ENVIRONMENTAL REVIEW
OF PETROLEUM INDUSTRY
EFFLUENTS ANALYSIS

Claire Faustine

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Abstract

The present report deals with environmental issues in refineries and petrochemical processes. More precisely gaseous, liquid and solid effluents from processes are analysed qualitatively and quantitatively when possible. Techniques to treat these effluents are reviewed or proposed when lacking and methods to do not produce these effluents are envisaged.

In the part A of the report general effluents that are released from all types of processes are studied. These effluents include fugitive emissions, flue gases from process heaters, blowdown systems emissions and wastewaters. Fugitive emissions, one of the greatest sources of VOCs can be qualified and quantified by the average emission factor approach and reduced thanks to the implementation of an LDAR program. Flue gases from process heaters, which are a major source of NOx, SOx and particulate matters can be characterized with emission factors and several techniques exist to treat or prevent these emissions. Concerning blowdown systems emissions, which are difficult to quantify, methods to minimize these emissions are given. Finally, wastewaters treatment in petroleum industry is shortly described before best management practices and pollution prevention methods are enounced.

In the part B of the report four families of processes are studied: naphtha hydrotreatment, naphtha isomerization, catalytic reforming and hydrogenation in olefin plants. Each of these processes is firstly described, the process flow diagram is explained and continuous and intermittent effluents are characterized. In addition to general effluents dealt with in part A, it has been found that processes can produce other effluents such as dioxins in isomerization or catalytic reforming units or green oils during catalyst regeneration operations.
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List of Acronyms

API- American Petroleum Institute
BOOS- Burner Out Of Service
CCR- Continuous Catalytic Reforming
CO- Carbon Monoxide
CO2- Carbon Dioxide
DMDS- Dimethyl Disulfur
EPA- United States Environmental Protection Agency
ETBE- Ethyl Tertiary-Butyl Ether
FCC- Fluid Catalytic Cracking
FG- Fuel Gas
FGR- Flue Gas Recirculation
FO- Fuel Oil
GHU- Gasoline Hydrogenation Unit
HAP- Hazardous Air Pollutant
HC- Hydrocarbon
LDAR- Leak Detection And Repair
LEA- Low Excess Air
LNB- Low NOx Burner
LPG- Liquefied Petroleum Gas
MA- Methyl Acetylene
MTBE- Methyl Tertiary-Butyl Ether
NOx- Nitrogen Oxide
NO2- Nitrogen dioxide
OFA- Over Fire Air
PD- Propadiene
PCDD- Polychlorodibenzo-p-dioxin
PCDF- Polychlorodibenzo-p-furan
PM- Particulate Matter
RPG- Raw Pyrolysis Gasoline
SCA- Staged Combustion Air
SCR- Selective Catalytic Ceduction
SNCR- Selective Non Catalytic Reduction
SOx- Sulfur Oxide
SO2- Sulfur dioxide
SR- Semi Regenerative
TAME- Tert-Amyl-Methyl-Ether
TOC- Total Organic Compound
VHAP- Volatile Hazardous Aromatic Product
VOC- Volatile Organic Compounds
WI/SI- Water Injection / Steam Injection
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Introduction

Refineries and petrochemical processes are responsible for many emissions both into the air and into the water. Most relevant emissions into the air are nitrous oxides (NOx), sulfur oxides (SOx), carbon monoxide (CO), methane and volatile organic compounds (VOC). Waste water from petroleum industry contains organic compounds, phenols, toxic metals and other pollutants such as iron, dissolved and suspended solids, oil, cyanides, sulfides and chlorine. In order to reduce these emissions, an accurate analysis of processes is necessary. The analysis of some processes leads to two conclusions:

On the one hand, we can see that major part of emissions always come from the same sources:
- Fugitive emissions, responsible for VOC releases to the atmosphere.
- Process heaters and boilers, responsible for NOx, SOx and particulate matters releases to the atmosphere.
- Blowdown systems
For each of these sources, theoretical methods to qualify and quantify pollutants emitted, and treatment methods available and pollutant production reduction methods are analyzed.

On the other hand, we can see that particular pollutants are emitted from some processes, in normal or intermittent functioning. For example, dioxins can be produced during catalyst regeneration of reforming and isomerization units. Usually these kinds of emissions are not taken into account for different reasons: the formation mechanism of these pollutants is not well-known (dioxins), the emission occurs rarely (catalyst in-situ regeneration), etc.

Aim and objectives

The aim of this study is to carry out a general environmental assessment of refineries and petrochemical processes. The first part of this report emphasizes on major emissions sources and gathered general solutions available and applicable. The second part of this report lightens particular processes. A methodology to analyze processes is proposed.

Methodology

This report is based on a bibliographic study for general considerations. Process books produced by Axens are used for the analysis of particular processes. When it comes to characterize emitted pollutants, only theoretical methods are given, it means that measurements or monitoring techniques are not taken into account.
Part A: Major emission sources of refineries and petrochemical industry

1. Fugitive emissions \(^{1,2,3,4}\)

Equipment leaks in refinery processes are responsible for significant amount of emissions. Even if each individual leak is generally small, according to EPA, it is the largest source of emissions of volatile organic compounds (VOCs) and volatile hazardous air pollutants (VHAPs) from petroleum refineries and chemical manufacturing facilities. The US EPA (United States Environmental Protection Agency) emitted in 1995 a protocol for equipment leak emission estimates based on emission factors or correlation approaches. The emission factors approach is the only method available that allows estimation without monitoring. This method is described below. The implementation of an LDAR (Leak Detection And Repair) programme will then be dealt with.

1.1. Average Emission Factor Approach

The Average Emission Factor Approach is a combination of average emission factors and unit-specific data: number of each type of equipment (valves, pump seals, etc.), the service each equipment is in (gas, light liquid, heavy liquid), the Total Organic Compound (TOC) concentration of the stream and time period each equipment is in that service. The emission rate of TOC from all equipment can be calculated with the following formula:

\[ E_{TOC} = F_A \times W_{TOC} \times N \]

Where:
- \( E_{TOC} \) = emission rate of TOC from all equipments in the stream of a given equipment type (kg/hr)
- \( F_A \) = applicable average emission factor for the equipment type (kg/hr/source)
- \( W_{TOC} \) = average weight fraction of TOC in the stream
- \( N \) = number of pieces of equipment of the applicable equipment type in the stream

Average emission factors are divided into four categories: SOCMI factors, oil and gas production factors, refinery factors, and factors for petroleum marketing terminals (this last category is not applicable here). Within each category, factors depend on equipment type and material in service (light or heavy liquid or gas). Heavy liquid factor is used if the stream's vapor pressure is less than or equal to 0.003 bars at 20°C. If the vapor pressure is greater than 0.003 bars at 20°C, light liquid factor must be used.

Appendix 1 gathers all the Average Emission Factors and Appendix 2 shows an example of calculation.

Total TOC fugitive emission from a unit process can be known by summing emissions from each type of components, from each stream.

Average factors generally determine total hydrocarbon emissions. In order to determine total VOC emissions, the calculated emission rates must be multiplied by the stream’s weight percentage of VOC compounds. (Indeed, it can happen that not all organic compounds present in the stream be classified as VOCs, for instance methane or ethane.)
If some of the organic compounds in the stream are not classified as VOCs total VOCs emission can be calculated with the following formula:

\[ E_{VOC} = E_{TOC} \times \left( \frac{WP_{VOC}}{WP_{TOC}} \right) \]

Where:
- \( E_{VOC} \) = the VOC mass emissions from the equipment (kg/hr)
- \( E_{TOC} \) = the TOC mass emissions from the equipment (kg/hr)
- \( WP_{VOC} \) = the VOC concentration in the equipment in weight percent
- \( WP_{TOC} \) = the TOC concentration in the equipment in weight percent

If, for a stream, estimating emissions of a specific VOC in the mixture is necessary, the following formula can be used:

\[ E_X = E_{TOC} \times \left( \frac{WP_X}{WP_{TOC}} \right) \]

Where:
- \( E_X \) = the organic chemical “X” mass emissions from the equipment (kg/hr)
- \( E_{TOC} \) = the TOC mass emissions from the equipment (kg/hr)
- \( WP_X \) = the organic chemical “X” concentration in the equipment in weight percent
- \( WP_{TOC} \) = the TOC concentration in the equipment in weight percent

Three other methods emitted from the protocol for equipment leak emission estimates are available. However these methods necessitate on-site monitoring so they are not included into the scope of this study.

1.2. Implementation of a Leak Detection and Repair (LDAR) program

Still according to EPA, the implementation of an LDAR program could lead to a reduction by 63% of emissions from equipment leaks. The following describes the procedure to implement this program.

1.2.1. Identifying components

Each regulated component must be assigned a unique identification number, recorded and located in the facility and on the Piping and Instrumentation Diagrams.

1.2.2. Leak definition

Leak definition means the threshold standard (in ppm). It depends on regulation, component type, service and monitoring interval. Leak definition can also be based on visual inspections and observations, sound and smell. A leak is detected whenever the measured concentration (ppm) exceeds the leak definition.

1.2.3. Monitoring components

For many regulations with leak detection provisions, the method for monitoring to detect leaking components is EPA Reference Method 21. This procedure uses a portable detecting
instrument. Monitoring intervals depend on component type and periodic leak rate but are typically weekly, monthly, quarterly, and yearly.

1.2.4. Repairing components

Components have to be repair as soon as possible after the leak is detected. The following practices can be applied:
- Tightening bonnet bolts.
- Replacing bonnet bolts.
- Tightening packing gland nuts.
- Injecting lubricant into lubricated packing.
If the repair of any component is technically infeasible without a process unit shutdown, the component may be placed on the Delay of Repair list.

1.2.5. Record keeping

For each regulated process, a list of ID number for all equipment subject, detailed schematics, equipment design specifications, piping and instrumentation diagrams and results of performance testing and leak detection monitoring must be maintain.
For leaking equipment, records, instrument and operator ID numbers and the date the leak was detected must be maintained. The dates of each repair attempt and an explanation of the attempted repair method is noted. Dates of successful repairs and results of monitoring tests to determine if the repair was successful are included.

2. Flue gases from process heaters and boilers

Fuel combustion in process heaters and boilers is an important pollutants and greenhouse gases emission source. Carbon dioxide (CO₂) is the principal gas released but nitrogen and sulfur oxides (NOx and SOx), carbon monoxide (CO), organic compounds and particulate matters (PM) are also released in non negligible quantities. In order to reduce the overall air emissions of a refinery or a petrochemical plant, these emissions must be taken into account. Several technologies exist to reduce these emissions. The present report synthesizes them.

2.1. General

In process heaters and boilers in refineries and petrochemical plants, two major types of fuel are burned by combustion sources: fuel gas and fuel oil.

Refinery fuel gas is a collection of light gases generated in a number of processing units in the refinery. It contains principally hydrogen and methane and variable amounts of light hydrocarbons such as ethane, ethylene or propane. It can also contain hydrogen sulfide in trace amounts.

Fuel oil is a fraction obtained from petroleum distillation. It can be divided in two categories: distillate oils and residual oils, further distinguished by grade numbers with 1 and 2 being distillate oils and 5 and 6 being residual oils:
- Grade 1: Light domestic fuel oil-distillate.
- Grade 2: Medium domestic fuel oil-distillate.
- Grade 3: Heavy domestic fuel oil-distillate.
- Grade 4: Light industrial fuel oil.
- Grade 5: Medium industrial fuel oil.
- Grade 6: Heavy industrial fuel oil.

There are four major types of boilers used in industrial applications: watertube, firetube, cast iron and tubeless design. Boilers design and size, orientation of heat transfer surfaces and burner configuration are factors that influence strongly emissions and the potential for controlling emissions.

Emissions depend also on type and composition of the fuel. Because the combustion characteristics are different, their combustion can produce significantly different emissions. Among these emissions can be found:
- Particulate emissions, filterable or condensable, which depends on the completeness of combustion and the initial fuel ash content.
- Nitrogen oxides emissions, due either to thermal fixation of atmospheric nitrogen in the combustion air (thermal NOx), or to the conversion of chemically bound nitrogen in the fuel (fuel NOx).
- Sulfur oxides emissions, that are generated during combustion from the oxidation of sulfur contained in the fuel.
- Carbon monoxide and organic compounds emissions, which depends on the combustion efficiency of the fuel.
- Trace metals emissions, which depend on the initial fuel metals content.

All these emissions can be estimated thanks to emission factors available in EPA literature.

Control techniques for the reduction of NOx, SOx and particulate matters are described and compared below as these three types of emission are the most relevant.

2.2. Control techniques for NOx emissions reduction

NOx reduction in boilers and process heaters can be achieved with combustion modification and flue gas treatment or a combination of these. The choice of the technique depends on the type and size of the boiler or heater, the fuel characteristics and the flexibility for modifications. Practically, NOx reductions consist in thermal NOx* reduction and fuel NOx** reduction. When fuel with low nitrogen content is used, such as fuel gas or distillate oil, thermal NOx is the only component that can be controlled.

* Thermal NOx is produced by combination at high flame temperature of nitrogen and oxygen contained in the combustion air supply. It is produced during the combustion of both fuel gases and fuel oils.

