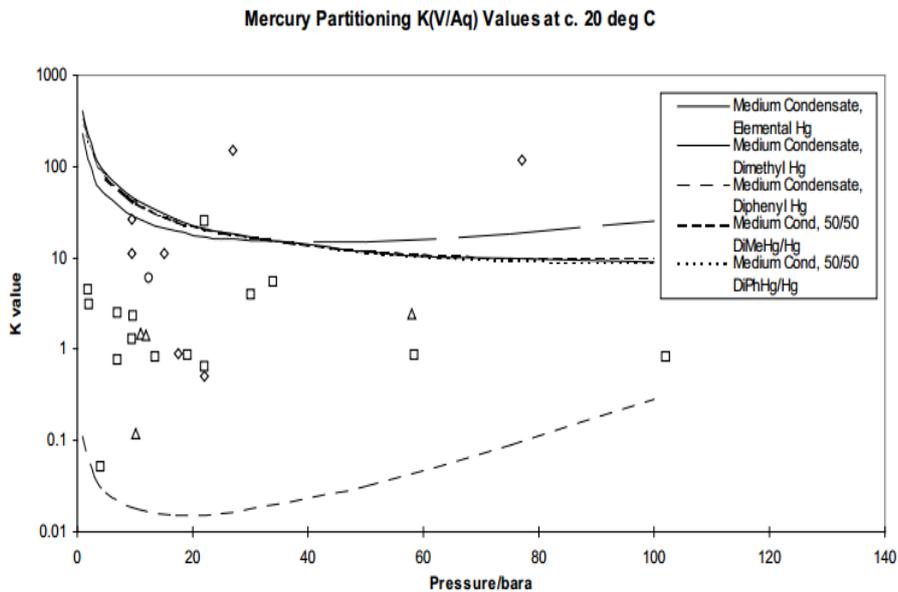


Figure 19. Vapor-aqueous K values against pressure [12].

- Partitioning between condensate phase and aqueous phase

Figure 20 presents elemental mercury and dimethylmercury data but not diphenylmercury data because is off scale.

As well as the last plot, the majority of experimental data is below the both curves. This seems to indicate that other mercury species are present in the aqueous phase.

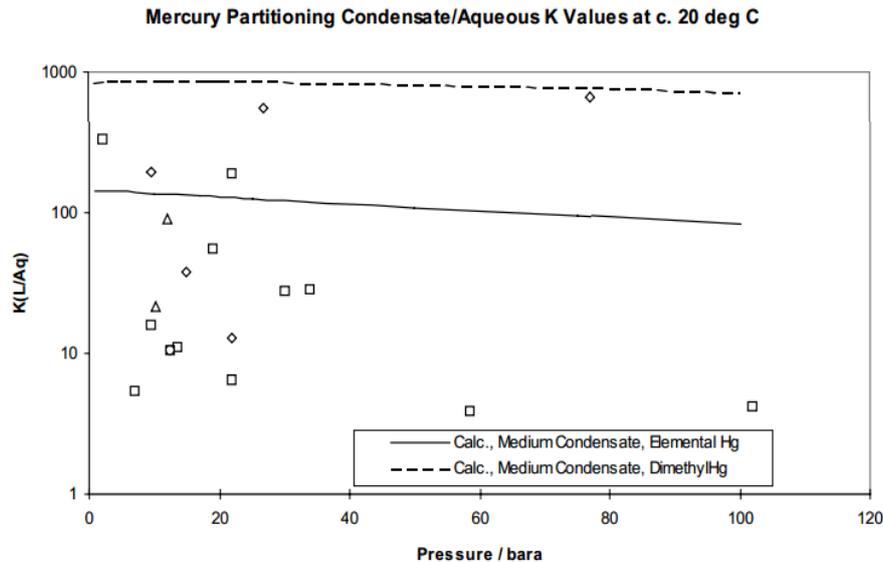


Figure 20. Condensate-aqueous K values against pressure [12].

According to [12] the general observations are:

- Condensate-aqueous K values are more sensitive to condensate composition than vapour-condensate and vapour-aqueous K values.
- Liquid phase mercury analysis is generally more reliable than gas phase analysis; observed condensate-aqueous K values should be of better quality than the corresponding vapour-aqueous K values.

Simulation using Honeywell Unisim Design R390

Honeywell Unisim Design R390 has been used to simulate the partitioning of mercury in gas, oil and water.

The simulation has been done following five different stages:

- 1) Definition of the composition of the crude oil
- 2) Justification of the fluid package used
- 3) Specification of the work conditions
- 4) Design of the separation system
- 5) Results

Definition of the composition of the crude oil

The composition of crude oil is defined according to [13]. The processing stream is a mixture of two streams:

- 60 wt % Reservoir oil stream: Composed by hydrocarbons, nitrogen and CO₂ (see table 11)
- 40 wt % Water and mercury stream (see table 12)

Table 11. Reservoir oil stream composition data [13]

Component	Mole fraction
Methane	0,330
Ethane	0,0622
Propane	0,0749
Isobutane	0,0117
N-butane	0,0304
Isopentane	0,0150
N-pentane	0,0231
N-hexane	0,0286
N-heptane	0,0403
N-octane	0,0428
N-nonane	0,0291
N-decane	0,2634
Nitrogen	0,0304
CO₂	0,0058

Table 12. Water and mercury stream composition.

Component	Mole fraction
Water	0,95
Mercury	0,05*

*Although mercury is present in trace levels in crude oil (the concentration moves from 0,5 to 5000 ng/g) I have decided to increase the amount of mercury in crude oil in order to observe easily the distribution in the different phases.

Justification of the fluid package used

Once defined the composition of the crude oil, is necessary to specify the mathematic model or the fluid package of the separation unit.

One method used to choose the more suitable fluid package is using the J.D. Seader tree diagram (figure 21)

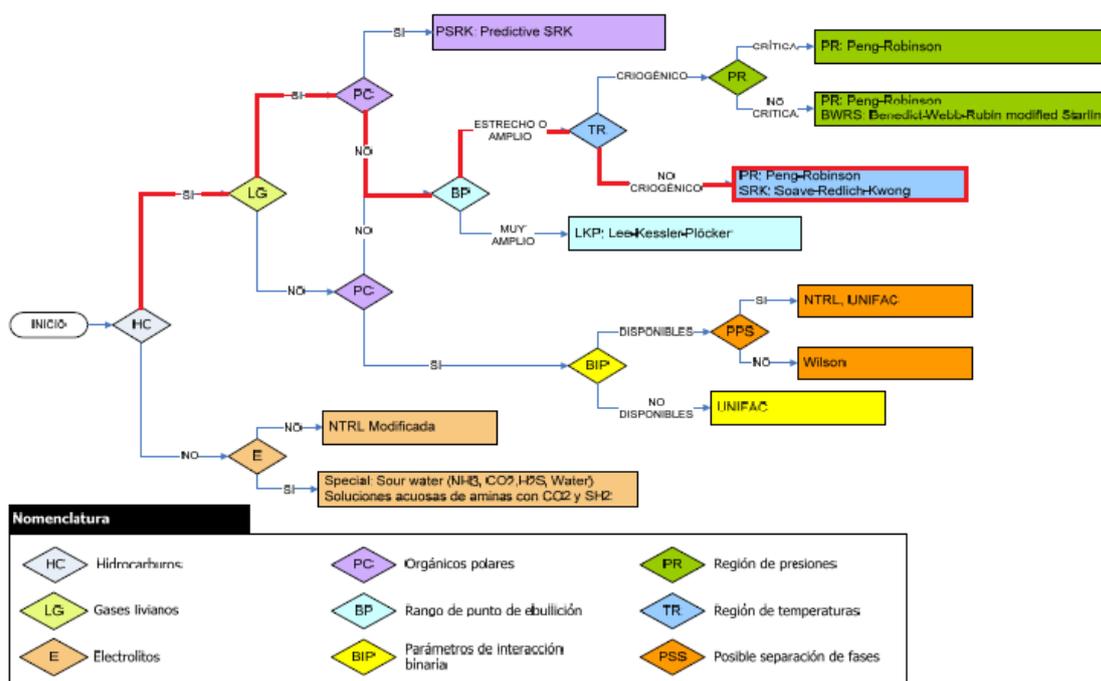


Figure 21. J.D. Seader tree diagram [14]

