

"Capacity Building and Strengthening Institutional Arrangement"

Workshop: Quantitative risk assessment of oil and gas plants

EU and Italian standards for Oil and Gas industries evaluation impacts 2nd part

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EU and Italian standards for Oil and Gas industries evaluation impacts

• <u>EU</u>:

Integrated Pollution Prevention and Control (IPPC)- Reference Document on Best Available Techniques (**BAT**) for Mineral Oil and Gas Refineries - **BREF**, February 2003.

Italy:

IPPC - Guidelines for identification of BAT

MTD, October 2005.



- The purpose of refining is to convert natural raw materials such as crude oil and natural gas into useful saleable products.
- Crude oil and natural gas are naturally occurring hydrocarbons found in many areas of the world in varying quantities and compositions.
- In refineries, they are transformed into different products as: fuels for cars, trucks, aeroplanes, ships and other forms of transport combustion fuels for the generation of heat and power for industry and households raw materials for the petrochemical and chemical industries speciality products such as lubricating oils, paraffins/waxes and bitumen energy as a by-product in the form of heat (steam) and power (electricity).



- In order to manufacture these products, these raw materials are processed in a number of different refining facilities.
- The combination of these processing units to convert crude oil and natural gas into products, including its supporting units and facilities, is called a refinery.



- The market demand for the type of products, the available crude quality and certain requirements set by authorities influence the size, configuration and complexity of a refinery.
- As these factors vary from location to location no two refineries are identical.



EU approach

Amongst the many environmental issues addressed in the BREF, the five that are dealt with below are probably the most important:

- increase the energy efficiency (~32 BAT identified);
- reduce the nitrogen oxide (NOx) emissions (~17 BAT id.);
- reduce the sulphur oxide (SOx) emissions (~38 BAT id.);
- reduce the volatile organic compounds (VOC) emissions (~19 BAT identified);
- reduce the contamination of water (~21 BAT identified).



- <u>Emerging techniques</u>: include the techniques that have not yet been commercially applied and are still in the research or development phase.
- The environmental situation of European refineries varies greatly across the European Community, so the starting point for each case is very different.
- Different environmental perceptions and priorities are also evident.



- In preparation for future BREF reviews, all interested parties should continue to collect data on the current emission and consumption levels and on the performance of techniques to be considered in the determination of BAT.
- For the review it is also important:

- to collect more data on the achievable emission and consumption levels and the economics of all production processes under analysis;

- it is also important to continue collecting information on energy efficiency.



Main environmental issues in the refining sector

- Refineries are industrial sites that manage huge amounts of raw materials and products and they are also intensive consumers of energy and water used to carry out the process;
- In their storage and refining processes, refineries generate emissions to the atmosphere, to the water and to the soil, to the extent that environmental management has become a major factor for refineries;
- The refining industry is a mature industry and pollution abatement programmes have been carried out in most refineries for a long time to different extends;
- The emissions generated by refineries have declined per tonne of crude processed and are continuing to decline.



- It is important to know, with respect to the quality and quantity of refinery emissions, that on a macro scale the crude oils vary only to a certain extent in their composition;
- Moreover, refineries are often limited to a comparatively narrow range of crude oil diets;
- Normally, when switching from one crude oil to another within this range, large variations in refinery emissions are not usually expected;
- Consequently the type and quantity of refinery emissions to the environment are well known during normal operations;
- However, from time to time, processing of crude oils previously unknown to the refinery can have unforeseen impacts on the performance of refinery processes, leading to an increase in emissions;
- This is particularly likely to affect aquatic emissions and to a lesser extent air emissions.