** Fuel NOx is produced by combination of nitrogen contained in the fuel with excess oxygen contained in the combustion air. It is only a problem with fuel oils containing bound nitrogen.

Combustion control involves consequently three main strategies:
- Reducing peak temperatures in the combustion zone.
- Reducing the gas residence time in the high-temperature zone.
- Reducing oxygen concentrations in the combustion zone.
These changes can be achieved with process modifications or operating conditions modifications.

Finally, the flue gas treatment allows reducing NOx emissions.

Here below different technologies are generally and shortly described. The table synthesized information available concerning efficiency and applicability of these technologies on process heaters or boilers in petroleum industry, using fuel oil or fuel gas. Only methods that have been used for industrial process heaters or boilers are considered here but many others techniques exist.

### 2.2.1. Low-NOx burners (LNB)

Low-NOx burner is a technology allowing a controlled mixing of fuel and air, resulting in a cooler flame and consequently less thermal NOx formation. It is designed as a stage combustion with either staged air or staged fuel. It is applicable to tangential and wall-fired boilers of various sizes and heaters. It reduces emissions from 40 to 60%.

The basic principle of Low-NOx burner is the separated injection of air and fuel in the furnace resulting in the destruction of NOx in the flame (fuel-rich combustion zones) and the peak flame temperature suppression. Moreover the better air flow distribution allows fuel ignition and flame stability.

### 2.2.2. Staged combustion air (SCA)

Staged combustion air allows the reduction of fuel NOx by suppressing the amount of air below that required for complete combustion. It is achieved by injecting a portion of the total combustion air downstream of the fuel-rich primary combustion zone.

The SCA can be accomplished by several means such as burners out of service (BOOS), biased firing or overfire air (OFA), depending on the type of boiler. The SCA technique is highly effective on high nitrogen fuels such as residual oil. It reduces NOx emissions by 20 to 50%.

### 2.2.3. Flue gas recirculation (FGR)

Flue gas recirculation consists in the rerouting of a portion of flue gases from the stack back to the furnace. Thus, furnace temperature and oxygen concentration are reduced and so is thermal NOx formation. Large modifications to the burner and windbox in old boilers are expensive so this technique is better for new boilers.

### 2.2.4. Water or steam injection (WI/SI)

Water or steam injection in the flame reduces thermal NOx formation by lowering the peak temperature of the flame. This technique has a relatively low initial cost so it is considered as quite efficient for smaller boilers. However this technique can lead to thermal losses and increase in CO emissions.
2.2.5. Selective non catalytic reduction (SNCR)

SNCR is a postcombustion technique consisting in injecting ammonia or urea into combustion flue gases. A reaction with NOx occurs to produce nitrogen and water. There are not many experiences to evaluate effectiveness of this technique.

2.2.6. Selective catalytic reduction (SCR)

SCR is another postcombustion technique consisting in injecting ammonia into the combustion zone in presence of a catalyst to reduce NOx into nitrogen and water. This method allows achieving NOx emission reduction by 75 to 90%. This technique is rather common.

Both SNCR and SCR are influenced by sulfur content of the flue gas.

The table below (table 2-1) summarizes available techniques for NOx control for process heaters. It uses information from the “Alternative Control Techniques Document - NOx Emissions from Industrial/Commercial/Institutional (ICI) Boilers” published by the US EPA. This table can help in a first approach for identifying the best technology to use in function of the type of boiler and the fuel. However, many other parameters are to be taken into account such as the NOx emissions threshold wanted, the budget, etc.
<table>
<thead>
<tr>
<th>Fuel / boiler</th>
<th>NOx control</th>
<th>% NOx reduction</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Residual oil / watertube</strong></td>
<td>LNB</td>
<td>20 - 50</td>
<td>- Relatively inexpensive</td>
<td>- Specific emissions data from industrial boilers with LNB are lacking.</td>
</tr>
<tr>
<td></td>
<td>FGR</td>
<td>4 - 30</td>
<td>- Available</td>
<td>- Staged air burners could result in flame impingement on furnace walls of smaller units.</td>
</tr>
<tr>
<td></td>
<td>SCA</td>
<td>5 - 50</td>
<td>- Best suited for new units</td>
<td>- Requires extensive modifications to the burner and windbox.</td>
</tr>
<tr>
<td></td>
<td>LNB + FGR</td>
<td>N.A.</td>
<td></td>
<td>- Possible flame instability at high FGR rates.</td>
</tr>
<tr>
<td></td>
<td>LNB + SCA</td>
<td>N.A.</td>
<td></td>
<td>- BOOS applicable for boilers with multiple burners only.</td>
</tr>
<tr>
<td></td>
<td>SNCR</td>
<td>40 - 70</td>
<td>- Commercially offered.</td>
<td>- Retrofit is not feasible or not available for all design types.</td>
</tr>
<tr>
<td></td>
<td>SCR</td>
<td>N.A.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Distillate oil / watertube</strong></td>
<td>LNB</td>
<td>20 - 50</td>
<td>- New burners generally applicable to all boilers.</td>
<td>- Specific emissions data from industrial boilers equipped with LNB are lacking.</td>
</tr>
<tr>
<td></td>
<td>FGR</td>
<td>20 - 68</td>
<td>- Available</td>
<td>- Requires extensive modifications to the burner and windbox.</td>
</tr>
<tr>
<td></td>
<td>SCA</td>
<td>17 - 44</td>
<td>- Best suited to new units</td>
<td>- Possible flame instability at high FGR rates.</td>
</tr>
<tr>
<td></td>
<td>LNB + FGR</td>
<td>N.A.</td>
<td>- Most common technique.</td>
<td>- Limited application except BOOS, Bias and OFA for large watertube.</td>
</tr>
<tr>
<td></td>
<td>LNB + SCA</td>
<td>N.A.</td>
<td>- Common technique.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SNCR</td>
<td>40 - 70</td>
<td>- Commercially offered.</td>
<td>- Not widely demonstrated on large boilers.</td>
</tr>
<tr>
<td></td>
<td>SCR</td>
<td>N.A.</td>
<td></td>
<td>- Elaborate reagent injection, monitoring, and control system required.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Must have sufficient residence time at proper temperature.</td>
</tr>
<tr>
<td><strong>Natural gas / watertube</strong></td>
<td>WI</td>
<td>50 - 77</td>
<td></td>
<td>- Thermal efficiency loss of 0.5 to 2.5% and CO increase is expected.</td>
</tr>
<tr>
<td></td>
<td>SCA</td>
<td>15 - 50</td>
<td></td>
<td>- BOOS applicable for boilers with multiple burners only.</td>
</tr>
<tr>
<td></td>
<td>LNB</td>
<td>40 - 85</td>
<td>- Popular technique. Many designs and vendors available.</td>
<td>- LEA LNBs more applicable to single-burner systems.</td>
</tr>
<tr>
<td></td>
<td>FGR</td>
<td>50 - 75</td>
<td></td>
<td>- Staged air burners could result in flame impingement on furnace walls.</td>
</tr>
<tr>
<td></td>
<td>LNB + FGR</td>
<td>55 - 90</td>
<td>- Most popular technique for clean fuels.</td>
<td>- Requires extensive modifications to the burner and windbox.</td>
</tr>
<tr>
<td></td>
<td>LNB + SCA</td>
<td>N.A.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SNCR</td>
<td>10 - 40</td>
<td></td>
<td>- Applicable principally to multi-burner boilers.</td>
</tr>
<tr>
<td></td>
<td>SCR</td>
<td>80 - 90</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Residual oil / firetube</strong></td>
<td>LNB</td>
<td>30 - 60</td>
<td></td>
<td>- No data available.</td>
</tr>
<tr>
<td></td>
<td>SCA</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Distillate oil / firetube</strong></td>
<td>LNB</td>
<td>20 - 50</td>
<td>- Several designs are available.</td>
<td>- Specific emissions data from industrial boilers with LNB are lacking.</td>
</tr>
<tr>
<td></td>
<td>FGR</td>
<td>55 - 75</td>
<td>- Effective technique for clean fuels.</td>
<td>- Requires extensive modifications to the burner and windbox.</td>
</tr>
<tr>
<td><strong>Natural gas / firetube</strong></td>
<td>SCA</td>
<td>5</td>
<td></td>
<td>- Technique not practical unless incorporated in new burner design.</td>
</tr>
<tr>
<td></td>
<td>LNB</td>
<td>30 - 80</td>
<td></td>
<td>- Specific emissions data from industrial boilers with LNB are lacking.</td>
</tr>
<tr>
<td></td>
<td>FGR</td>
<td>55 - 75</td>
<td>- Effective technique used in many applications.</td>
<td>- Requires extensive modifications to the burner and windbox.</td>
</tr>
<tr>
<td></td>
<td>LNB + FGR</td>
<td>N.A.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A-2-1: Comparison of available techniques for NOx control for process heaters
2.3. Control techniques for SOx emissions reduction

On the contrary to NOx, SOx emissions are directly linked to the initial sulfur content of the fuel and the combustion parameters do not influence on the amount of SOx emitted. Two strategies can be used to reduce SOx emissions: the formation prevention (low sulfur fuel usage, fuel desulfurization) or the flue gas desulfurization (wet or dry scrubbing, dual-alkali, spray drying, Wellman-Lord process, etc.).

There are many post-combustion flue gas desulfurization techniques. Almost all techniques are based on the acid-alkaline reaction between SO2 (and SO3) and an alkaline agent such as often lime or limestone, caustic soda, magnesium hydroxide or ammonia. Other techniques are selective adsorption or absorption.

Flue gas desulfurization is mostly used in thermal power plant. Few refineries have a flue gas desulfurization, except in Japan where principally dry processes are used. The principles of four major techniques are given below.

2.3.1. Lime and limestone process

Lime and limestone scrubblings are non-regenerative wet processes producing gypsum. Lime and limestone scrubbing are very similar. The use of lime (CaO) instead of limestone (CaCO3) for the slurry preparation is the only difference. The alkaline slurry is sprayed in the absorber and reacts with the SO2 in the flue gas. Following chemical reactions occur:

SO2 dissociation:

\[
\text{SO}_2 \text{(gaseous)} \rightarrow \text{SO}_2 \text{(aqueous)}
\]

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3
\]

\[
\text{H}_2\text{SO}_3 \rightarrow \text{H}^+ + \text{HSO}_3^- \rightarrow 2\text{H}^+ + \text{SO}_3^-
\]

Lime or limestone dissolution:

\[
\text{CaO}_{(solid)} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \text{(aqueous)} \rightarrow \text{Ca}^{2+} + 2\text{HO}^-
\]

or

\[
\text{CaCO}_3_{(solid)} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{HO}^-
\]

Reaction between ions:

\[
\text{Ca}^{2+} + \text{SO}_3^{2-} + 2\text{H}^+ + 2\text{HO}^- \rightarrow \text{CaSO}_3_{(solid)} + 2\text{H}_2\text{O}
\]

The following reactions can occur if there is excess oxygen:

\[
\text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-}
\]

\[
\text{SO}_4^{2-} + \text{Ca}^{2+} \rightarrow \text{CaSO}_4_{(solid)}
\]

Lime and limestone processes are the most popular flue gas desulfurization system for utility boilers. Some system has achieved SO2-removal efficiency greater than 95%. Another advantage is that these processes produce gypsum, which is saleable. However, these processes have limited usage in refineries.
2.3.2. Dual-alkali scrubbing

Dual-alkali scrubbing is a non-regenerative process using sodium-based solution and lime or limestone to remove SO₂ from flue gases. Following chemical reactions occur:

Main absorption reactions:

\[
\begin{align*}
2NaOH + SO_2 & \rightarrow Na_2SO_3 + H_2O \\
NaOH + SO_2 & \rightarrow NaHSO_3 \\
Na_2CO_3 + SO_2 + H_2O & \rightarrow 2NaHSO_3 \\
Na_2CO_3 + SO_2 & \rightarrow Na_2SO_3 + CO_2 \\
Na_2SO_3 + SO_2 + H_2O & \rightarrow 2NaHSO_3 \\
2NaOH + SO_3 & \rightarrow Na_2SO_4 + H_2O \\
2Na_2SO_3 + O_2 & \rightarrow 2Na_2SO_4
\end{align*}
\]

Regeneration:

\[
\begin{align*}
2NaHSO_3 + Ca(OH)_2 & \rightarrow Na_2SO_3 + CaSO_3 + \frac{1}{2} H_2O + \frac{3}{2} H_2O \\
Na_2SO_3 + Ca(OH)_2 + \frac{1}{2} H_2O & \rightarrow 2NaOH + CaSO_3 + \frac{1}{2} H_2O \\
Na_2SO_4 + Ca(OH)_2 & \rightarrow 2NaOH + CaSO_4
\end{align*}
\]

This method is attractive because it has a high SO₂-removal efficiency and it reduces scaling problems.

2.3.3. Activated char process

Activated char process is the principal dry process used in refineries. The circulating activated char absorbs SO₂ at a temperature comprised between 100 and 200°C. This process has the advantage to also eliminate NOx present in the flue gases. The following chemical reactions occur:

Absorption on char and conversion into sulphuric acid:

\[
SO_2 + \frac{1}{2} O_2 + H_2O \rightarrow H_2SO_4
\]

NOx reduction with ammonia:

\[
4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O
\]

Char regeneration at 400°C:

\[
\begin{align*}
H_2SO_4 & \rightarrow H_2O + SO_3 \\
2SO_3 + C & \rightarrow 2SO_2 + CO_2
\end{align*}
\]

After concentration, SO₂ is sent to the Claus unit.