If the choice of the equation of state is not correct, then the results give it by the simulation won't be acceptable [15]

A priori could seem that, according to the figure 10, the more suitable equation of state would be Peng-Robinson because most of the components of the mixture are light gases, organic polar hydrocarbons and the region of temperatures are not cryogenic. However, if the final choice is using Peng-Robinson, the presence of mercury as a metal wouldn't be taken into account. Moreover, *Honeywell Unisim Design R390* gives an advice message informing that the fluid package is not a good option if mercury is one of the components of the mixture.

This is because Peng-Robinson is ideal for Vapor Liquid Equilibrium calculations as well as calculating liquid densities but it is not suitable for highly non-ideal systems as it occurs in this case [16]

The solution could be to make modifications to the original Peng-Robinson model to increase the range of applicability and to improve its predictions for some non-ideal systems.

These modifications haven't been done so the results obtained don't be reliable. The comparison between the results of [12] and the results of the simulation allow to distinct the veracity of them.

Specification of the work conditions

The specification of the work conditions (pressure and temperature) is summarized in table 13.

Table 13. Pressure and temperature conditions for the operational streams.

	Pressure (bar)	Temperature (°C)
Reservoir oil stream	10	50
Water + mercury stream	10	50
Process stream	10	50

The pressure and temperature conditions have been modified to observe the different mercury partitioning in oil, water and gas streams.

Design of the separation system

The separation system includes the following equipment:

- Mixer
- Cooler
- Three phase separator

The mixer combines reservoir oil stream and water and mercury stream to form the process stream. This stream passes through a cooler (E-102) in order to control the temperature inside the three phase separator. This equipment separates the process stream in three other currents (gas, oil and water).

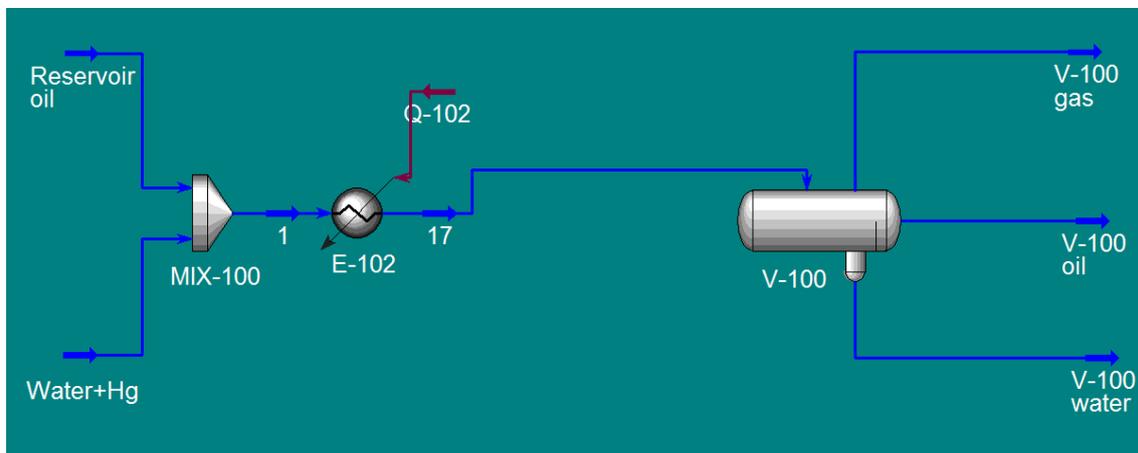


Figure 22. Simulation environment with Honeywell Unisim Design R390.

Results

Results obtained with *Honeywell Unisim Design R390* show the portioning of mercury in gas, oil and water streams (V-100 gas, V-100 oil and V-100 water) in function of the inlet temperature of the 3 phase separator and the arrival pressure of the mercury and water stream.

- Partitioning in function of the temperature

The temperature range has been varied from 20°C to 250°C and the evolution of the proportion of mercury in each phase shows in the figure 23, 24 and 25.

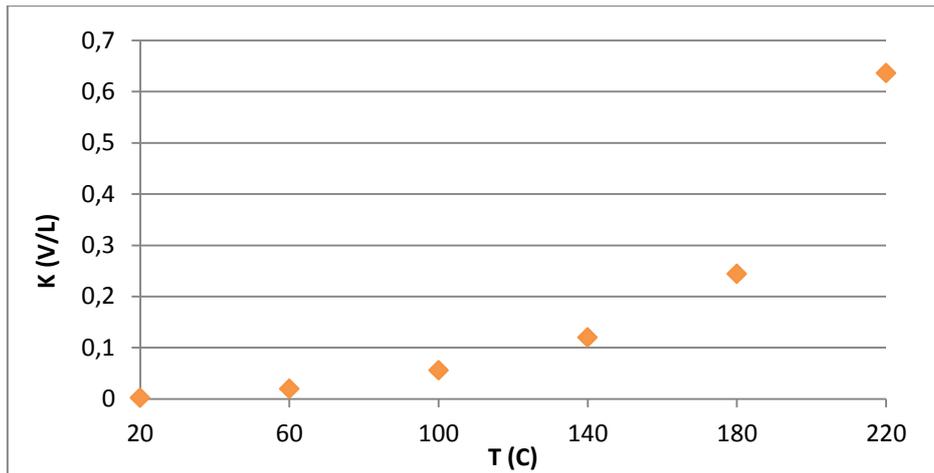


Figure 23. Gas/condensate mercury partitioning in function of the temperature.

According to figure 23, if the temperature increases the amount of mercury in the vapour phase rises. It is important to notice that the amount of mercury in vapour phase grow up at 40°C. In that moment, elemental mercury starts to vaporize.

The growth of mercury in the gas phase is very slow and although the temperatures are high, the majority of the mercury concentrates in the condensate.

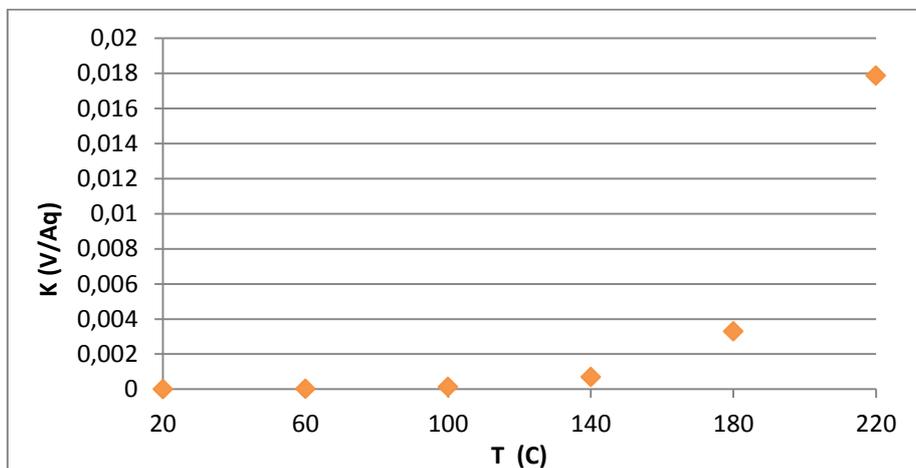


Figure 24. Gas/water mercury partitioning in function of the temperature.