Emissions to the atmosphere

- Refinery processes require a lot of energy; typically more than 60 % of refinery air emissions are related to the production of energy for the various processes.
- Sulphur recovery units and flares also contribute to those emissions.
- Catalyst changeovers and cokers release particulates.
- Volatile organic compounds (VOCs) are released from storage, product loading and handling facilities, oil/water separation systems and, as fugitive emissions, from flanges, valves, seals and drains.
- Other emissions to the atmosphere are H2S, NH3, BTX, CS2, COS, HF and metals as constituents of the particulates (V,Ni and others).
- Main air pollutants emitted by refineries and their main sources are:



Main air pollutants	Main sources			
Carbon dioxide	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Flare systems Incinerators			
Carbon monoxide	Process furnaces and boilers Fluidised catalytic cracking regenerators CO boilers Sulphur recovery units Flare systems Incinerators			
Nitrogen oxides (N ₂ O, NO, NO ₂)	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Incinerators Flare systems			
Particulates (including metals)	Process furnaces and boilers, particularly when firing liquid refinery fuels Fluidised catalytic cracking regenerators CO boilers Coke plants Incinerators			
Sulphur oxides	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Sulphur recovery units (SRU) Flare system Incinerators			
Volatile organic compounds (VOCs)	Storage and handling facilities Gas separation units Oil/water separation systems Fugitive emissions (valves, flanges, etc.) Vents Flare systems			



- Particulate emissions have become a focus of attention because of their potential adverse health effects.
- Particulate emissions are caused by combustion of fuel oils, especially when there is sub-optimal combustion.
- Another source is the catalytic cracker (catcracker).

Emissions to water

- Water is used intensively in a refinery as process water and for cooling purposes.
- Its use contaminates the water with oil products mainly increasing the oxygen demand of the effluent.



- Refineries discharge waste water which originates from:
 - Process water, steam and wash water.
 - Cooling water, once-through or circulating systems.
 - Rainwater from process areas.
 - Rainwater from non-process areas.
- Oil and hydrocarbons are the main pollutants found in waste water generated by refineries.
- Other pollutants found in waste water generated by refineries are hydrogen sulphide, ammonia, phenols, benzene, cyanides and suspended solids containing metals and inorganic compounds (e.g. halides, sulphates, phosphates, sulphides).



Summary of the main water pollutants as well as their main sources:

Water pollutant	Source		
Oil	Distillation units, hydrotreatment, visbreaker, catalytic cracking,		
	hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)		
H ₂ S (RSH)	Distillation units, hydrotreatment, visbreaker, catalytic cracking,		
	hydrocracking, lube oil, spent caustic		
NH ₃ (NH ₄ ⁺)	Distillation units, hydrotreatment, visbreaker, catalytic cracking,		
	hydrocracking, lube oil, sanitary/domestic		
Phenols	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast		
	water		
Organic chemicals	Distillation units, hydrotreatment, visbreaker, catalytic cracking,		
(BOD, COD, TOC)	hydrocracking, lube oil, spent caustic, ballast water, utilities (rain),		
	sanitary/domestic		
CN', (CNS')	Visbreaker, catalytic cracking, spent caustic, ballast water		
TSS	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast		
	water, sanitary/domestic		



 Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted to prevention and reduction.

Waste generation

- The amount of waste generated by refineries is small if it is compared to the amount of raw materials and products that they process;
- Oil refinery waste normally covers three categories of materials:

- *sludges*, both oily (e.g. tanks bottoms) and non-oily (e.g. from waste water treatment facilities);



- other refinery wastes, including miscellaneous liquid, semi-liquid or solid wastes (e.g. contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator ash, spent caustic, spent clay, spent chemicals, acid tar);
- non-refining wastes, e.g. domestic, demolition and construction.
- Summary of the main types of solid wastes generated in a refinery and their sources:



Type of waste	Category	Source
Oiled materials	oily sludges	tank bottoms, biotreatment sludges, interceptor sludges, waste water treatment sludges, contaminated soils, desalter sludges
	solid materials	contaminated soils, oil spill debris, filter clay acid, tar rags. filter materials, packing, lagging, activated carbon
Non-oiled materials	spent catalyst (excluding precious metals)	Fluid catalytic cracking unit catalyst, hydrodesulphurisation / hydrotreatment) catalyst, polymerisation unit catalyst, residue conversion catalyst
	other materials	resins, boiler feed water sludges, desiccants and absorbents, neutral sludges from alkylation plants, FGD wastes
Drums and containers		metal, glass, plastic, paint
Radioactive waste (if used)		catalysts, laboratory waste
Scales		leaded/unleaded scales, rust
Construction/demolition debris		scrap metal, concrete, asphalt, soil, asbestos, mineral fibres, plastic/wood
Spent chemicals		laboratory, caustic, acid, additives, sodium carbonate, solvents, MEA/DEA (mono/di-ethanol amine), TML/TEL (tetra methyl/ethyl lead)
Pyrophoric wastes		scale from tanks/process units
Mixed wastes		domestic refuse, vegetation
Waste oils		lube oils, cut oils, transformer oils, recovered oils, engine oils