This process can achieve an SO₂-removal efficiency of 90% and a NOx-removal efficiency of 70%.
2.3.4. Wellman-Lord process

The Wellman-Lord process consists in the SO$_2$ neutralisation by a sodium-based solution which is then regenerated. The following chemical reactions occur:

SO$_2$ capture:

\[
\text{SO}_2 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3
\]

\[
\text{Na}_2\text{SO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4
\]

Regeneration:

\[
2\text{NaHSO}_3 \rightarrow \text{SO}_2 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}
\]

SO$_2$-rich gas treatment:

\[
2\text{SO}_2 + 6\text{H}_2 \rightarrow 2\text{H}_2\text{S} + 4\text{H}_2\text{O}
\]

\[
2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}
\]

The final effluent is sent to the Claus unit.

This process has been often used for utility and industrial boilers. It has the advantage to regenerate the scrubbing solution and to produce a saleable product. However, installation and maintenance costs are higher than lime, limestone or dual-alkali systems.

2.4. Control techniques for particulate matters emissions

For large boilers, a good design and good maintenance can minimize soot and condensable organic compounds emissions. However, fly ash is still emitted, and in this case a postcombustion PM control is needed. Four common methods are described below.

2.4.1. Inertial collectors

Inertial collectors allow separating particles from gas thanks to mechanical forces such as centrifugation, gravitation or inertia. The three major types of inertial collectors are settling chambers, baffle chambers and centrifugal chambers.

2.4.1.1. Settling chambers

A settling chamber is a large box which, by a large size, reduces the speed of the gas stream. Thus, heavier particles settle down.

![Figure A-2-1: Settling chamber](image)

This technique is quite simple and easily manufactured, however it needs a large space and it has a low efficiency.
2.4.1.2. Baffle chambers

In baffle chambers, gas stream changes its direction. Heavier particle do not follow the stream and settle down.

![Figure A-2-2: Baffle chamber](image)

This technique is better used as precleaner.

2.4.1.3. Centrifugal collectors

Centrifugal collectors use the cyclonic action to separate particles from the gas stream. Particles, which are heavier, are directed towards the wall of the cyclone and fall down.

![Figure A-2-3: Cyclone](image)

Single or multicyclones are available.

2.4.2. Electrostatic precipitators

This technique uses electrostatic forces to separate particles from gases. The gas passes through a passage formed by the discharge and collecting electrodes. Particles receive a negative charge and are then attracted to a positively charged electrode. Collected particles are then removed by rapping or vibrating electrodes continuously or intermittently.

2.4.3. Fabric filtration

Fabric filters use filtration to separate particles from gas. The gas stream enters the baghouse and passes through fabric bags that act as filters. The fabric used can be cotton, synthetic or glass-fibre materials. This technique is very efficient and cost effective.
Fabric filters are classified according to their cleaning methods (mechanical shaking, reverse air injection).

2.4.4. Scrubbing systems

This technique uses a scrubbing liquid (generally water) that comes into contact with the gas stream. The three basic operations of wet scrubbers are gas humidification, gas-liquid contact and gas-liquid separation. The outlet liquid is either cleaned and discharged or recycled into the scrubber.

2.4.5. Selection of the control technique for PM emissions

Design, effectiveness, space requirements, investment, operating, and maintenance costs differ widely according to the technique. A compromise must be done in function of advantages and drawbacks of each technique and SOx level emitted. Moreover, general factors influent the selection of the PM-control technique. These factors are:
- PM concentration and particle size.
- Degree of particle removal required.
- Characteristics of gas stream.
- Characteristics of particles.
- Methods of disposal.

The table below (Table 2-2) indicates some advantages and drawbacks concerning each technique.
<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inertial collectors</td>
<td>- Low-cost equipment</td>
<td>- Primary technique</td>
</tr>
<tr>
<td></td>
<td>- Continuous or batch unloading</td>
<td>- Abrasion problems for high particle concentrations</td>
</tr>
<tr>
<td>Electrostatic precipitators</td>
<td>- High efficiency</td>
<td>- High-cost equipment</td>
</tr>
<tr>
<td>Fabric filtration</td>
<td>- High efficiency</td>
<td>- Can be damaged by high temperatures or water</td>
</tr>
<tr>
<td></td>
<td>- Moderate-cost equipment</td>
<td></td>
</tr>
<tr>
<td>Scrubbing systems</td>
<td>- High efficiency</td>
<td>- Corrosion problems</td>
</tr>
<tr>
<td></td>
<td>- Moderate-cost equipment</td>
<td>- Wet slurry production</td>
</tr>
<tr>
<td></td>
<td>- Control also SOx emissions</td>
<td>- Water pollution</td>
</tr>
</tbody>
</table>

Table A-2-2: Comparison of SOx-removal techniques

2.5. Carbon dioxide

The major gas emitted during combustion is obviously carbon dioxide. These emissions have generally to be minimised due to actual context. Frequent measures to reduce carbon dioxide emissions in plants are Energy Management Systems (tool used to control and optimize the energetic performance) and cogeneration (use of heat engine to produce both electricity and heat). A good optimization of processes is a way to recover all energy available, thus reducing CO₂ generation.

Conclusion

Many methods exist to reduce emissions from process heaters and boilers. Usage of a cleaner fuel, better combustion, low-NOx burners, or postcombustion control techniques contribute all to emit less pollutants into the atmosphere.

3. Blowdown systems¹,¹⁴,¹⁵

Petroleum industry process units are equipped with a collection unit called the blowdown system. It allows the safe disposal of liquid and vapor hydrocarbons that are vented in pressure relief valves or drawn from the unit. This system can also be used to purge the unit in case of shutdowns. Blowdown materials are partly liquid and partly vapor. The liquid cut is either recycled into the refinery or sent to the waste water treatment. The vapor cut is either recycled or discharged directly to the atmosphere or flared. When discharged directly to the atmosphere, emissions consist principally in hydrocarbons. When flared, sulfur oxides are emitted. The emission rate of the blowdown system depends on the amount of equipment considered, the frequency of discharges, and the blowdown system controls.

3.1. Emissions to the flare

Flaring is a safety measure used in petroleum industries to ensure that gases are safely disposed of. A flare is a device that burn hydrocarbons emitted from emergency process vents or pressure relief valves. It is usually assumed that flares have a combustion efficiency of at least 98%.
The combustion reaction is:

\[ C_xH_y + (x + y/4) O_2 \rightarrow x CO_2 + y/2 H_2O \]

Principally carbon dioxide is emitted from flares, but also organic compounds and carbon monoxide, NOx, SOx and soot. It is actually impossible to estimate flare emissions, however, several measures can be adopted to minimise these emissions:
- Use of efficient flare tips, and optimization of the size and number of burning nozzles.
- Maximization of flare combustion efficiency by controlling and optimizing flare fuel/air/steam ratio.
- Minimization of flaring from purge without compromising safety, through measures such as purge gas reduction devices, flare gas recovery units, inert purge gas.
- Installation of high integrity instrument pressure protection systems, where appropriate, to reduce over pressure events and avoid or reduce flaring situations.
- Minimization of liquid entrainment in the gas flare stream with a suitable liquid separation system.
- Implementation of burner maintenance and replacement programs to ensure continuous maximum flare efficiency.

3.2. Liquid emissions

In order to minimize liquid emissions, it is important to recycle as much as possible drained liquids. If recycle is not possible, segregation of process drained liquid from relatively clean water can reduce the quantity of oily sludge generated. Moreover, it is easier to recover oil from smaller and concentrated streams.

4. Wastewater\textsuperscript{12,20}

Wastewaters from petroleum industries are various. They can be process waters such as crude oil desalting waters or sour waters from hydrocracking or hydrotreatment processes, general effluents such as drained oily waters, washing waters and finally spent caustics. In order to meet quality requirements about wastewater releases, the best way is to segregate these different waters. In this chapter, common techniques for wastewater treatments in refineries are shortly described and then, best management practices for process wastewater are given.

4.1. Wastewater treatment techniques

4.1.1. Sour waters stripping

This operation is a pre-treatment operation before release to the principal wastewater treatment. It is necessary due to high content of NH\textsubscript{4}\textsuperscript{+} and H\textsubscript{2}S. It consists firstly in an acidification with a strong acid to dissociate HSNH\textsubscript{4} into H\textsubscript{2}S and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and then in a vapor stripping of H\textsubscript{2}S and NH\textsubscript{3}. This operation results in sulfur elimination of about 90 to 98% and ammonium elimination of about 92 to 97%. Phenols are however not well-stripped and only 30% of linked ammonia is stripped.
4.1.2. Oil water separation

Oil water separation is the first step of general treatment of residuals refinery waters. Its purpose is to eliminate insoluble hydrocarbons and suspended matters. It is classically carried out by gravity. Several separators are available which can be longitudinal (API separators), circular, or lamellar.

4.1.3. Physical and chemical purification

This step is necessary before biological treatment. This technique associates one chemical reaction with a physical separation. Most used techniques are coagulation, flocculation, air flotation and filtration. It allows elimination of colloidal suspended matters and insoluble hydrocarbons.

4.1.4. Biological treatment

After physical and chemical treatment, dissolved pollutants are still to be removed. These pollutants include soluble hydrocarbons, soluble CODs and BODs, phenols and nitrogen compounds. They are biodegradable and can be removed with biological treatment techniques such as activated sludge or trickling filters.

4.2. Best management practices

Treatment techniques are quite well-known and widely used in refineries to treat wastewater. However liquid effluents may also result from accidental releases or leaks. In order to prevent prevention from these events, management practices can be applied:
- Regularly inspect and perform maintenance of storages and equipment for prevention and control of accidental releases.
- Maximize recovery into the process and avoid massive discharge of process liquids into the oily water drainage system.
- Construct storage containment basins with impervious surfaces to prevent contamination of soil and groundwater.
- Segregate process water from other wastewaters.
- Direct spent caustic soda to caustic oxidation before wastewater treatment system.
- Install a closed process drain system to collect and recover spills of MTBE, ETBE and TAME.
4.3. Pollution prevention

In addition to these management practices, some pollution prevention solutions can be noticed:
- Control solids entering sewers, which produced more oily sludges.
- Improve recovery of oils from oily sludges.
- Identify benzene sources and install upstream water treatment.
- Recycle and regenerate spent caustics.
- Use oily sludges as feedstock for coking or crude distillation units.
- Recycle lab samples.
Part B: Analysis of processes

1. Naphtha hydrotreating unit

In gasoline production, naphtha hydrotreating is an essential step. Its purpose is to reduce sulfur, nitrogen and olefins contents in naphtha before it is fed in paraffin isomerization and catalytic reforming as catalysts used in these processes are very sensitive to impurities. Approximately 200 processes have been commercialized by Axens.

1.1. Purpose of the unit

The purpose of the unit is to produce clean desulfurized naphtha cut able to be processed in isomerization and reforming units. Indeed these processes involve catalysts that are very sensitive to impurities such as sulfur, nitrogen, water, halogen, diolefins, olefins, arsenic, mercury and other metals. The high performances of isomerization and reforming units are very much dependent upon the efficiency of the naphtha pretreater. Naphtha hydrotreating unit is located after the crude oil distillation and before isomerization and catalytic reforming units. It pretreats different types of naphtha such as straight run naphthas (paraffinic naphthas from crude oil distillation), coker naphtha (from coking unit), wild naphtha and naphtha from hydrocraking unit.

1.2. Raw materials and resources input characteristics

1.2.1. Naphtha feeds

The feed of the naphtha hydrotreating unit is a blend of different raw naphtha feeds. It contains many different compounds such as paraffins, isoparaffins, olefins, naphtenes and aromatics, from C1 to C_{11}. Raw naphtha feeds impurities are principally sulphur, nitrogen and diolefins. Finally, silicon, mercury, lead, arsenic, chlorine, fluorine, oxygenates and oxygen, and mercaptans can be present in trace amounts.

The following table indicates the typical properties of a crude oil distillation naphtha:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>55.6 % vol.</td>
</tr>
<tr>
<td>Olefins</td>
<td>0.2 % vol.</td>
</tr>
<tr>
<td>Naphtenes</td>
<td>37.5 % vol.</td>
</tr>
<tr>
<td>Aromatics</td>
<td>6.7 % vol.</td>
</tr>
<tr>
<td>Sulfur</td>
<td>500 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1 ppm</td>
</tr>
</tbody>
</table>

*Table B-I-I: Typical properties of crude oil distillation naphtha*

Naphtha molecular weight is generally between 100 and 215 g/mol. Its boiling point is comprised between 80 °C and 180 °C.
1.2.2. Hydrogen make-up

The hydrogen make-up is supplied from the isomerization unit or from another unit. It contains about 95% hydrogen, and hydrocarbons from \( \text{C}_1 \) to \( \text{C}_5 \). Impurities that can be found are sulphur, nitrogen compounds, carbon oxides, carbonyl sulphide, olefins and chlorides, all these compounds present in trace amount.