The tendency followed by figure 25 data is similar to figure 24 data but the difference is that there is a high amount of mercury in the aqueous phase than in the condensate phase.

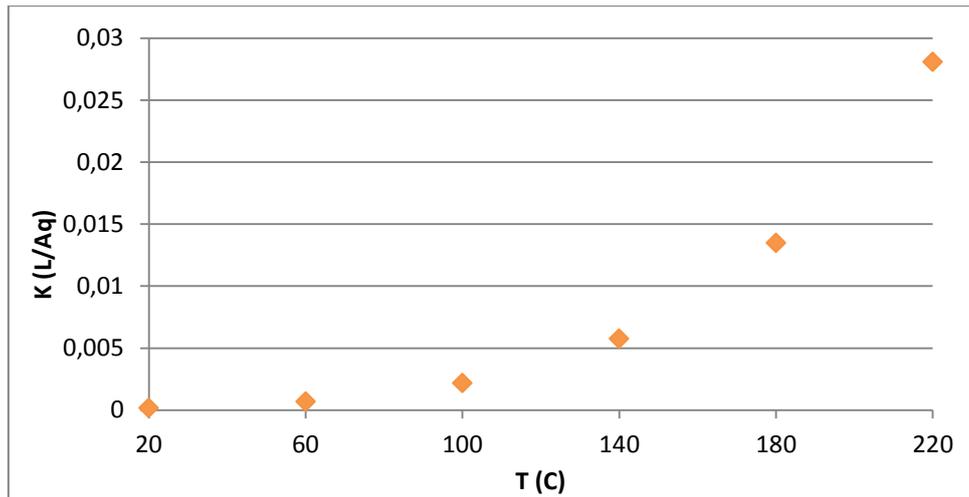


Figure 25. Condensate/water mercury partitioning in function of the temperature.

Figure 25 demonstrates that as well as the temperature increase, the quantity of mercury in the condensate rise. However, this growth is very slow and the majority of the mercury is present in the aqueous phase.

- Partitioning in function of the pressure

The amount of mercury in gas phase decrease when the pressure rises. According to figure 26, for pressures higher than 1 bar, the proportion of mercury in the liquid phase is larger than in the vapour phase.

K values are expected to increase as pressure falls because more mercury evaporates into the gas phase.

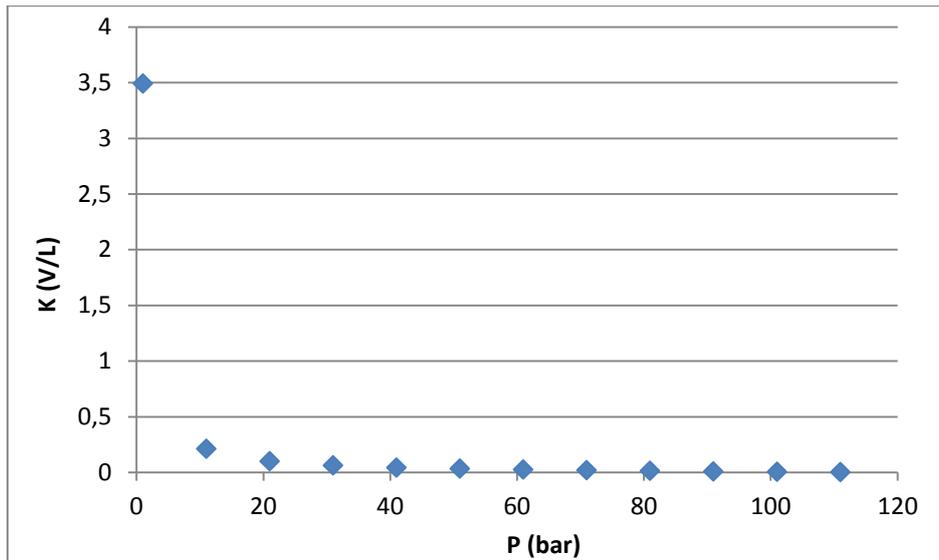


Figure 26. Vapour/condensate mercury partitioning in function of the pressure.

Low values of K means that the majority of the mercury is contained in the aqueous phase despite of the vapour phase.

Comparing figure 26 and figure 27, mercury mobility in vapour phase is higher in the condensate rather in the aqueous phase.

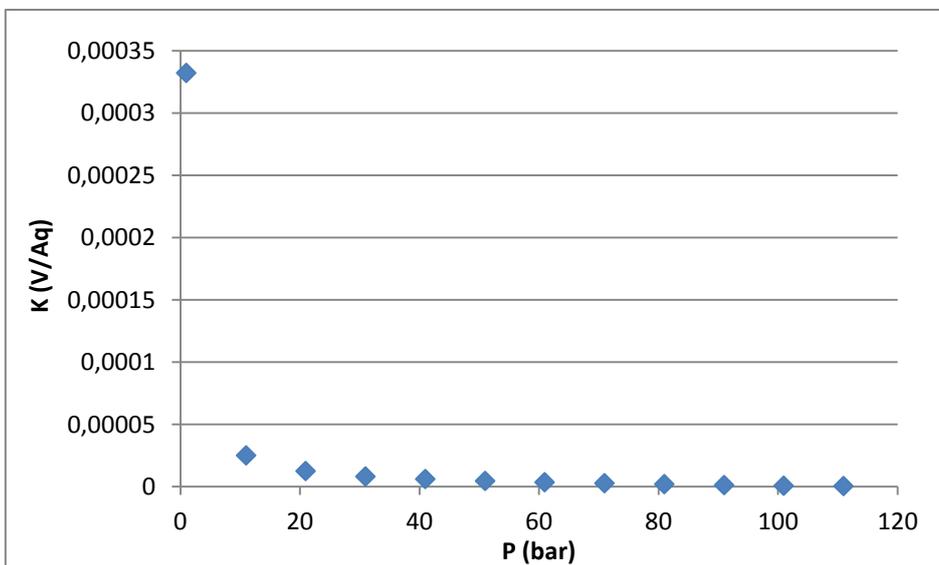


Figure 27. Vapor/aqueous mercury partitioning in function of the pressure.

Figure 28 shows that when the pressure increases, the proportion of mercury in the liquid phase rises. But this growth is very slow, so the mercury has low mobility from the liquid phase to the aqueous phase.

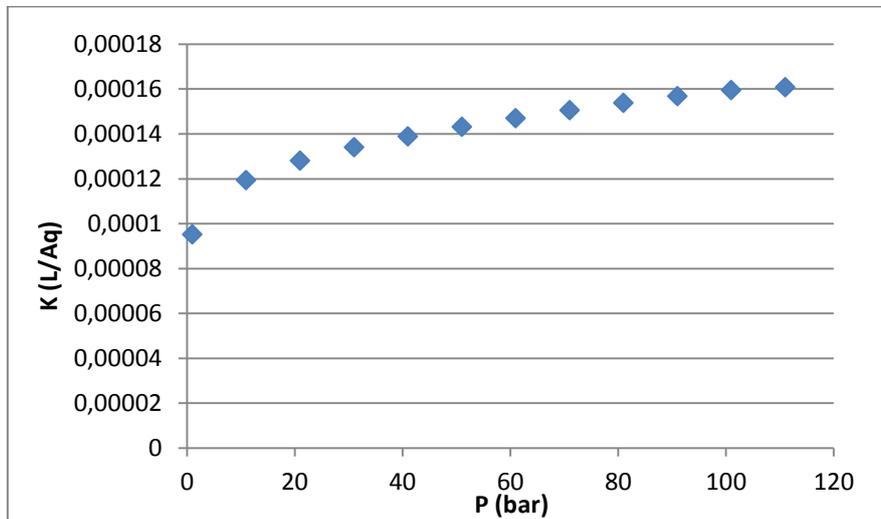


Figure 28. Condensate/aqueous mercury partitioning in function of the pressure.