- Oil retained in sludges or other type of wastes represents a loss of product and, where possible, efforts are made to recover such oil;
- Waste disposal depends very much on its composition and on the local refinery situation;
- Because of the high operating costs of waste disposal, much priority has been given to waste minimisation schemes.



- Waste generation trends during the last ten years show that oily sludge production is declining, mainly through housekeeping measures, whereas biological sludge generation has increased as a result of increased biotreatment of refinery effluent.
- Spent catalysts production is also increasing through the installation of new hydrocrackers, hydrotreatment facilities and catalytic cracker dust collectors.
- For all these waste categories increased use is made of third party waste contractors for off-site treatment and disposal.



Soil and Groundwater contamination

- Most refineries have some areas that are contaminated by historical product losses. Current refinery practices are designed to prevent spillages and leaks to ground.
- In the past, the awareness of the potential risks of these contaminated areas was low.
- The two main topics here are prevention of new spills and remediation of historic contamination.
- Increased knowledge about soil sciences and the difficulty of soil remediation on a site that is still in operation, has lead to the pragmatic approach of managing the risks of these contaminated sites to ensure their fitness for use and ensuring that pollution does not spread beyond the site.



- There are a number of ongoing research initiatives for improving the performance of on-site remediation techniques.
- The main sources of contamination of soil and groundwater by oil are typically those places along the handling and processing train of crude to products where hydrocarbons can be lost to the ground.
- These are commonly associated with the storage, transfer, and transport of the hydrocarbons themselves or of hydrocarbon-containing water.
- The possibility of contamination by other substances such as contaminated water, catalysts and wastes also exists.



Other environmental issues

- Nuisance has become an issue of discussion with both local authorities and with representatives of the local population in so-called neighbourhood councils.
- Topics such as noise, light and smoke emission (flaring) and smell which directly impact the residents receive much more emphasis in these neighbourhood councils than the abovementioned 'major' emissions which tended to receive more attention historically.
- Nuisance by light can be caused through flaring at night by refineries and petrochemical plants located near densely populated areas.



- Occupational health is included in the operational safety procedures aimed at protecting workers from exposure to toxic materials and providing them with all necessary facilities which contribute to their wellbeing and their sense of security and safety.
- Instructions, information exchange and training of personnel, the provision of personal protection equipment as well as strict adherence to stringent operational procedures have contributed to a steady decrease in accidents and health incidents.
- Typical refinery pollutants and products with a health risk include hydrogen sulphide, BTEX (of which benzene is the most prominent), ammonia, phenol, HF, NOx and SOx, for which legally binding Maximum Acceptable Concentrations values prevail.



- The design of the refinery installations and the process control systems needs to include provisions for a safe shut-down with minimum emissions from the unit involved.
- During unplanned operational upsets, these provisions should guarantee that feed supply is terminated followed by subsequent pre-programmed automated activation of pumps, relief systems, purging systems, flares and other equipment.
- Examples of such occurrences are utility failure, breakdown of equipment, a fire or an explosion.



- Emergency situations leading to direct spills occurring in parts of the plant which are neither fully contained nor fully automated, such as pipeline and tank bottom rupture, have to be addressed with standing emergency procedures.
- These are directed to minimisation and containment of the spills, followed by rapid clean-up in order to minimise the environmental impact.



BAT and Environmental approaches

•**Bottom-up approach**: each <u>process/activity</u> of the industrial sector is analysed from the environmental point of view. Some issues need to be analysed across the whole installation.