1.2.3. Catalyst

Hydrotreating catalysts are oxide supported (generally Al\( _2 \)O\(_3 \)) and the active phase is molybdenum or tungsten sulfur with cobalt or nickel.

1.3. Products characteristics

There are two products from naphtha hydrotreating unit: heavy naphtha that goes to catalytic reforming unit, and light naphtha that goes to isomerization unit.

The following table indicates the typical properties of naphtha hydrotreating products:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isomerization product</th>
<th>Reforming product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parraffins</td>
<td>82.5 % vol.</td>
<td>47.8 % vol.</td>
</tr>
<tr>
<td>Olefins</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>16.5 % vol.</td>
<td>48.6 % vol.</td>
</tr>
<tr>
<td>Aromatics</td>
<td>1 % vol.</td>
<td>8.6 % vol.</td>
</tr>
<tr>
<td>Sulfur</td>
<td>&lt; 0.5 ppm</td>
<td>&lt; 0.5 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&lt; 0.5 ppm</td>
<td>&lt; 0.5 ppm</td>
</tr>
</tbody>
</table>

*Table B-1-2: Typical properties of naphtha hydrotreating products*

1.4. Normal operations

The figure B-1-1 is an example of a process flow diagram for a naphtha hydrotreating unit in normal operations. The process flow diagram can be separated into two sections: the reaction section and the separation section. Before entering the reaction circuit, naphthas from different sources are mixed together and with hydrogen.
1, 2, 3, 4, 5, 6: different sources of naphtha

Figure B-1-1: Naphtha hydrotreating process flow diagram
1.4.1. Reaction section

Hydrotreating is performed in two steps: the first one is the partial hydrogenation of diolefins into olefins, and the second one is hydrogenation of olefins, desulfurization and denitrification.

Catalyst in the first reactor selectively hydrotreats the naphtha feed. Diolefins and a part of olefins present in the feed are hydrogenated in liquid phase.

In the second reactor, two catalysts are present: The first one (first bed of the reactor) for hydrogenation and silica removal and the second one (second and third bed of the reactor) for aromatic hydrogenation, desulfurization and denitrification.

Reactions occurring within the process are principally desulfurization, denitrification, hydrogenation and elimination of metals.

Desulfurization
Principal sulfur compounds in naphthas are mercaptans, aliphatic and cyclic sulfides and disulfides. These compounds react readily with hydrogen to produce the corresponding saturated compound, releasing H₂S.

Denitrification
Typical nitrogen compounds in naphthas are methylpyrrol and pyridine. Nitrogen is removed by the breaking of the C-N bond producing an aliphatic compound and ammonia.

Hydrogenation
Hydrogenation is the addition of hydrogen to an unsaturated hydrocarbon to produce a saturated product.

Elimination of arsenic and other metals
In naphthas, arsenic and other metals are usually in organo-metallic form. After hydrogenation in the hydrotreater reactor, the hydrogenated form reacts with the hydrotreater catalyst forming a bimetallic compound. Arsenic and other metals are physically adsorbed on the catalyst.

Prior to the air condenser, water is injected in order to dissolve chloride, sulphide and ammonium salts, which precipitate at low temperature. Water is recovered in the boot of the separator drum.

1.4.2. Separation section

The function of this section is to split the full range naphtha into light naphtha, to feed the isomerization unit, and heavy naphtha, to feed the reforming unit.

1.4.3. Influents / effluents scheme

The following scheme represents simply what enters and what goes out the battery limit during normal operations.
1.5. Intermittent operations

1.5.1. Catalyst sulfiding

The metals of catalysts used in this process are in the oxide form. They must undergo a treatment to recover the active sulfide form. If sulfiding is not complete, it could lead to metal sintering resulting in poor activity of the catalyst and heavy coke deposits. This operation is achieved by injection of the sulfiding agent (dimethyl disulfide (DMDS)) in a circulation of hydrogen and raw feed. The required amount of DMDS is determined from the decomposition of DMDS into H₂S.

1.5.2. Catalyst regeneration

When catalysts activity becomes too low, they must be regenerated. This regeneration can be in-situ or ex-situ.

If the regeneration is in-situ, the procedure includes:
- Commissioning of ammonia injection lines and caustic soda injection lines to the circuit.
- A first coke combustion step with 0.5% vol. oxygen in the reactor inlet gas.
- A second coke combustion step with 1% vol. oxygen in the reactor inlet gas.
- A finishing phase with 1% vol. oxygen.
- The shut-off of ammonia injection and caustic scrubbing.
- Cooling down of the reactor temperature using the recycle gas circulation to prepare the unit for the new start-up.

Chemical reactions occurring during catalysts regeneration are:
- Coke combustion to produce carbon dioxide and water.
- Oxidation of the metallic sulfides on the catalyst to produce sulfur oxides.
- Neutralization reactions.
  \[
  \begin{align*}
  \text{SO}_3 + 2 \text{NH}_3 + \text{H}_2\text{O} & \rightarrow (\text{NH}_4)\text{SO}_4 \\
  \text{CO}_2 + 2 \text{NaOH} & \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \\
  \text{SO}_2 + 2 \text{NaOH} & \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}
  \end{align*}
  \]

In case of ex-situ regeneration, the catalyst has to be unloaded from the reactor without previous coke combustion.

1.6. Effluents characterization

In this part, each effluent (except products from the process) is the most precisely as possible characterized with data available.
1.6.1. Normal operations

Fugitive emissions

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Valves, pump seals, flanges, open-ended valves, relief valves, compressor seals, drains, sample connections.</td>
</tr>
<tr>
<td>Destination</td>
<td>Diffuse in the atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be estimated with the Average Factor Method</td>
</tr>
<tr>
<td>Composition</td>
<td>VOCs, sulfur compounds</td>
</tr>
</tbody>
</table>

Fugitive emissions are not negligible. They can be estimated thanks to the Average Factor Method which is explained in part A of this report.

Gas relieves

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Relief valves</td>
</tr>
<tr>
<td>Destination</td>
<td>Flare and then atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>?</td>
</tr>
<tr>
<td>Composition</td>
<td>CO2, VOCs, SOx, NOx</td>
</tr>
</tbody>
</table>

Off-gases

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Separator and reflux drums</td>
</tr>
<tr>
<td>Destination</td>
<td>Sour gas treatment or sulfur recovery units</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be known from material balance</td>
</tr>
<tr>
<td>Composition</td>
<td>Light fuel gas, H2S (see material balance)</td>
</tr>
</tbody>
</table>

Off-gases are very rich in hydrogen sulphide and light hydrocarbons. It is typically sent to the sour gas treatment unit and sulfur recovery unit.

Flue gas from furnaces

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Fuel oil or fuel gas combustion in heaters</td>
</tr>
<tr>
<td>Destination</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be known from process data</td>
</tr>
<tr>
<td>Composition</td>
<td>CO2, SOx, NOx, PM, VOCs, metals - Calculated with Emission Factors</td>
</tr>
</tbody>
</table>

These emissions are indirect emissions from the process. They come from the fuel combustion in heaters. These emissions can be estimated thanks to Emission Factors. They depend on the type of fuel burned, firing practice and post combustion controls. The choice of fuel oil or fuel gas burned in furnaces depends on the fuel available on-site.
Sour waters

<table>
<thead>
<tr>
<th>Media</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Separators</td>
</tr>
<tr>
<td>Destination</td>
<td>Sour waters treatment</td>
</tr>
<tr>
<td>Quantity</td>
<td>6 to 12 % of the charge</td>
</tr>
<tr>
<td>Composition</td>
<td>Salts (≈5%)</td>
</tr>
</tbody>
</table>

Sour waters come from stripping steam injected after reactors. Sulfur is converted into H₂S and mercaptans, nitrogen compounds are converted into NH₃ and cyclic hydrocarbons are converted into phenols. These waters are sent to sour waters treatment.

1.6.2. Intermittent operations

Spent caustic stream from catalyst regeneration

<table>
<thead>
<tr>
<th>Media</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Separator drum</td>
</tr>
<tr>
<td>Destination</td>
<td>Spent caustic treatment unit</td>
</tr>
<tr>
<td>Quantity</td>
<td>Estimated in process book</td>
</tr>
<tr>
<td>Composition</td>
<td>Estimated in process book – H₂O (≈92%), Salts (≈8%), HC &lt; 50 wt ppm</td>
</tr>
</tbody>
</table>

During regeneration, a spent caustic stream is drained from the separator drum and sent to the spent caustic treatment unit.

Waste vapor from catalyst regeneration

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Separator drum</td>
</tr>
<tr>
<td>Destination</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Estimated in process book</td>
</tr>
<tr>
<td>Composition</td>
<td>N₂, CO₂, O₂ (traces), VOCs (traces)</td>
</tr>
</tbody>
</table>

During regeneration, a waste vapor stream is routed from separator to atmosphere at safe location under pressure control.

1.6.3. Solid wastes

Catalyst

<table>
<thead>
<tr>
<th>Media</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Reactors</td>
</tr>
<tr>
<td>Destination</td>
<td>Metals regeneration, reclamation or reuse</td>
</tr>
<tr>
<td>Quantity</td>
<td>Depends on reactor size</td>
</tr>
<tr>
<td>Composition</td>
<td>Contaminated catalyst</td>
</tr>
</tbody>
</table>
1.7. Emissions reduction proposals

Air emissions from naphtha hydrotreating in normal operations arise from process heaters, vents and fugitive emissions.

In order to reduce fugitive emissions, a leak detection and repair program can be established (refer to part A of this report).

Concerning process heaters, old furnaces that produce NOx, SOx and particulate matters should be replaced with emission controls furnaces.

During catalyst regeneration, waste vapor is sent to the atmosphere. These vapors contain coke, VOC and carbon monoxide in trace amount and carbon dioxide. Before being released in the atmosphere, this gas should be treated. For example, it could go through a first boiler to burn carbon monoxide and VOCs, and then through a particulate matters removing apparatus, such as an electrostatic separator or a cyclone separator.

2. Naphtha isomerization

Isomerization is a conversion process which aim is to raise octane number by transforming straight chains C₅-C₆ paraffins into branched paraffins (isoparaffins). Axens offers a complete range of isomerization solutions that can increase C₅-C₆ naphtha cut octane number up to 92. Isomerization schemes available are once-through, recycle with diisopentanizer or with deisohexanizer, advanced recycle (IPSORB®, HEXORB®). The choice of the process depends on criteria such as feed composition or desired octane number.

2.1. Purpose of the unit

The purpose of the unit is to produce high-octane number isoparaffins by isomerising normal C₅-C₆ paraffins. The isomerization unit can also include a benzene hydrogenation step in the first reactor. Naphtha isomerization unit is located after the hydrotreating unit because the catalyst is very sensitive to impurities. The product obtained (isomerate) enters in gasoline composition.

2.2. Raw materials and resources input characteristics

2.2.1. Naphtha feeds

The feed of the naphtha isomerization unit depends a lot on the refinery. It can be either the hydrotreated naphtha from the crude oil distillation, either light naphtha cut from reforming unit. A typical isomerization naphtha feed contains principally C₅ and C₆ paraffins. It contains also between 0 and 3% of C₄ paraffins and other hydrocarbons such as benzene, napthenes, olefins and C₇+.
The following table indicates the typical properties of an isomerization naphtha feed:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopentane</td>
<td>20 % wt.</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>29 % wt.</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>1 % wt.</td>
</tr>
<tr>
<td>2.2-Dimethylbutane</td>
<td>0.3 % wt.</td>
</tr>
<tr>
<td>2.2-Dimethylbutane</td>
<td>1.5 % wt.</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>11 % wt.</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>8.2 % wt.</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>19.5 % wt.</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>5 % wt.</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.5 % wt.</td>
</tr>
<tr>
<td>Benzene</td>
<td>2 % wt.</td>
</tr>
<tr>
<td>$C_7+$</td>
<td>1 % wt.</td>
</tr>
</tbody>
</table>

Table B-2-1: Typical properties of isomerisation naphtha feed

Isomerization naphtha feed boiling point is generally comprised between 70 °C and 80 °C.

2.2.2. Hydrogen

Hydrogen is necessary in order to avoid a coke deposit on the catalyst. Moreover, the quantity of hydrogen must be high enough to hydrogenate benzene and to favorize isomerization reactions.

2.2.3. Catalyst

Metallic platinum on chlorinated alumina based catalyst, that must be used in inert conditions and with continuous chlorine injection is the current isomerization catalyst.

2.2.4. Dryers molecular sieves

Synthetic zeolite containing sodium and calcium is used as dryer.

2.3. Products characteristics

High-octane isomerate product is the principal product from this process. By-product is the fuel gas produced at the head of the stabilization column and washed with caustic soda before being sent to the fuel gas network.

2.4. Normal operations

2.4.1. Reactions

With platinum on chlorinated alumina based catalyst, the process must include feed and hydrogen dryers and continuous chlorine injection.

Figure B-2-1 is an example of simplified process flow diagrams for a naphtha isomerization unit in normal operations.
Chlorine injection is necessary to maintain the chlorine amount on the catalyst. Carbon tetrachloride (CCl₄) and tetrachloroethylene (C₂Cl₄) are usually utilized. A scrubber with caustic soda and feed water is necessary to eliminate chlorhydric acid present in gases.