Comparison of the two methods

The conclusions extracted with the *Honeywell Unisim Design R390* don't be reliable because of a bad choice of the fluid package so it is not possible to link both results.

However, the results obtained for the mercury partitioning between vapour-condensate phase, and mercury partitioning between vapour-aqueous phase have similarities with the results of [12].

The difference between the mercury partitioning in vapour-aqueous phase is the order of magnitude. In the simulation the K values are very low whereas in [12] K values are higher.

The distribution of mercury among the vapour-condensate phase follows similar tendencies in both cases.

The partitioning of mercury between condensate and aqueous phase can't be compared because while in the simulation K values increases with the pressure in [12] K decreases when the pressure rise.

Chapter 5: Material balance of the mercury in the UK refineries

The presence of mercury in crude oil and natural gas has a direct impact on the three different stages (extraction, transportation and processing) of the transformation of the raw material.

Release of mercury during the extraction

During crude oil and gas extraction mercury is released to the ocean in solid drill cuttings and produced water. Furthermore, the contaminant release to the atmosphere when natural gas is combusted to produce power.

Drilling process use the mineral barite (BaSO_4) to regulate the hydrostatic pressure in the well. In 2010, in UK, the total amount of mineral used was 29200 tonnes; its mercurial concentration was between 400 and 750 $\mu\text{g Hg/Kg}$ in consequence, the total amount of mercury extracted in the drilling process was 12-22 kg Hg. [7]

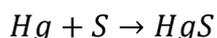
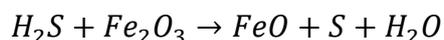
Produced water is removed during the primary separation of hydrocarbons into oil and gas streams. In 2009, in UK, the total volume of produced water discharged was 197 million m^3 , the concentration was 0,94 $\mu\text{g Hg/dm}^3$ so it means that the total amount of mercury extracted from the produced water was 186 kg. [7]

Gas flaring is the burning of unwanted gas at the production platform to remove waste gas that is not economical. In 2009, in UK, the total volume of flared gas was 1,3 billion m^3 , the concentration was 1 $\mu\text{g Hg/dm}^3$ so the quantity of mercury was 1,3 kg. [7]

Oil and gas platforms produce their own power using as a combustible the gas from the wells. This gas is not treated so the amount of mercury that releases is higher than the gas combusted after the refining. In 2009 in UK, the total volume of untreated gas used to supply energy to the platform was 5,6 billion m^3 ; again, the concentration was 1 $\mu\text{g Hg/dm}^3$ so the quantity of mercury was 5,6 kg.

Release of mercury during the transportation

According to recent studies, mercury from oil and natural gas reacts with metal surfaces such as steel pipelines, container walls and pipes. This reaction is catalysed by the presence of H₂S in trace quantities and driven by the following reactions: [7]



Mercury absorbs up to 1mm across the whole pipeline system, it means that the total amount of contaminant in UK pipelines is up to 207 kg. [7]

On the other hand, there is amount of mercury that removes via “pigging” but the quantities are very small compared with pipelines chemisorption.

Release of mercury during the process

Crude oil

Generally, crude oil refining is based on separate crude oil into product streams of different density, which are then treated and cleaned to saleable products.

The refinement of crude oil generates three waste streams: atmospheric, solid and liquid waste. The quantity of mercury distributed in each stream shows in table 14. [7]

Table 14. Release of mercury during the crude oil refining [7]

	Percentatge	Kg Hg/year
Wastewater	0,4-3%	1,1-25
Atmospheric emissions	8-23%	22-190
Solid waste	15-79%	41-650
Refined products	13-58%	35-480

Furthermore, in the refining process there is an additional release due to the combustion of the products occurs on the refineries. So, according to a 2008

UK National Atmospheric Emissions Inventory study, 500 kg of mercury release to the atmosphere proceeding from fuels from refineries. [7]

Natural gas

Natural gas processing is more simply than crude oil processing because only treats and separates the raw material into saleable products without using any molecular transformation.

Gas processing is summarized in the following steps [7]:

- 1) Water removal using TEG or molecular sieve absorbents.
- 2) Gas cleans through acid gas scrubbers.
- 3) Gas treats in a cryogenic distillation, based on cooling the gas in an aluminium exchanger and then heats it progressively, allowing the individual products to be boiled off and separated in towers.
- 4) The liquid product streams are sent to petrochemical manufacturers or sold as LPG.

The most important losses associated with natural gas processing come from dryers and acid gas scrubbers.

The majority of mercury concentrates in vented and flared gas from the heat exchangers and there is a small amount of mercury concentrated in glycol. [7]

Mercury that enters in a gas processing plant distributes in the different stages of the process as it shows the table 15.

Table 15. Release of mercury during the natural gas processing [7]

	Kg Hg/year	Percentage
Acid Removal Vent	22	10%
Dryer Vent	3	1,4%
Condensate	45	20,5%
Sales Gas	150	68%

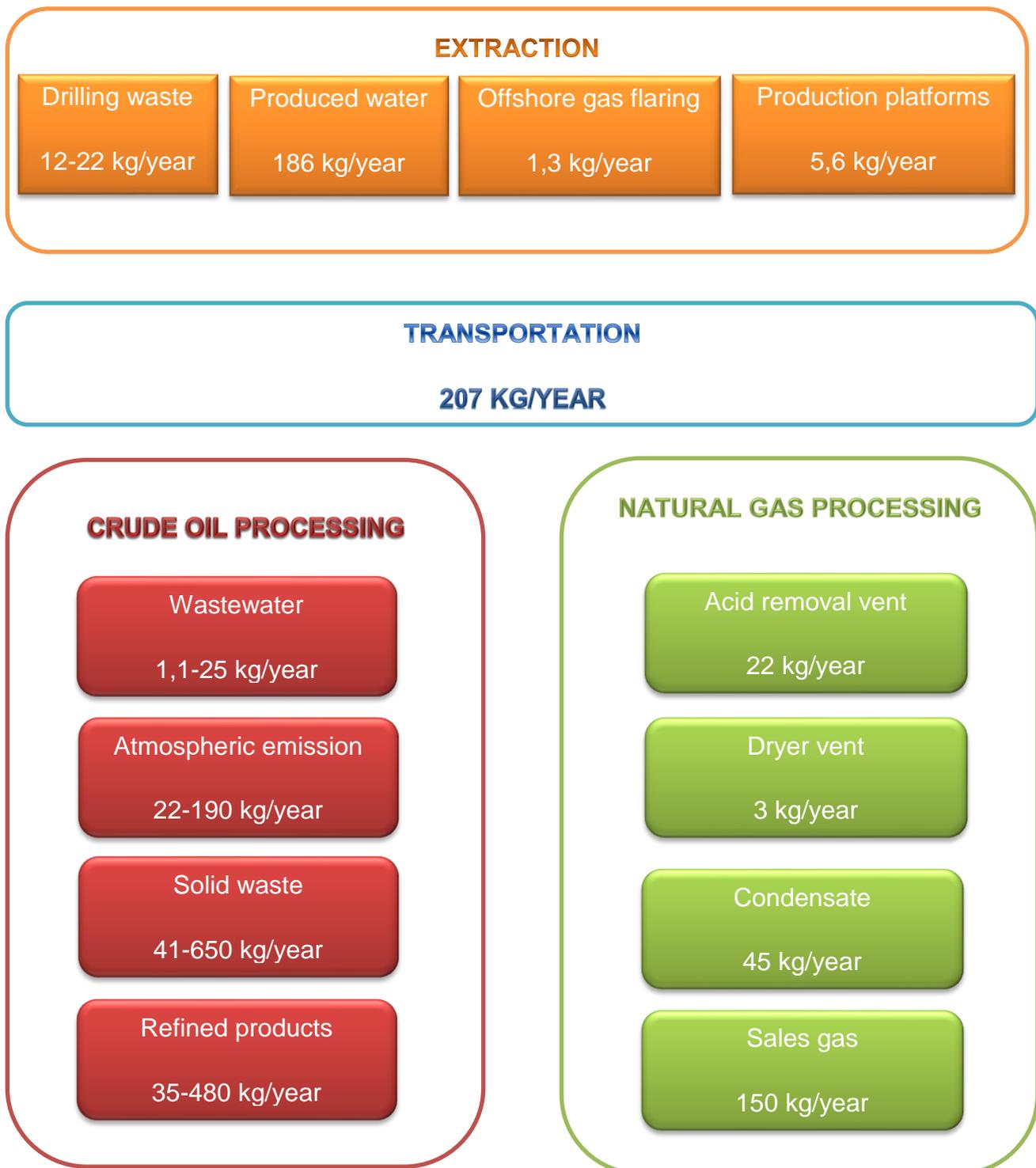


Figure 29. Amount of annual mercury in the different stages of crude oil and natural gas processing

To summarize the chapter, figure 30 shows the mercury release in the different stages of the extraction and processing of crude oil and natural gas.

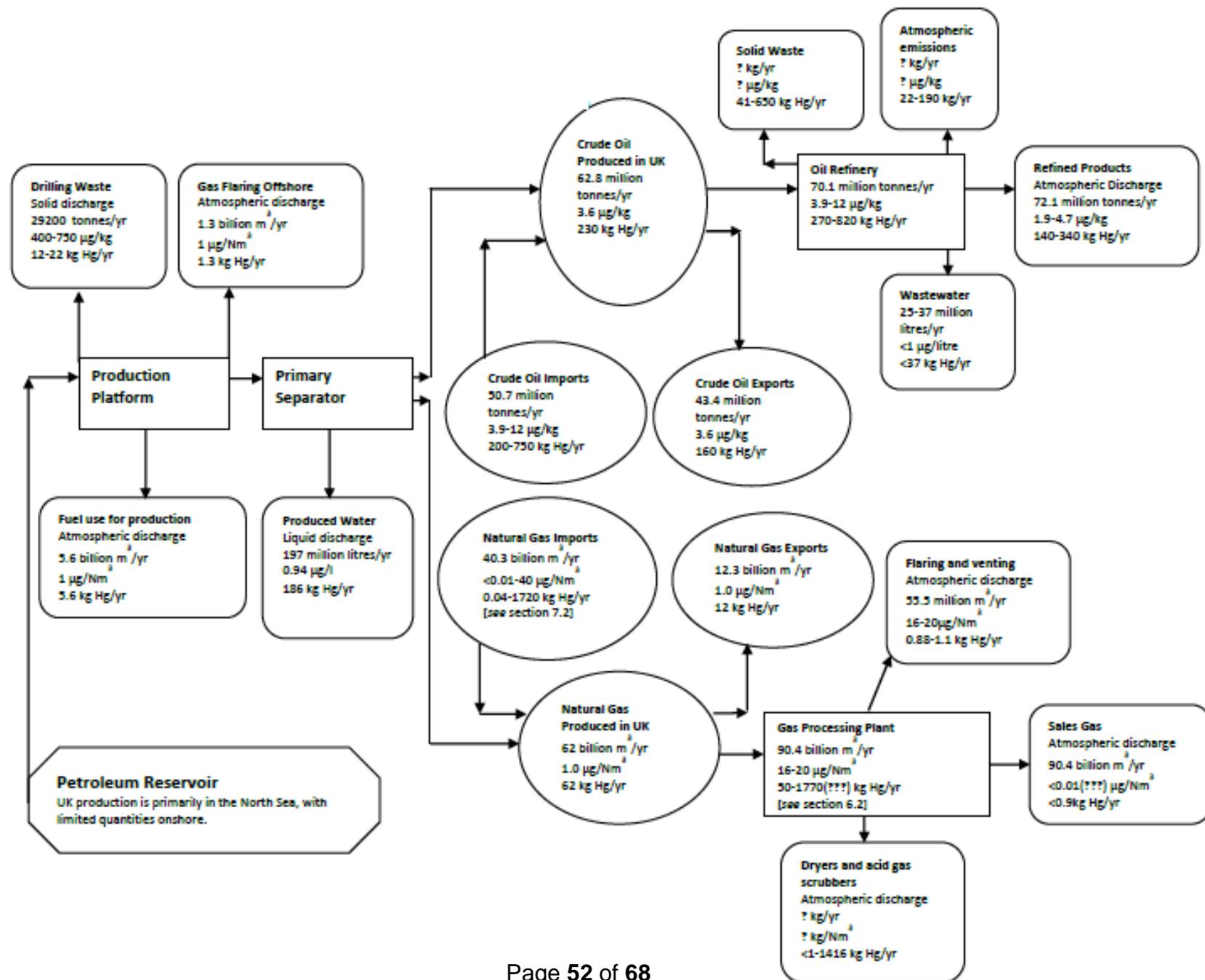


Figure 30. Mercury release in the processing of gas natural and crude oil [7]

Chapter 6: Impacts of mercury

The main impact of the mercury concentrates in three different fields:

- Processing operations impacts
- Health impacts
- Environmental impacts

Processing operation impacts

The main impacts in processing operations according to [11] are:

- Mercury deposits in cryogenic equipment causing cracking of welded aluminium heat exchangers.
- Gas plants products used for chemical manufacture such as olefins, ethylene, aromatics and MTBE are at risk in process feeds due to equipment problems and catalyst poisoning.
- Mercury contaminates treatment processes such as molecular sieve and glycol dehydration units and amine acid gas removal systems.
- Mercury sorbent materials used for gas or liquid treatment constitute a hazardous waste that plant operators must store or process for disposal.
- Mercury deposition in equipment is a health and safety risk for workers involved in maintenance or inspection activities.
- Sludge containing mercury from water treatment systems, separators, desalters and heat exchangers represents a toxic waste stream that is difficult to store or process for disposal.
- Waste water streams that contain high levels of mercury must be treated to remove mercury prior to discharge thus adding significant costs to plant operational expense.

Health impacts

The pathways which mercury could introduce inside of the body are due to inhalation, ingestion or dermal adsorption. [17]

The impacts of the mercury are different in function of the exposure time so, short term exposure to high concentrations of mercury vapours causes harmful effects on the nervous, digestive, renal and respiratory systems whereas for

chronicle exposures results in psychological anomalies, physical symptoms and diseases related with the nervous system such as arrhythmias, cardiomyopathies, kidney damage, loss of memory, excitability or fever. [17]

In the industry, the most common locations for elemental mercury accumulation are separators, heat exchangers and inside the vessels. Furthermore, accumulation mechanisms include adsorption on equipment surfaces and dissolution in sludge. [11]

Organic mercury compounds are more toxic than their elemental form. They have been implicated in causing brain and liver damage.