Axens offers several types of isomerization processes: one through or recycle. In order to recycle n-paraffins which have not been transformed, it is necessary to separate it from isoparaffins. This separation can be achieved either by distillation (diisopentanizer or deisohexaniser) which is big energy consumer or by adsorption on molecular sieve. A combination of both can also be designed (IPSORB® and HEXORB®). (See figures B-2-2 and B-2-3).
Examples of reactions occurring are given below:

\[
\text{CH}_3 - (\text{CH}_2)_3 - \text{CH}_3 \quad \rightarrow \quad \text{CH}_3 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qu
2.5. Intermittent operations

2.5.1. Dryers regeneration

Molecular sieves in dryers have to be regenerated on a regular time basis. It is consequently a cyclic regeneration. For this operation, the deisohexanizer distillate product is generally used as regenerant. After heating it flows on the sieve and it is recycled after the regenerant degasser where light components are flared and free water is drained and sent to oily water sewer.

2.5.2. Influents / effluents scheme

The following scheme represents simply what enters and what goes out the battery limit during dryers regeneration.
2.6. Effluents characterization

In this part, each effluent (except products from the process and by-products) is the most precisely as possible characterized with data available.

2.6.1. Normal operations

Fugitive emissions

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Valves, pump seals, flanges, open-ended valves, relief valves, compressor seals, drains, sample connections.</td>
</tr>
<tr>
<td>Destination</td>
<td>Diffuse in the atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be estimated with the Average Factor Method</td>
</tr>
<tr>
<td>Composition</td>
<td>VOCs, Cl</td>
</tr>
</tbody>
</table>

Fugitive emissions are not negligible. They can be estimated thanks to the Average Factor Method which is explained in part A.

Chlorine is involved in the process, consequently chlorine can be released in the atmosphere with fugitive emissions.

Gas relieves

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Relief valves, reflux drum</td>
</tr>
<tr>
<td>Destination</td>
<td>Flare and then atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>?</td>
</tr>
<tr>
<td>Composition</td>
<td>CO₂, VOCs, SOₓ, NOₓ, Cl</td>
</tr>
</tbody>
</table>

Chlorine is also emitted in case of gas relieves. This chlorine could be released in form of dioxins (see specific paragraph later).

Flue gas from furnaces

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Fuel oil or fuel gas combustion in heaters</td>
</tr>
<tr>
<td>Destination</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be known from process data</td>
</tr>
<tr>
<td>Composition</td>
<td>CO₂, SOₓ, NOₓ, PM, VOCs, metals - Calculated with Emission Factors</td>
</tr>
</tbody>
</table>

These emissions are indirect emissions from the process. They come from the fuel combustion in heaters. These emissions can be estimated thanks to Emission Factors. They depend on the type of fuel burned, firing practice and postcombustion controls. The choice of fuel oil or fuel gas burned in furnaces depends on the fuel available on-site.
Spent caustic

<table>
<thead>
<tr>
<th>Media</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Caustic scrubber</td>
</tr>
<tr>
<td>Destination</td>
<td>Battery limit</td>
</tr>
<tr>
<td>Quantity</td>
<td>Batch operation (see process book)</td>
</tr>
<tr>
<td>Composition</td>
<td>2 % wt NaOH, 10% wt NaCl, dissolved HC, H₂O</td>
</tr>
</tbody>
</table>

2.6.2. Dryers regeneration

Oily water

<table>
<thead>
<tr>
<th>Media</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Discharge from regenerant degasser</td>
</tr>
<tr>
<td>Destination</td>
<td>Oily water sewer</td>
</tr>
<tr>
<td>Quantity</td>
<td>Maximum quantity estimated with maximum water content of feeds</td>
</tr>
<tr>
<td>Composition</td>
<td>H₂O, hydrocarbons</td>
</tr>
</tbody>
</table>

Light components

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Regenerant degasser</td>
</tr>
<tr>
<td>Destination</td>
<td>Flare</td>
</tr>
<tr>
<td>Quantity</td>
<td>?</td>
</tr>
<tr>
<td>Composition</td>
<td>CO₂, VOCs, NOx</td>
</tr>
</tbody>
</table>

2.6.3. Solid wastes

Catalyst

<table>
<thead>
<tr>
<th>Media</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Reactors</td>
</tr>
<tr>
<td>Destination</td>
<td>Disposal in landfill or regeneration</td>
</tr>
<tr>
<td>Quantity</td>
<td>Depends on reactor size</td>
</tr>
<tr>
<td>Composition</td>
<td>Contaminated catalyst</td>
</tr>
</tbody>
</table>

Used catalysts from isomerization are either disposed of in landfill or regenerated ex-situ. These wastes are generally reclaimed due to their precious metal content.

Spent platinum chloride and spent aluminium chloride catalysts are expected to have a small concentration of contaminants as these catalysts require a clean feed. However, they are expected to contain dioxins because of the presence of chlorine in the process.
### Adsorbent

<table>
<thead>
<tr>
<th>Media</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Naphtha and H₂ feeds purification, product separation.</td>
</tr>
<tr>
<td>Destination</td>
<td>Disposal in landfill, recycling / reuse, or regeneration</td>
</tr>
<tr>
<td>Quantity</td>
<td>Depends on dryers / column size</td>
</tr>
<tr>
<td>Composition</td>
<td>Contaminated molecular sieves</td>
</tr>
</tbody>
</table>

Solid adsorbents are used in three locations in the isomerization process: naphtha feed purification, hydrogen feed purification and separation of the product. These adsorbents are regularly regenerated but when they are no longer efficient, they are replaced by fresh adsorbents. Used adsorbents are either disposed of in landfill or reused in cement plant and road materials or stored in pile.

### 2.7. Emissions reduction proposals

#### 2.7.1. Air emissions

Air emissions from isomerization unit in normal operations arise from process heaters, vents and fugitive emissions.

In order to reduce fugitive emissions, a leak detection and repair program can be established (see part A of this report).

Concerning process heaters, old furnaces that produce NOₓ, SOₓ and particulate matters should be replaced with emission controls furnaces.

#### 2.7.2. Water emissions

Two types of water emissions occur in this process: spent caustics and oily water.

Spent caustics do not contain sulfur and phenols but about 10% of NaCl salt and dissolved hydrocarbons. These hydrocarbons can be removed and recycled. These spent caustics are free of phenols and sulfur compounds so it should not be mixed with other spent caustics (which can be sent to phenol recovery units for example).

Oily water removed from the regeneration degasser is also expected to be free from impurities such as sulfur or nitrogen compounds. It represents a very small amount.

#### 2.7.3. Solid wastes

Concerning the catalyst, source reduction methods are those that extend its life. Its time life is comprised between three and five years but it can sometimes be replaced after more years. Currently, recycling of the spent catalyst by sending to metals reclamation is a common practice since the catalyst is platinum.

Adsorbents are used to extend catalyst life; they are consequently a source reduction technique for other residuals. They do not have themselves source reduction methods. Their time life is about three years.
2.8. Dioxins emissions

Dioxin compounds are in fact polychlorodibenzo-p-dioxins (PCDD), which include also furans and pyralens. PCDD are aromatic tricyclic chlorinated molecules. Below is an example of a compound from this family:

![Image of 2,3,7,8-Tetrachlordibenzodioxin]

Figure B-2-6: 2,3,7,8-Tetrachlordibenzodioxin

Dioxins and furans are formed only in two refining processes: naphtha catalytic reforming and isomerization units.

Three major mechanisms are nowadays identified for the formation of dioxins. The first mechanism involves PCDDs/PCDFs (polychlorinated dibenzo-p-dioxin/polychlorinated dibenzofuran) contained in the feed and released intact to the environment after combustion, the second mechanism (precursor mechanism) involves the formation of PCDDs/PCDFs from the thermal breakdown and molecular rearrangement of aromatic precursors either originating in the feed or forming as a product of incomplete combustion and the third mechanism involves the heterogeneous solid-phase formation of PCDDs/PCDFs in the post-combustion environment on the surface of fly ash.

The formation of dioxins occurs then in case of combustion. It can be supposed nevertheless that the second mechanism could occur in an isomerization process in the petroleum industry.

An aromatic compound like benzene reacts with chlorine, causing hydrogen abstraction and the formation of chlorobenzenes and chlorophenols. Homogeneous gas-phase formation of PCDDs/PCDFs occurs from these precursor compounds at temperatures higher than 500°C, catalyzed by the presence of copper compounds or other heavy metals. Heterogeneous formation of PCDDs/PCDFs from gas-phase precursors has been observed at temperature comprised between 200 and 450°C and by the presence of a transition metal.

Dioxin formation mechanisms are not well-known so we can suppose that the heating of organic molecules in presence of a chlorine source in industrial processes can produce dioxins that are released to the atmosphere in case of gas relieves or depressurization.

However, in the literature, source of dioxins concerning petroleum industry is the reforming and isomerization catalyst regeneration (isomerization catalyst regeneration is very rare).

Nothing either is specified in the European Legislation concerning dioxins emissions in the petroleum industry.

Conclusion

The isomerization process is different from the others because of the presence of chlorine. This chlorine is scrubbed in normal operation but can be released in case of gas relieves and depressurization.
3. Catalytic reforming\textsuperscript{9,14,15,16,17,18,19}

Catalytic reforming is a key process in gasoline production. It allows upgrading naphtha cut to high-octane products by the obtaining of aromatic products. These compounds are formed through complex series of reactions such as cyclohexanes dehydrogenation, cyclopentanes isomerization and dehydrogenation, paraffins isomerization and dehydrocyclization. Moreover, catalytic reforming is great source of hydrogen. Axens offers several types of catalytic reforming: semi-regenerative process, cyclic process (Dualforming\textsuperscript{®}) and continuous process (Octanizing).

3.1. Purpose of the unit

The purpose of the unit is to produce high-octane products thanks to different type of reaction explained later in this chapter. Catalytic reforming unit is located after the hydrotreating unit because the catalyst is very sensitive to impurities. The product obtained (reformate) enters in gasoline composition. It can also be sent to the isomerization unit.

3.2. Raw materials and resources input characteristics

3.2.1. Naphtha feed

The feed of the catalytic reforming unit is the heavy naphtha from the crude distillation. It often goes through the hydrotreating unit before reforming in order to get naphtha free from sulfur, nitrogen and olefins. Catalytic reforming naphtha feed contains C\textsubscript{5} to C\textsubscript{10} paraffins, naphtenes and aromatics.

Also, gasolines from visbreaking, coking, hydrocracking or fluid catalytic cracking (FCC) units can be sent to reforming.

The following table indicates the characteristics of two typical charges in weight percent.

<table>
<thead>
<tr>
<th></th>
<th>Paraffins</th>
<th>Naphtenes</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charge A</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{5}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C\textsubscript{6}</td>
<td>5.49</td>
<td>2.30</td>
<td>0.41</td>
</tr>
<tr>
<td>C\textsubscript{7}</td>
<td>16.83</td>
<td>5.80</td>
<td>3.18</td>
</tr>
<tr>
<td>C\textsubscript{8}</td>
<td>21.38</td>
<td>8.27</td>
<td>6.80</td>
</tr>
<tr>
<td>C\textsubscript{9}</td>
<td>17.26</td>
<td>5.95</td>
<td>3.08</td>
</tr>
<tr>
<td>C\textsubscript{10}</td>
<td>2.59</td>
<td>0.63</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>63.55</td>
<td>22.95</td>
<td>13.47</td>
</tr>
<tr>
<td><strong>Charge B</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{5}</td>
<td>0.16</td>
<td>0.27</td>
<td>-</td>
</tr>
<tr>
<td>C\textsubscript{6}</td>
<td>3.31</td>
<td>5.78</td>
<td>0.20</td>
</tr>
<tr>
<td>C\textsubscript{7}</td>
<td>6.13</td>
<td>14.24</td>
<td>1.20</td>
</tr>
<tr>
<td>C\textsubscript{8}</td>
<td>9.79</td>
<td>14.47</td>
<td>3.54</td>
</tr>
<tr>
<td>C\textsubscript{9}</td>
<td>3.89</td>
<td>17.14</td>
<td>4.29</td>
</tr>
<tr>
<td>C\textsubscript{10}</td>
<td>3.59</td>
<td>11.17</td>
<td>0.88</td>
</tr>
<tr>
<td>Total</td>
<td>26.81</td>
<td>63.07</td>
<td>10.10</td>
</tr>
</tbody>
</table>

*Table B-3-1: Typical properties of two charges for catalytic reforming unit*
3.2.2. Catalyst

Catalysts used are bimetallic platinum - rhenium (Pt/Re) or platinum – tin (Pt/Sn) catalysts. Pt/Re is mostly used for semi-regenerative process and Pt/Sn for circulating bed process. Reforming catalysts activate many different reactions. However, they are very sensitive to impurities and require the feed pre-treatment. Another drawback is that these catalysts produce coke at a non negligible speed. This speed can nevertheless be reduced with high pressure of hydrogen.

3.3. Products characteristics

Catalytic reforming generates three main products: reformate stream, hydrogen rich gas stream and LPG stream. There is also a by-product which is a fuel gas stream from the LPG absorber.