Dialkylmercury, for example, is many times more toxic than elemental mercury. However, their effects are uncertain because of lack of data on dermal absorption efficiency and the lack of data of prevalent concentrations. This contaminant is less likely to enter via respiratory ways than elemental mercury. However, there are more probabilities to be absorbed by the skin because of the lipid solubility. [11]

Methylmercury accumulates in the tissues of tuna or swordfish. The period between exposure to methylmercury and the appearance of symptoms in adult poisoning cases is long but when the symptoms appears, it is followed rapidly by more severe effects, sometimes ending in coma and death.

Inorganic mercury occurs as salts such as mercury (II) chloride. This contaminant affects the gastrointestinal system and the kidneys but it is not able to cross the blood-brain barrier easily. Its solubility in water is very high; it is for this reason that is easily absorbed by the gastrointestinal tract. [18]

Environmental impacts

The main environmental impact of mercury is its ability to build up in the organisms and up along the food chain. Although all forms of mercury can accumulate to some degree, methylmercury is absorbed and accumulates to a greater extent than other forms. Inorganic mercury can also be absorbed, but is generally taken up at a slower rate and with lower efficiency than is methylmercury. [19]

There are two terms that have a great impact on animals and humans:

- **Bioaccumulation:** The net accumulation over time of metals within an organism from both biotic (other organisms) and abiotic (soil, air, and water) sources [19]
- **Biomagnification:** The progressive build up of some heavy metals (and some other persistent substances) by successive trophic levels – meaning that it relates to the concentration ratio in a tissue of a predator organism as compared to that in its prey. [19]

Mercury is responsible for a reduction of micro-biological activity vital to the terrestrial food chain. The critical limits to prevent ecological effects have been set at 0,07-0,3 mg/Kg for the total mercury content in soil. [20]

Many governments and private groups have made efforts to regulate heavily the use of mercury, or to issue advisories about its use. Unfortunately there is no regulation in mercury concentration for oil and gas industries. Moreover, there are no limitations on the presence of highly mercury species such as organomercury species, either in the oil or gas production industries. [21]

Table 16 summarizes the maximum amount of mercury species allowed for regulating agencies in the different mediums.

Table 16. Maximum amount of mercury species allowed for regulating agencies [21]

Regulating agency	Medium	Mercury compound	Limit
Occupational safety and health administration	Air	Elemental mercury	$\leq 0,1 \text{ mg/m}^3$
Occupational safety and health administration	Air	Organic mercury	$\leq 0,05 \text{ mg/m}^3$
Food and drug administration	Sea food	Methylmercury	$\leq 1 \text{ ppm}$
Environmental protection agency	Water	Inorganic mercury	$\leq 2 \text{ ppb}$

Chapter 7: Technologies to mitigate the impact

There are different kind of technologies used to remove Hg for oil and natural gas. The most used is the adsorbent technology. However, other technologies, like precipitation, chemical oxidation, ion exchange, incineration and solidification have good removal efficiency.

Precipitation process

One of the most effective techniques to remove mercury from water (not gas and oil) is precipitation.

In this method, mercury ions in solutions can be precipitated easily using hydrogen sulfide or alkali metal sulfides salts (e.g: sodium sulfide or other sulfide salt). These last components are added to the wastestream to convert the soluble mercury to the relatively insoluble mercury sulfide form through the following reaction [22]:

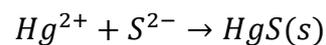


Figure 31 shows a typical process flow diagram for sulfide precipitation. The process is usually combined with pH adjustment and flocculation, followed by solids separation.

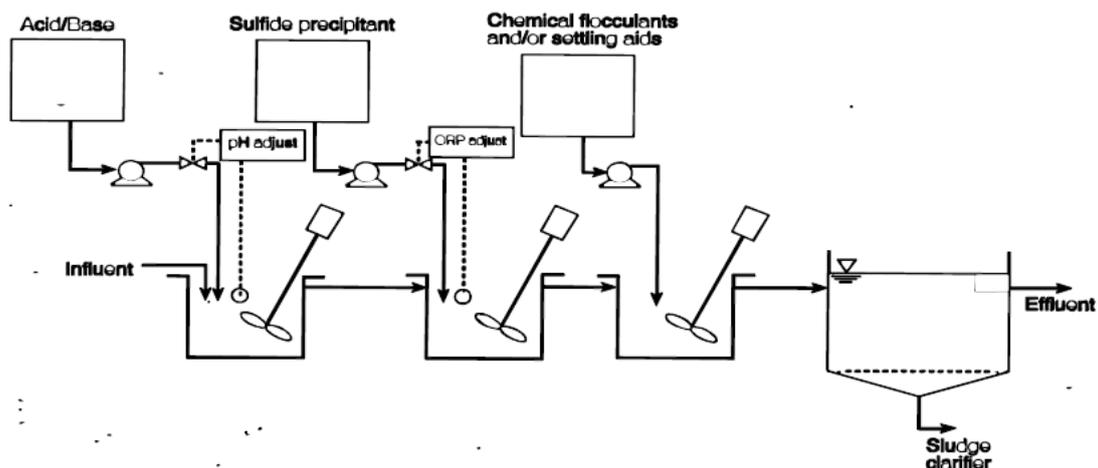


Figure 31. Sulfide precipitation process [22].

The main advantage of this technology is its high efficiency that varies from 95 to 99,9% and its low economic cost due to the sludge management. However, there are different drawbacks to take into account, as for example: the sludge

contains stockpiles of mercury-laden that can resolubilize under conditions that can exist in landfills in consequence; more leaching tests should be done. [22]

Adsorbent technology

One of the most effective tools to remove mercury from oil and natural gas based on adsorbent technology is the use of sorbent beds. They are used to remove mercury from liquids and gases. [25]

A sorbent bed is the union between a substrate support (zeolite, activated carbon, metal oxide or alumina) and a reactant (sulfur, metal sulfide, and iodide). It is important to control the size of porous of the substrate support in order to avoid the adsorption of high molecular weight hydrocarbons. [25]

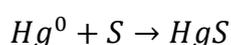
When the mercury and mercury compounds adsorbs physically by the sorbent bed, the metal reacts with the reactive component to form a complex (HgS, HgI₂ or amalgam) chemically inert to the components of process stream. [25]

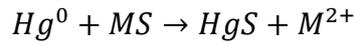
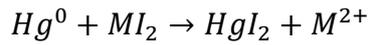
Nowadays, there are several commercial mercury removal technologies available in the market. Some are targeted to remove mercury from a gaseous stream whereas others are destined to separate this metal from a liquid (table 17).

Table 17. Mercury sorbent technologies [25]

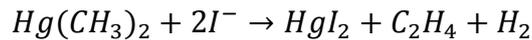
Substrate	Reactant	Complex	Application
Sulfur	Carbon	HgS	Gas (Hg ⁰)
Metal Sulfide	Alumina	HgS	Gas (Hg ⁰)
Iodide	Carbon	HgI ₂	Gas/liquid
Iodide	Alumina	HgI ₂	Liquid

The reactions taking place in the different adsorbent technologies and targeted on gas streams polluted by elemental mercury (Hg⁰), are based on the following reactions [25]:

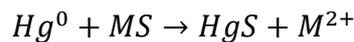
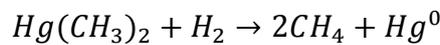




If the contaminant stream contains organic mercury (for example: $Hg(CH_3)_2$ normally liquids) then metal sulfides or sulfur on carbon will not scavenge organic mercury. In this case, the using of iodide as a substrate give very good results [25]:



An other effectiveness method is based on two step process based on an hydrogenation and a metal sulfide reaction [25].