3.4. Reaction section

Reactions occurring in catalytic reforming are numerous. Desired reactions are:

- Dehydrogenation

\[
\text{Cyclohexane} \quad \text{↔} \quad \text{Benzene} \quad + 3 \text{H}_2
\]

- Isomerization/dehydrogenation

\[
\text{Octane} \quad \text{↔} \quad \text{Nonane} \quad \text{↔} \quad \text{Isobutane} \quad + 3 \text{H}_2
\]

- Paraffins isomerization

\[
n\text{C}_7\text{H}_{16} \quad \text{↔} \quad i\text{C}_7\text{H}_{16}
\]

- Dehydrocyclization

\[
n\text{C}_7\text{H}_{16} \quad \text{↔} \quad \text{Benzene} \quad + 4 \text{H}_2
\]

Other parasite reactions are promoted with the catalyst. These reactions are dismutation, alkylation, hydrocracking, hydrodealkylation and coking.

Different technologies exist for catalytic reforming. These differences concern mainly the reactor type: the catalytic bed can be either fixed or mobile. With fixed bed, two processes exist: semi-regenerative or cyclic. With a mobile bed, a continuous process is proposed by Axens. Simplified process schemes and basic information are given below.
3.4.1. Semi-regenerative fixed bed

In this process, the catalyst regeneration implies unit shutdown.

![Figure B-3-1: Simplified scheme of semi-regenerative process for catalytic reforming](image)

The pre-treatment section is necessary to purify the feed as catalyst is very sensitive to impurities such as nitrogen, sulfur and oxygenated compounds and metals. A molecular sieve can also be used in order to eliminate water traces.

Hydrogen recycling (from the stabilization section) is necessary to prevent a rapid catalyst deactivation.

Finally, light hydrocarbons produced are separated from the product in the stabilization section.

3.4.2. Continuous Catalyst Regeneration reforming process

Nowadays, units are generally Continuous Catalyst Regeneration (CCR) reforming process named octanizing®. The scheme of this process is quite similar to semi-regenerative process except that the catalyst bed is moving from one reactor to another, before regeneration and introduction back to the first reactor. The scheme below is a simplified representation of the catalyst circulation in reactors.
Two different lift gases are usually used: hydrogen rich gas or nitrogen gas. These gases are recovered and recycled so are not effluents of the process.

### 3.4.3. Influents / effluents scheme

The following scheme represents simply what enters and what goes out the battery limit during normal operations.

![Diagram of Influents/effluents scheme for catalytic reforming reaction section](image)

#### 3.5. Regeneration section

In continuous catalytic regeneration, the process utilizes moving catalyst bed technology. The purpose is to regenerate continuously the catalyst during normal operation and keep optimum operating conditions for the unit. The scheme below represents a simplified process flow diagram for the catalyst regeneration.
Before entering the regenerator, the catalyst is sent in a lock hopper where fresh catalyst can be loaded in case of catalyst attrition. The pressure in this lock hopper is automated and depressurizations happen during around 5 minutes every 20 to 50 minutes.

The regeneration of catalyst is achieved through the following operations:
- Coke burning.
- Catalyst oxychlorination.
- Catalyst calcination.
- Catalyst cooling.
- Catalyst reduction.

The first three steps are performed in the regenerator, the fourth one in a hopper located up to the first reactor and the last one in a reduction chamber located between the hopper and the reactor.

Coke burning, oxychlorination and calcination effluents are all directed to a washing drum where gases are stripped with caustic soda. Reduction gas (hydrogen from another unit) is recycled in the reaction section.

The following scheme represents simply what enters and what goes out the battery limit during regeneration.
3.6. Effluents characterization

In this part, each effluent (except products from the process and by-products) is the most precisely as possible characterized with data available.

3.6.1. Reaction section

Reaction section of the catalytic reforming process does not have any waste effluent. Emissions come from fugitive emissions and process heaters.

**Fugitive emissions**

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Valves, pump seals, flanges, open-ended valves, relief valves, compressor seals, drains, sample connections.</td>
</tr>
<tr>
<td>Destination</td>
<td>Diffuse in the atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be estimated with the Average Factor Method</td>
</tr>
<tr>
<td>Composition</td>
<td>VOCs, HAPs, chlorinated compounds</td>
</tr>
</tbody>
</table>

Fugitive emissions are not negligible. They can be estimated thanks to the Average Factor Method which is explained in part A.

The volatile nature of toluene, xylene, benzene and other HAPs which are formed during catalytic reforming makes fugitive emissions HAPs largest release source.

**Gas relieves**

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Relief valves, reflux drum</td>
</tr>
<tr>
<td>Destination</td>
<td>Flare or atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>?</td>
</tr>
<tr>
<td>Composition</td>
<td>CO₂, VOCs, HAPs</td>
</tr>
</tbody>
</table>
Flue gas from furnaces

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Fuel oil or fuel gas combustion in heaters</td>
</tr>
<tr>
<td>Destination</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be known from process data</td>
</tr>
<tr>
<td>Composition</td>
<td>CO₂, SOₓ, NOₓ, PM, VOCs, metals - Calculated with Emission Factors</td>
</tr>
</tbody>
</table>

These emissions are indirect emissions from the process. They come from the fuel combustion in heaters. These emissions can be estimated thanks to Emission Factors. They depend on the type of fuel burned, firing practice and postcombustion controls. The choice of fuel oil or fuel gas burned in furnaces depends on the fuel available on-site.

3.6.2. Regeneration section

As in reaction section, there are similar fugitive emissions and gas relieves in regeneration section. Other effluents are described below.

Caustic purge

<table>
<thead>
<tr>
<th>Media</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Washing drum</td>
</tr>
<tr>
<td>Destination</td>
<td>Effluent treatment system</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be found in material balance</td>
</tr>
<tr>
<td>Composition</td>
<td>H₂O, Sodium salts (0.25% wt): NaCl + Na₂CO₃ + NaOCl, NaOH (1mg/l max), HCl (1mg/l max), H₂CO₃, CO₂ (3g/l max), dioxins</td>
</tr>
</tbody>
</table>

Trace amounts of dioxins have been observed in catalytic reforming process effluents. This can be due to coke burning, high temperatures and chlorine presence. More information is given in paragraph 3.8.

Regeneration loop purge

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Washing drum</td>
</tr>
<tr>
<td>Destination</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be found in material balance</td>
</tr>
<tr>
<td>Composition</td>
<td>N₂, CO₂, O₂, H₂O. Possible presence of CO, HCl, SO₂.</td>
</tr>
</tbody>
</table>

Lock hopper depressurization

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Lock hopper</td>
</tr>
<tr>
<td>Destination</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be found in process book</td>
</tr>
<tr>
<td>Composition</td>
<td>N₂, possible presence of alumina dust</td>
</tr>
</tbody>
</table>
3.6.3. Solid wastes

Catalyst

<table>
<thead>
<tr>
<th>Media</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Reactors</td>
</tr>
<tr>
<td>Destination</td>
<td>Regeneration, metal recovery</td>
</tr>
<tr>
<td>Quantity</td>
<td>Depends on reactor size</td>
</tr>
<tr>
<td>Composition</td>
<td>Contaminated catalyst</td>
</tr>
</tbody>
</table>

Catalyst from reforming process is regenerate every 6 to 24 months for SR process and continuously for CCR. Catalysts used are generally very expensive so precautions are taken to ensure a long lifetime and losses. When the catalyst has lost its activity, metals are recovered off-site.

3.7. Emissions reduction proposals

3.7.1. Air emissions

Air emissions from isomerization unit in normal operations arise from process heaters, vents and fugitive emissions.

In order to reduce fugitive emissions, a leak detection and repair program can be established (see part A of this report).

Concerning process heaters, old furnaces that produce NOx, SOx and particulate matters should be replaced with emission controls furnaces.

3.7.2. Solid wastes

Concerning the catalyst, source reduction methods are those that extend its life. Currently, recycling of the spent catalyst by sending to metals reclamation is a common practice since the catalyst is platinum and other expensive metals.

3.7.3. Spent caustic

In order to minimize spent caustic, contact between caustic and gas must be optimized.

3.8. Dioxins emissions

According to limited testing performed in the United States, catalyst regeneration in the reforming process is a potential source of PCDDs/PCDFs.

During the reforming process, coke formation onto the catalyst lower its activity. This coke can be removed by regeneration via burning at temperatures around 400°C followed by a reactivation at temperatures around 500°C using chlorine or chlorinated compounds. This coke burning produces exhaust gases that are vented to the atmosphere or scrubbed with caustic or water.
Studies have been conducted in order to determine PCDDs and PCDFs concentrations in waste streams. However no regulation law has been emitted by European or American legislation concerning dioxins in petroleum industry.

Once dioxins are produced, it is difficult to eliminate them as treatment methods or disposal systems just transfer dioxins from a medium to another (for example, to scrub a gas transfer dioxins to liquid). Decomposition of dioxins seems to not be widely used.

A better option would be to prevent dioxins formation, which is also difficult as formation mechanisms are not well-known and chlorinated compounds are necessary in this process.

4. Hydrogenation in olefin plants

Hydrogenations are simple and relatively similar units present in olefin plants. They are purification steps whose aim is to selectively hydrogenate dienes, alkynes and olefins which are unstable compounds into olefins and alkanes. These processes generally do not produce a lot of effluents. The main issue is basically effluents produced during the catalyst regeneration. Axens has a strong experience with all types of hydrogenation.

4.1. Purpose of units

The C₃ hydrogenation unit is a sub-process in an olefin plant. It is designed to selectively hydrogenate Methylacetylene (MA) and Propadiene (PD) contained in the C₃ stream from the depropaniser overhead, before it is fed to Propylene Towers. Indeed, in addition to up to 90% propylene, the raw C₃ cut contains a non negligible quantity of MA and PD that have to be removed in order to meet the propylene product specification. The reactions involved are hydrogenations of MA and PD with hydrogen. The MAPD hydrogenation to propylene can be carried out in either the vapour or liquid phase. All modern steam crackers for which the C₃ cut is separated before hydrogenation ("tail end hydrogenation") use liquid-phase hydrogenation as it requires lower investment and has lower operating costs compared to gas-phase processing.

The C₄ hydrogenation unit is a sub-process in an olefin plant. It is designed to selectively hydrogenate butadiene contained in the C₄ stream from the debutanizer overhead, before it is fed to isobutylene and butane-1 removal units. The reaction involved is hydrogenation of butadiene with hydrogen.

The gasoline hydrogenation unit is a sub-process in an olefin plant. It is designed to totally hydrogenate raw pyrolysis gasoline (RPG) which is the bottom product of the ethylene plant debutanizer. The purpose of this unit is to eliminate unstable components such as diolefins and styrenics, and olefins in order to meet the product specification. Indeed cracked gasoline typically exhibits high aromatics content, about 50% being benzene. It is an ideal feedstock for benzene production. However, treatment steps with adequate fractionation facilities are required upstream of the benzene process in order to meet sulphur, olefins and diolefins content specifications. The treatment process operates in two stages. About 90 first stages and 60 second stages of gasoline hydrogenation have been licensed by Axens.
4.2. Raw materials and resources input characteristics

4.2.1. Raw C3 cut

The feed of the C3 selective hydrogenation units is a blend of different C3 compounds with a major percentage of propane and propylene. Sulfur, nitrogen, arsenic and mercury can be present in trace amounts.

The following table indicates the typical proportion of the raw C3 cut:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane + propylene</td>
<td>90 to 95% wt.</td>
</tr>
<tr>
<td>Methylacetylene (MA)</td>
<td>1.5 to 4 % wt.</td>
</tr>
<tr>
<td>Propadiene (PD)</td>
<td>1.5 to 3 % wt.</td>
</tr>
<tr>
<td>(C2−) + (C4+)</td>
<td>0.25 % wt.</td>
</tr>
</tbody>
</table>

*Table B-4-1: Typical composition of a raw C3 cut entering a selective hydrogenation unit*

4.2.2. Raw C4 cut

In addition to C4 components, raw C4 cut contains C3 and C5 components in minority proportions. It can also contain impurities in trace amount such as sulphur, nitrogen, C8+ and polymers, carbonyl compounds, acetone, mercury or arsenic.

4.2.3. Raw pyrolysis gasoline

Raw pyrolysis gasoline has a high aromatics content, about half of this figure being benzene. It contains also diolefins, olefins and sulphur in variable amounts. Impurities such as nitrogen, arsenic, antimony, or mercury can also be present.

4.2.4. Hydrogen make-up

The hydrogen make-up can contain trace amounts of light hydrocarbons (CH4, C2H6), carbon oxides, chlorhydric and sulfuric acids and mercury. These compounds are in very little quantity but contaminate the catalyst. They can be consequently present in effluents from regeneration.

4.2.5. Catalyst

These hydrogenations are promoted with a palladium or nickel-on-alumina catalyst.

4.3. Products characteristics

Hydrogenated C3 cut is mainly composed of propylene (85%) and propane (15%). It shall have an MAPD content inferior to 500 ppm (vol). It is routed to the next unit of the olefin plant. There is no by-product from this unit.