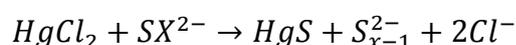
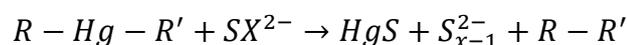
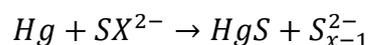


In general, the choice of substrate and the reactant depends on many factors such as: the composition of inlet feeds, the desired bed life, the process design and numerous economic considerations.

However, according to the studies made by Tsoung [23], a new efective process have been developed to remove all kinds of mercury (organic and inorganic).

This technology is based on the combination of solvent extraction and solid adsorption.

In this method, polysulfide converts all Hg compounds to HgS. This last component is easily formed in inorganic Hg and elemental Hg because it reacts with sulfur. However, the problem is that organic mercury is too stable to react with sulfur so, in order to form HgS (an insoluble and innocuous compound) it uses a polysulfide solution able to react with all Hg compounds. [23]



The reactions are based on keep in touch an aqueous phase that contains polysulfides and oil phases that contains mercury compounds. The two phases contact each other by centrifugal pumps and mixers. [23]

There is a high interfacial tension between oil and aqueous phase that complicates the mixing. However, by heating, the interfacial tension decreases and the two phases become miscible. [23]

Activated carbon offers a high surface area that concentrates mercury compounds and polysulfide facilitating the reaction. Furthermore, this material is very effective to separate the excess of water that difficulties the cooling.

This method is composed by [23]:

- a. Reactor
- b. Product/feed heat exchanger
- c. Feed heat exchanger
- d. Make-up solution tank
- e. Chemical feeding pump
- f. Solenoid valve

The reactor is filled with activated carbon and polysulfide solution. Then, the condensate feed, previously heated at 70°C enters to the reactor from the bottom and rises through the bed of aqueous phase to react with polysulfide. Finally, the interphase between the oil and aqueous maintains at desire level by using a solenoid valve. [23]

By using this technique, the mercury content could be reduced from 3000 to 10 ppb. It represents over 99,7% of mercury removal. [23]

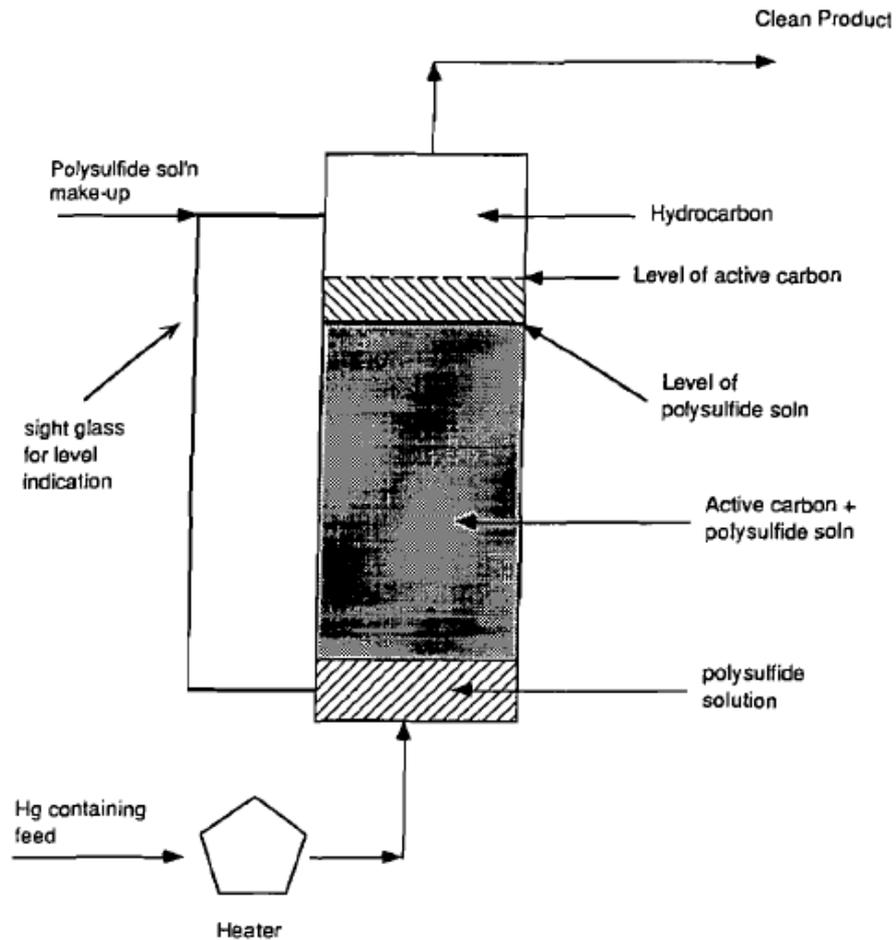


Figure 32. Activated carbon column for mercury adsorption.

The columns could adopt different design configurations as it shows in Figure 33 [22]

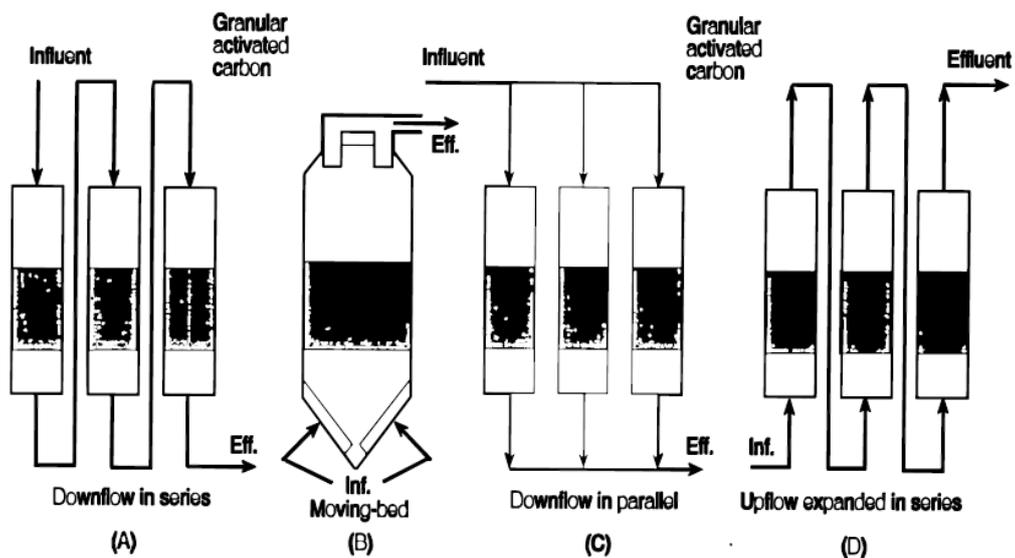


Figure 33. Different design configurations for adsorption columns [22]

Ion exchange treatment

Ion exchange techniques are used in water purification processes to clean up cations and anions.

Referring to [22], ion exchange treatment is a technology that operates in a packed column in four operation steps:

- 1) Service: The water containing mercury to be removed is introduced into the packed column.
- 2) Backwash: The bed expands and it removes fines that may be clogging the packed bed.
- 3) Regeneration: A concentrated solution of the original exchange ion pass throughout the bed and a revers change process occurs.
- 4) Rinse: Removes excess regeneration solution before the column.