C4 product is mainly composed of butenes and routed to the next unit of the olefin plant. It contains also butane and traces amount of C3 and lighter, C5 dienes and acetylenes, acetonitrile, sulfur and water. Waste effluents are produced: water and purge gas from recycle and reflux drums.
The hydrogenated raw pyrolysis gasoline should be olefin, diene and sulphur free.

4.4. Normal operations

Simple flow sheets of each process are represented below.

4.4.1. Selective hydrogenation of C₃

Feed section
The feed to the reactor consists of both fresh and recycle C₃ cut streams. The recycle stream comes from the separator. The recycle stream and the fresh stream are first mixed together before being mixed with the hydrogen make-up in the static mixer.

Reactor section
The total stream enters the reactor top and flows downwards through the fixed catalyst bed. The hydrogenation of MA and PD occurs selectively according to the following reaction:

\[
\begin{align*}
CH_3\equiv C≡CH & + H_2 \rightarrow CH_3\equiv CH = CH_2 \\
CH_2 = C≡CH_2 & + H_2 \rightarrow CH_3\equiv CH = CH_2
\end{align*}
\]

The reactor effluent is then condensed and cooled down in a cooler.

A spare reactor is foreseen in order to allow the catalyst reduction, reactivation or in-situ regeneration operations in one reactor while the other one is in operation.
For catalyst reduction, reactivation or regeneration operations, the gas is sent into the reactor at the required temperature and the effluent is sent to battery limit for disposal (flare or cracker furnace fire box).

**Separator section**
The reactor effluent is then received in a separator where the off-gas is purged if necessary (the off-gas purged is recycled). Finally the liquid phase is pumped out and divided into two streams: the recycle to the reactor and the product routed to battery limit.

### 4.4.2. Selective hydrogenation of C₄

**Figure B-4-2: Flow sheet of the C₄ selective hydrogenation process**

#### Feed section
The feed to the reactor consists of both fresh and recycle C₄ cut streams. The recycle stream comes from the recycle drum. The recycle stream and the fresh stream are first mixed together before being mixed with the hydrogen make-up.

#### Reactor section
The total stream enters the first reactor top and flows downwards through the fixed catalyst bed. The hydrogenation of butadiene occurs selectively according to the following reaction:

\[
\text{CH}_2 \equiv \text{CH} - \text{CH} \equiv \text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_2 \equiv \text{CH} - \text{CH}_2 - \text{CH}_3
\]

The reactor effluent is then sent in the recycle drum where free water is purged if necessary. In case of two phase mixture, vapor shall be partially condensed in the condenser. The resulting liquid falls back to the condenser and the purge gas is sent to the flare. Liquid from
the recycle drum is then pumped, cooled split into two streams, the recycle C4 cut and the stage 2 feed, that goes to the second reactor.

The stage 2 feed is mixed with a second hydrogen make-up and enters the second reactor bottom and flows upwards through the catalytic bed. The remaining butadiene is hydrogenates selectively and the effluent is sent to the C4 stabilizer.

**Stabilization section**
The stage 2 effluent is preheated in a heat exchanger with the stabilizer bottom and feed the stabilizer. In the stabilizer, light compounds of the products due to the H2 make-up quality are removed. The column overhead is partially condensed and collected in the reflux drum where vapor is purged and water drained. The liquid returns back to the column as reflux.

The column bottom stream constitutes the final product. This stream is cooled down and routed to product storage.

**4.4.3. Gasoline hydrogenation**

![Flow sheet of the gasoline hydrogenation process](image)

*Figure B-4-3: Flow sheet of the gasoline hydrogenation process*

**First stage reaction section**
The raw pyrolysis gasoline coming from the debutanizer bottom is routed to the feed drum where a boot allows trapping and draining water if any. It is then mixed with hydrogen make-
up and recycle diluent from separators, enters the reactor top and flows downwards through two beds of the same catalyst. Reactions occur in mixed phase (mainly liquid).

Main reactions happening are:
- Hydrogenation of diolefins.
- Hydrogenation of alkenyl aromatics (hydrogenation of the linear side chain).
- Isomerization of olefins.
- Hydrogenation of olefins
- Thermal and catalytic polymerization of unstable compounds.
The two last reactions must be avoided.

After being cooled, reactor effluent is sent to hot separator. Vapor from the separator, which contains light hydrocarbons, is partially condensed and sent to cold separator. Vapor from the cold separator is sent to second stage reaction section as hydrogen make-up. Liquid effluents from hot and cold separators are mixed together. Part of this liquid is recycled, the remaining is sent to the second stage reaction section.

Second stage reaction section
The feed coming from the first stage reaction section is mixed with the recycle gas. The mixture is heated before entering the second reactor top and flows downward through two types of catalysts: the first one to finish hydrogenation, the second one for desulphurization.

Main desirable reactions occurring are:
- Hydrogenation of olefins.
- Hydrogenation of sulphur compounds.

After consecutive cooling, reactor effluent enters a separator in which the vapour phase is partly purged, partly recycled, and the liquid phase is partly recycled, partly fed to stabilizer column.

Stabilization section
The purpose of this column is to eliminate light components such as hydrogen and hydrogen sulphide dissolved in the gasoline.

The stabilizer overhead is condensed and sent in a reflux drum where vapour and liquids phases are separated. Vapour phase is routed to sour gas and decanted water is sent to battery limit.

The column bottom stream constitutes the final product. This desulphurized product is cooled down and routed to battery limit.

4.4.4. Influen ts / effluents scheme
The following schemes represent simply what enters and what goes out the battery limit during normal operations.
Figure B-4-5: Influent/effluent scheme for \( C_3 \) selective hydrogenation during normal operations

![Diagram](image)

Figure B-4-6: Influent/effluent scheme for \( C_4 \) selective hydrogenation during normal operations

![Diagram](image)

Figure B-4-7: Influent/effluent scheme for gasoline hydrogenation during normal operations

![Diagram](image)
4.5. Intermittent operations

4.5.1. Catalyst reduction / reactivation / hot hydrogen stripping

Catalyst reduction
Before the first use of the catalyst, and after generations, the catalyst is in the oxide form, which is inactive. It has to be reduced with hydrogen to recover its active form. The reduction reaction is the following:

\[ \text{MeO} + \text{H}_2 \rightarrow \text{Me} + \text{H}_2\text{O} \]

(Me corresponds here to the metal used as catalyst, for instance palladium Pd)

The flow of dry reduction gas through the catalyst allows the elimination of the water contained in the catalyst.

Catalyst reactivation / hot hydrogen stripping
Reactivation is hot hydrogen stripping used when the catalyst is deactivated by free water carry-over. These two operations are similar to reduction except the operating temperature.

![Figure B-4-8](image)

*Figure B-4-8: Influents/effluents scheme for C₃ selective hydrogenation during catalyst reduction or reactivation*

![Figure B-4-9](image)

*Figure B-4-9: Influents/effluents scheme for C₄ selective hydrogenation during catalyst reduction, reactivation or stripping*
4.5.2. Catalyst regeneration

The catalyst regeneration can be proceeded in-situ or ex-situ the process. In case of in-situ regeneration or oxidation, effluents are a non negligible issue even if they do not occur often. Indeed these gaseous effluents contain a lot of pollutants that have never really been qualified and quantified and the treatment method currently used seems to not be efficient.

Origin of contaminants

a) Impurities in raw materials

Feed to selective hydrogenation units come from steam cracking or other olefins sources, consequently many impurities are present, that come from upstream processes. In the same way, hydrogen contains impurities. Even if these impurities are in very little quantity, they can fix themselves on the catalyst. When the catalyst is regenerated or oxidised, all these impurities, which are no longer in trace amount as they concentrated, leave the catalyst and go out with the gaseous effluent.

These contaminants are various:
- Sulphur compounds (H₂S, COS, disulphides and mercaptans)
- Methanol and oxygenated compounds
- Nitrogen compounds (HCN, NH₃, amines …)
- Inorganic chlorides and other mineral salts
- Arsenic
- Mercury
- Chlorhydric acid

b) Parasite reactions

As described before, catalyst and operating conditions in selective hydrogenation aim at privilege the hydrogenation of dienes or alkynes into olefins and disadvantage other chemical reactions that could occur. However dimerization (chemical union of two identical molecules) and then oligomerization can occur. It is assumed that 10% of dienes and alkynes are dimerized. In case of C₄ hydrogenation, the product of dimerization is called green-oils. These molecules (C₄ to C₂₀) coat the catalyst and deactivate it but can be removed by regeneration.

Catalyst regeneration principle

During catalyst regeneration procedure, a combustion (or oxidation) is performed in order to burn deposited coke (or green oils). Other impurities can also be stripped by this process.

Operations of catalyst regeneration are a bit different depending from the process. Nevertheless, main steps are more or less the same:
- Heating the catalyst bed by circulating heated nitrogen through the reactor.
- Catalyst bed stripping by establishing a steam circulation through the reactor (this step is not always performed).
- Catalyst pre-oxidation by slowly adding air to the steam.
- Catalyst impurities burning-off by raising temperature and injecting air again.
- Cooling and purge with steam first and then nitrogen.
The out coming gas is consequently contaminated with CO₂ and CO and also unburned coke and other impurities. Here below is a list of compounds that can be found in the effluent regeneration gas:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green oils</td>
<td>10 % of the compound that have to be hydrogenated.</td>
</tr>
<tr>
<td>Sulphur (H₂S, SO₂, SO₃)</td>
<td>(1)</td>
</tr>
<tr>
<td>Mercury</td>
<td>(1)</td>
</tr>
<tr>
<td>Arsenic (AsH₃)</td>
<td>(1)</td>
</tr>
<tr>
<td>Chloride (HCl)</td>
<td>(1)</td>
</tr>
</tbody>
</table>

(1) The quantity of contaminants deposited on the catalyst can not be known. The only data is the maximum content of contaminants in the raw materials.

*Table B-4-2: Compounds possibly present in catalyst regeneration effluents*

**Decoking drum**

The most usual way to treat in-situ regeneration gas in hydrogenation processes are currently decoking drum. This decoking drum is basically a drum in which the gas is simply washed with water before being released in the atmosphere. This washing appears to not be really efficient and pollutants are consequently released both in the atmosphere and in the waste water.

The following tables summarize effluents from each step of catalyst regeneration for each type of process.

<table>
<thead>
<tr>
<th>Gas components</th>
<th>Heating</th>
<th>Stripping</th>
<th>Pre-oxidation</th>
<th>Burning</th>
<th>Cooling 1</th>
<th>Cooling 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>N₂</td>
<td>Steam</td>
<td>Steam + air</td>
<td>Steam + air</td>
<td>Steam</td>
<td>N₂</td>
</tr>
<tr>
<td>Notice</td>
<td>Presence of HC and H₂O</td>
<td>Presence of HC</td>
<td>Presence of CO₂ and HC, impurities (2)</td>
<td>Presence of CO₂ and HC, impurities (2)</td>
<td>Presence of air, impurities (2)</td>
<td>-</td>
</tr>
<tr>
<td>Destination</td>
<td>Flare (3)</td>
<td>Flare (3)</td>
<td>Atmosphere via decoking drum (3)</td>
<td>Atmosphere via decoking drum (3)</td>
<td>Atmosphere via decoking drum (3)</td>
<td>Flare (3)</td>
</tr>
</tbody>
</table>

(1) Refer to operating instructions
(2) Impurities correspond to arsenic, mercury, and other compounds present in trace amount in raw materials and which are trapped on the catalyst.
(3) These are the usual destination but some units can have a special collecting drum.

*Table B-4-3: Gaseous effluents during catalyst regeneration in C₃ selective hydrogenation*
### Heating Oxidation I Oxidation II Air purge

<table>
<thead>
<tr>
<th>Gas components</th>
<th>Heating</th>
<th>Oxidation I</th>
<th>Oxidation II</th>
<th>Air purge</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>N₂ + air O₂ content: 0.3 % vol</td>
<td>N₂ + air O₂ content: 2 % vol</td>
<td>Air</td>
<td></td>
</tr>
</tbody>
</table>

| Flowrate | (1) | (1) | (1) | (1) |

| Notice | Presence of HC | Presence of CO₂ and HC, impurities (2) | Presence of CO₂ and HC, impurities (2) | - |

| Destination | Flare (3) | Decoking drum (3) | Decoking drum (3) | Decoking drum (3) |

(1) Refer to operating instructions
(2) Impurities correspond to arsenic, mercury, and other compounds present in trace amount in raw materials and which are trapped on the catalyst.
(3) These are the usual destination but some units can have a special collecting drum.

**Table B-4-4: Gaseous effluents during catalyst oxidation in C₄ selective hydrogenation**

First stage reactor:

<table>
<thead>
<tr>
<th>Gas components</th>
<th>Heating</th>
<th>Stripping</th>
<th>Pre-oxidation</th>
<th>Burning</th>
<th>Cooling 1</th>
<th>Cooling 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>Steam</td>
<td>Steam + air</td>
<td>Steam + air</td>
<td>Steam</td>
<td>N₂</td>
<td></td>
</tr>
</tbody>
</table>

| Flowrate | (1) | (1) | (1) | (1) | (1) | (1) |

| Notice | Presence of HC + H₂O | Presence of HC | Presence of HC, CO₂ | Presence of HC, CO₂, impurities (2) | - | - |

| Destination | Decoking drum or flare | Decoking drum | Decoking drum | Decoking drum | Decoking drum | Decoking drum or flare |

(1) Refer to operating instructions
(2) Impurities correspond to arsenic, mercury, and other compounds present in trace amount in raw materials and which are trapped on the catalyst.