Ion exchange treatment only uses when the concentration of mercury in the effluent is very low (from 1 to 10 ppb) and when the removal mercury is in form of anionic complexes. [22]

The majority of the anion exchange resins are composed by thiol. This function group has a high selectivity for mercury as well as a strong tendency to bind certain other metal ions such as copper, silver, cadmium, and lead. [22]

Immobilization

Different mercury immobilization technologies may be divided into the following two categories, stabilization and amalgamation.

Stabilization

According to [24], stabilization involves different steps:

- 1) The large mercury globules break providing a greater surface area.
- 2) A chemical reagent is added to produce mercury oxides or mercury sulfides
- 3) The reagent is mixed throughout the contaminated materials and there is an addition of cement.

- 4) The mercury oxides or sulfides are trapped in the cement mass, that reduce the mobility of mercury.

The main advantage of this technology is that it produces more stable mercury compounds. However, do not reduce total mercury concentration and the volume of the contaminated materials increase.

Amalgamation

Amalgamation is a physical immobilization technology where metals form a semisolid alloy with mercury. Mercury dissolves in the solid metal, forming a solid solution. [22]

Solidification improves the engineering properties of the materials and permeability, and it is for this reason that the release of contaminants from a solidified block can be reduced.

The main advantage is that a solid shape, allows manage, store and dispose the material easily. This process is not reversible so the use of additives is necessary. [22]

There are several metals able to form a semisolid alloy with mercury such as: tin, zinc, copper, sulfur and sulfur polymer cement. [22]

Thermal process

By heating mercury compounds, they volatilize to elemental mercury vapor. A thermal treatment can be viewed as a distillation process in which mercury vapor is condensed and collected in a relatively pure form.

There are several thermal processes, each one differentiates from the other in function of: the feed (batch or continuous), the energy input (gas fired or electric) and process carrier gas (inert gas, vacuum, oxidizing gas). [25]

The objective is to heat complex mixture containing mercury and/or mercury compounds to produce an inorganic solid residue containing less than 2 ppm Hg while simultaneously condensing elemental mercury separate from sulfur and hydrocarbons. [25]

Figure 34 shows a batch thermal process to remove mercury from soils. [25]

This method is based on:

- 1) A furnace vaporizes the mercury.
- 2) The mercury is condensed.
- 3) The vapor comes from the condenser heat and the results are the volatilization of: water vapor, hydrocarbons and a huge amount of mercury-containing portion.
- 4) A second heater is employed to vaporize the mercury containing portion.
- 5) An addition of metallic salts adds to the activated carbon bed. They react with elemental mercury to form a complex chemically inert.

With this method, the contaminant material is converted from one which is hazardous to one which is non-hazardous.

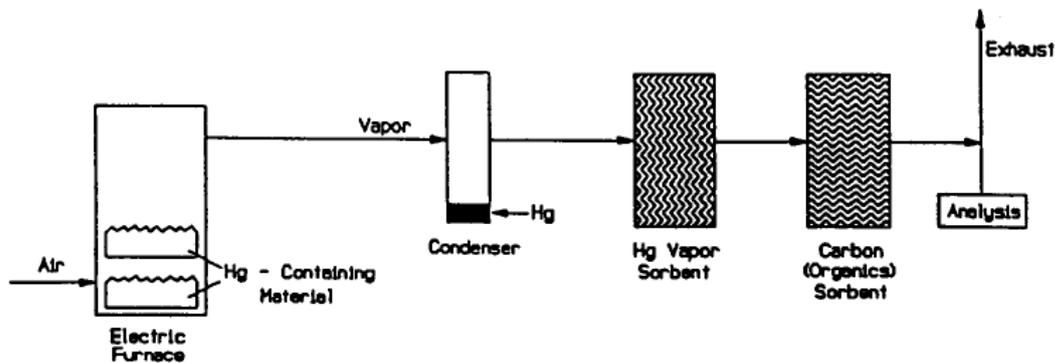


Figure 34. Batch thermal process to remove mercury from soils [25].

The main advantage of this removal system is that batch feeding is more portable than continuous whereas the major limitation is that are best suited for small to medium volumes of contaminated material based on economic considerations.

Thermal processes have some disadvantages as for example: the requirement of additional fuel, the maintenance of combustion temperature, the possibility of the appearance of other contaminants and their subsequent treatment for recovery.

Chemical reduction

Ionic mercury can be reduced in solution by other metals higher in the electromotive series and then separated by filtration or other solids separation techniques. Reducing agents include aluminum, zinc, iron, hydrazine, stannous chloride, and sodium borohydride. [22]

The major disadvantage of this process is that the residual mercury concentration after reduction is too high and probably requires a second-stage polishing. [22]

Chemical oxidation

This method is applied to convert elemental mercury and organomercury compounds to a soluble form, such as HgCl_2 or HgI_2 . These soluble forms can then be separated from the fluid and subsequently treated. Oxidising reagents used include sodium hypochlorite, ozone, hydrogen peroxide, chlorine dioxide and free chlorine plus other proprietary reagents. [22]

Biological treatment

Certain bacteria and plants are able to assimilate, accumulate mercury or convert from one type of mercury to another [26] [27].

There are two kinds of bacteria. The first one, convert soluble ionic mercury into elemental mercury whereas the second kind, utilize another detoxification mechanism to convert ionic mercury to methylmercury. This last component can be biologically converted to either dimethylmercury or to elemental mercury and methane. [22]

Different studies prove the existence of bacteria (*Escherichia coli*) that have been genetically engineered to take up mercury. Pilots tests demonstrate that this bacteria is capable of consuming 99,75% of the mercury in a solution containing 2 mg/L. [22]

Conclusions

The content of mercury in crude oil and natural gas is a present problem in all the refineries. The main impacts are related with its high toxicity and noxiousness and affect the process operations and the health of the operators. Although its relevance, there are few investigations that go into the detail of the question. In fact, this is because mercury is present into the crude oil and natural gas in trace levels and until now, these amounts hadn't considered detrimental for the refining process.

However, the tightening of the environmental and health laws and the optimization of the efficiency of oil and gas plants has converted this topic in one of the main concerns for process engineers.

According to the objectives considered on the introduction, the conclusions reached are:

- Mercury is a metal present in four different chemical forms: elemental mercury, organic mercury, inorganic salts and complexed mercury that is present in crude oil and natural gas in low concentrations (Between 0,1 and 20.000 $\mu\text{g}/\text{kg}$ in crude oil and between 0,05 and 5000 $\mu\text{g}/\text{Nm}^3$ in natural gas)
- In order to develop a model able to predict the partitioning of mercury in gas, oil and aqueous phase is necessary: a suitable equation of state according to the composition of the mixture, the solubility of mercury and their species in alkanes, vapor pressures of the mercury compounds and binary interaction parameters.
- According to the model analysed:
 - K values of mercury in vapor phase against aqueous and condensate phase are low when the pressure drops. This means that for low pressures and ambient temperature, the majority of the mercury remains in the aqueous or in the condensate phase and when the pressure increases the contaminant mobilizes to the gas phase.

- K values of mercury in condensate phase against aqueous phase shows that the proportion of mercury in the aqueous phase increase when the pressure rises.
- The simulation performed by *Honeywell Unisim Design R390* doesn't have reliable results because of a bad choice of the fluid package used.
- The presence of mercury in crude oil and natural gas has different impacts in the processing operations, the environment and the operator's health.
- Technologies used to remove mercury from crude oil and natural gas are based on: precipitation processes, adsorption, ion exchange treatments, chemical oxidation, chemical reduction, immobilization and biological processes.

In order to improve the results of the thesis would be interesting to make the simulation with the suitable fluid package. This would be a very powerful tool able to predict a wide variety of scenarios.

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