**Table B-4-5: Gaseous effluents during catalyst regeneration in GHU first reactor**
Second stage reactor:

<table>
<thead>
<tr>
<th>Gas components</th>
<th>Heating</th>
<th>Stripping</th>
<th>Pre-oxidation</th>
<th>Burning</th>
<th>Cooling 1</th>
<th>Cooling 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>N₂</td>
<td>Steam</td>
<td>Steam + air</td>
<td>Steam + air</td>
<td>Steam</td>
<td>N₂</td>
</tr>
<tr>
<td>Flowrate</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>Notice</td>
<td>Presence of HC + H₂O</td>
<td>Presence of HC, H₂S</td>
<td>Presence of HC, H₂S, CO₂</td>
<td>Presence of HC, H₂S, CO₂, impurities (2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Destination</td>
<td>Decoking drum or flare</td>
<td>Decoking drum</td>
<td>Decoking drum</td>
<td>Decoking drum</td>
<td>Decoking drum</td>
<td>Decoking drum or flare</td>
</tr>
</tbody>
</table>

(1) Refer to operating instructions
(2) Impurities correspond to arsenic, mercury, and other compounds present in trace amount in raw materials and which are trapped on the catalyst.

*Table B-4-6: Gaseous effluents during catalyst regeneration in GHU first reactor*

4.5.3. Catalysts sulfurization in the second reactor of gasoline hydrogenation unit

In the gasoline hydrogenation unit, metals of catalysts in the second reactor are in oxide form. They must undergo a treatment to recover the active sulphide form. The operation consists in sweeping the catalyst with a hydrogen steam which contains enough sulfiding agent to sulfurize catalysts.

<table>
<thead>
<tr>
<th>Gas components (%mol)</th>
<th>Sulfurization</th>
<th>Flowrate</th>
<th>Notice</th>
<th>Destination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂ + DMDS (dimethyldisulfide)</td>
<td>(1)</td>
<td>Presence of H₂O, H₂S</td>
<td>Flare</td>
</tr>
</tbody>
</table>

*Table B-4-7: Gaseous effluent during catalyst sulfurization in GHU*

4.6. Effluents characterization

In this part, each effluent (except products from the process) is the most precisely as possible characterized with data available.
4.6.1. Normal operations

Fugitive emissions

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Valves, pump seals, flanges, open-ended valves, relief valves, compressor seals, drains, sample connections.</td>
</tr>
<tr>
<td>Destination</td>
<td>Diffuse in the atmosphere</td>
</tr>
<tr>
<td>Quantity</td>
<td>Can be estimated with the Average Factor Method</td>
</tr>
<tr>
<td>Composition</td>
<td>VOCs</td>
</tr>
</tbody>
</table>

Fugitive emissions are not negligible. They can be estimated thanks to the Average Factor Method which is explained in the part A of this report.

Gas relieves

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Relief valves</td>
</tr>
<tr>
<td>Destination</td>
<td>Flare</td>
</tr>
<tr>
<td>Quantity</td>
<td>?</td>
</tr>
<tr>
<td>Composition</td>
<td>CO₂, VOCs, CO, SOx, NOx</td>
</tr>
</tbody>
</table>

Off-gas

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Recycle drums</td>
</tr>
<tr>
<td>Destination</td>
<td>Sour purge</td>
</tr>
<tr>
<td>Quantity</td>
<td>Estimated in process book</td>
</tr>
<tr>
<td>Composition</td>
<td>H₂, VOC, H₂S</td>
</tr>
</tbody>
</table>

4.6.2. Intermittent operations

Reduction / reactivation gas

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Reactor</td>
</tr>
<tr>
<td>Destination</td>
<td>Flare</td>
</tr>
<tr>
<td>Quantity</td>
<td>Flowrate in operating instruction</td>
</tr>
<tr>
<td>Composition</td>
<td>Presence of HC and H₂O</td>
</tr>
</tbody>
</table>

Regeneration

<table>
<thead>
<tr>
<th>Media</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Reactor</td>
</tr>
<tr>
<td>Destination</td>
<td>Atmosphere, decoking drum</td>
</tr>
<tr>
<td>Quantity</td>
<td>Flowrate in operating instruction</td>
</tr>
<tr>
<td>Composition</td>
<td>CO₂, CO, VOCs, coke, green oils</td>
</tr>
</tbody>
</table>
4.7. Emissions reduction proposals

Air emissions from hydrogenation processes in normal operations arise from fugitive emissions, process vents and process heaters for GHU.

In order to reduce fugitive emissions, a leak detection and repair program can be established (see part A of this report).

Catalyst regeneration is also responsible for air emissions. In order to minimize emissions, appropriate gas treatment systems must be used (such as scrubbers). This measure removes pollutants (green oils) from air to water which still need to be cleaned. Generally it is better to perform ex-situ regeneration in specific factories which have better techniques for catalyst regeneration and effluents treatment. Moreover, coke formation should be minimized by operating conditions control.

Conclusion

This study constitutes a first approach for the development of a complete and precise environmental study of Axens commercialized processes.

Part A of the report emphasizes on common emissions occurring in all refining processes. It allows a general point of view on several issues and gives some solutions to these issues. Fugitive emissions, flue combustion gases, blowdown systems and wastewater emissions are dealt with. Methods to qualify and quantify effluents are explains and environmental technical solutions are cited and shortly described. Part B of the report is more process oriented, and lightens problems concerning particular effluents. Several important processes are analysed. The methodology used to study each process can besides be widespread to analyse other processes.

This study is obviously non exhaustive and many points need to be completed and improved, however it can be used as the starting point to more focused environmental review for Axens processes.
References


### Appendix 1: Average Emission Factors

#### SOCMI Average Emission Factors

<table>
<thead>
<tr>
<th>Equipment type</th>
<th>Service</th>
<th>Emission Factor (kg/hr/source)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>0.00597</td>
<td></td>
</tr>
<tr>
<td>Light liquid</td>
<td>0.00403</td>
<td></td>
</tr>
<tr>
<td>Heavy liquid</td>
<td>0.00023</td>
<td></td>
</tr>
<tr>
<td>Pump seals / Agitator seals</td>
<td>Light liquid</td>
<td>0.0199</td>
</tr>
<tr>
<td></td>
<td>Heavy liquid</td>
<td>0.00862</td>
</tr>
<tr>
<td>Compressor seals</td>
<td>Gas</td>
<td>0.228</td>
</tr>
<tr>
<td>Pressure relief valves</td>
<td>Gas</td>
<td>0.104</td>
</tr>
<tr>
<td>Connectors</td>
<td>All</td>
<td>0.00183</td>
</tr>
<tr>
<td>Open-ended lines</td>
<td>All</td>
<td>0.0017</td>
</tr>
<tr>
<td>Sampling connections</td>
<td>All</td>
<td>0.0150</td>
</tr>
</tbody>
</table>

SOCMI factors are used to determine equipment leak emissions from chemical plants or chemical processes within refineries.

These factors are for total organic compound emission rates.

#### Refinery Average Emission Factors

<table>
<thead>
<tr>
<th>Equipment type</th>
<th>Service</th>
<th>Emission Factor (kg/hr/source)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>0.0268</td>
<td></td>
</tr>
<tr>
<td>Light liquid</td>
<td>0.0109</td>
<td></td>
</tr>
<tr>
<td>Heavy liquid</td>
<td>0.00023</td>
<td></td>
</tr>
<tr>
<td>Pump seals / Agitator seals</td>
<td>Light liquid</td>
<td>0.114</td>
</tr>
<tr>
<td></td>
<td>Heavy liquid</td>
<td>0.021</td>
</tr>
<tr>
<td>Compressor seals</td>
<td>Gas</td>
<td>0.636</td>
</tr>
<tr>
<td>Pressure relief valves</td>
<td>Gas</td>
<td>0.16</td>
</tr>
<tr>
<td>Connectors</td>
<td>All</td>
<td>0.00025</td>
</tr>
<tr>
<td>Open-ended lines</td>
<td>All</td>
<td>0.0023</td>
</tr>
<tr>
<td>Sampling connections</td>
<td>All</td>
<td>0.0150</td>
</tr>
</tbody>
</table>
Refinery factors are used to determine equipment leak fugitive emissions from a refinery process. For a chemical process located within a refinery that is not specifically considered a refinery process (for example, an MTBE production unit), the SOCMI factors must be used rather than the refinery factors.

These factors are for non-methane organic compound emission rates.

Oil and Gas Production Operations Average Emission Factors

<table>
<thead>
<tr>
<th>Equipment type</th>
<th>Service</th>
<th>Emission Factor (kg/hr/source)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td>Gas</td>
<td>4.5 E-03</td>
</tr>
<tr>
<td></td>
<td>Heavy oil</td>
<td>8.4 E-06</td>
</tr>
<tr>
<td></td>
<td>Light oil</td>
<td>2.5 E-03</td>
</tr>
<tr>
<td></td>
<td>Water / Oil</td>
<td>9.8 E-05</td>
</tr>
<tr>
<td>Pump seals</td>
<td>Gas</td>
<td>2.4 E-03</td>
</tr>
<tr>
<td></td>
<td>Heavy oil</td>
<td>Non available</td>
</tr>
<tr>
<td></td>
<td>Light oil</td>
<td>1.3 E-02</td>
</tr>
<tr>
<td></td>
<td>Water / Oil</td>
<td>2.4 E-05</td>
</tr>
<tr>
<td>Others</td>
<td>Gas</td>
<td>8.8 E-03</td>
</tr>
<tr>
<td></td>
<td>Heavy oil</td>
<td>3.2 E-05</td>
</tr>
<tr>
<td></td>
<td>Light oil</td>
<td>7.5 E-03</td>
</tr>
<tr>
<td></td>
<td>Water / Oil</td>
<td>1.4 E-02</td>
</tr>
<tr>
<td>Connectors</td>
<td>Gas</td>
<td>2.0 E-04</td>
</tr>
<tr>
<td></td>
<td>Heavy oil</td>
<td>7.5 E-06</td>
</tr>
<tr>
<td></td>
<td>Light oil</td>
<td>2.1 E-04</td>
</tr>
<tr>
<td></td>
<td>Water / Oil</td>
<td>1.1 E-04</td>
</tr>
<tr>
<td>Flanges</td>
<td>Gas</td>
<td>3.9 E-04</td>
</tr>
<tr>
<td></td>
<td>Heavy oil</td>
<td>3.9 E-07</td>
</tr>
<tr>
<td></td>
<td>Light oil</td>
<td>1.1 E-04</td>
</tr>
<tr>
<td></td>
<td>Water / Oil</td>
<td>2.9 E-06</td>
</tr>
<tr>
<td>Open-ended lines</td>
<td>Gas</td>
<td>2.0 E-03</td>
</tr>
<tr>
<td></td>
<td>Heavy oil</td>
<td>1.4 E-04</td>
</tr>
<tr>
<td></td>
<td>Light oil</td>
<td>1.4 E-03</td>
</tr>
<tr>
<td></td>
<td>Water / Oil</td>
<td>2.5 E-04</td>
</tr>
</tbody>
</table>

These factors are for total organic compound emission rates.
Appendix 2: Example calculation of fugitive emissions

Assuming a process operating gaseous product, calculation of fugitive emissions can be done like following.

Data for example calculation:

<table>
<thead>
<tr>
<th>Equipment type / service</th>
<th>Equipment count</th>
<th>Hours of operation* (hr/yr)</th>
<th>VOC wt. fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves / gas</td>
<td>272</td>
<td>8760</td>
<td>1</td>
</tr>
<tr>
<td>Compressors / gas</td>
<td>3</td>
<td>8760</td>
<td>1</td>
</tr>
<tr>
<td>Relief valves</td>
<td>37</td>
<td>8760</td>
<td>1</td>
</tr>
<tr>
<td>Open-ended lines</td>
<td>489</td>
<td>8760</td>
<td>1</td>
</tr>
<tr>
<td>Sampling connections</td>
<td>24</td>
<td>8760</td>
<td>1</td>
</tr>
</tbody>
</table>

* Hours of operation include all time in which material is contained in the equipment.

<table>
<thead>
<tr>
<th>Source</th>
<th>Equipment count</th>
<th>Emission factor (kg/hr/source)</th>
<th>VOC emissions rate (kg/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td>272</td>
<td>0.0268</td>
<td>7.2896</td>
</tr>
<tr>
<td>Compressor seals</td>
<td>3</td>
<td>0.636</td>
<td>1.908</td>
</tr>
<tr>
<td>Relief valves</td>
<td>37</td>
<td>0.16</td>
<td>5.92</td>
</tr>
<tr>
<td>Open-ended lines</td>
<td>489</td>
<td>0.0023</td>
<td>1.1247</td>
</tr>
<tr>
<td>Sampling connections</td>
<td>24</td>
<td>0.015</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Total VOC emissions (t/yr) 145.4

VOC emissions rate = equipment count * wt. fraction * emission factor

Total VOC emissions = sum [VOC emissions rate] * hours of operation