• **Top-down approach**: a certain environmental goal is given to the <u>whole</u> <u>installation</u>. This approach is applied in environmental regulation of refineries in particular for air emissions.



Generic (whole Refinery) BAT

Emissions to air are the most important environmental concern of refineries.

Reduction of Emissions to Air:

Overall reduction is achieved by a combined effort on the performance of the "processes/activities" (i.e. improved Sulfur Recovery Unit, application of low NOx techniques) and on the performance of the "integrated/whole" installation (i.e. energy efficiency, fuel management, S balance).

<u>BAT</u> is to:

- *Improve* the energy efficiency (reduction of all air pollutants generated by combustion) by enhancing heat integration and recovery throughout the refinery, applying energy conservation techniques and optimising the energy production/consumption;



Energy Intensity Index (EII)

is a measure used to compare energy consumption in refineries.

- for only 10 EU+ refineries, data range from 58 to 94.
- the index for the world refineries ranges between 55 and 165;
- lower values correspond to more energy-efficient refineries.
- the standard energy use is based on the energy consumption at about 300 refineries worldwide.

The average *Ell* obtained in a worldwide market survey (Solomon study, 1994) was <u>92</u>, with a range from 62 to 165 [Janson, 1999].



Egyptian and Italian Cooperation Programme on Environment Quantitative Risk Assessment of Oil and Gas Plants





BAT is to:

- **Use** clean refinery fuel gas (RFG) e liquid fuel (if necessary) combined with control and abatement techniques or other fuel gases such as natural gas or LPG.
- *Reduce* SOx emissions.
- Reduce NOx emissions.
- *Reduce* Particulate emissions.

Reduction of Discharges to Water

<u>BAT</u> for reduction of discharges to water is to:



- Apply a water management scheme aimed at reducing:
 - the volume of water used in the refinery by:
 - 1. re-using as much as possible the cleaned waste water;

2. applying techniques to reduce waste water generated within each specific process/activity;

- the contamination of water by:
 - 1. segregation of contaminated, low-contaminated or non-contaminated water streams and drainage systems;
 - 2. segregation of "once-through" cooling water;
 - 3. good housekeeping in operation and maintenance of existing facilities;
 - 4. spill prevention and control;

5. applying techniques to reduce contamination of waste water within each specific process/activity.



Achieve the following water parameters in the Waste Water Treatment Plant (WWTP) effluent:

Parameters	Concentration	Load
	(mg/l)	(g/tonne crude oil or
	(monthly average) ²	feedstocks processed)*
		(yearly averages)
Total hydrocarbon content	0.05 - 1.51	0.01 - 0.754
Biochemical oxygen demand (5 day ATU @ 20 °C)	2 - 20	0.5-11
Chemical oxygen demand (2 hour)	30 - 1253	3 - 703
Ammoniacal ninogon (as N)	$0.25 - 10^{4}$	0.1 - 6
Total mitrogen	$1.5 - 25^3$	0.5 - 156
Suspended solids (dried @ 105 °C)	2 - 50'	1-25
Total matals (As. Cd. Co. Cr. Cu. Hg. Ni. Pb. V. Zn) [#]	<0.1 - 4	



Solid Waste Management (SWM)

<u>BAT</u> for SWM is to:

- implement a SWM System that includes: an annual reporting of waste quantities, a plan with measures for waste reduction (recycling and/or recovery), an operation of WWTP so as to maximise performance with the mimimum of sludge production;
- minimise oil spills and exclude oil spills that contaminate the soil by:

1. a plan to exclude leakage from pipework and tanks including inspection, corrosion monitoring, leak detection instruments, double bottoms, etc.;

2. a risk analysis to rank where an accidental leak may occur;

3. a designing of new installations with the minimum of underground piping;



 apply techniques to reduce SW generated within each specific process/activity.

BAT for Process/Activity

- BAT for Alkylation
- BAT for Base Oil Production
- BAT for Bitumen Production
- BAT for Catalytic Cracking
- BAT for Catalytic Reforming
- BAT for Coking Processes
- BAT for Cooling Sytems
- BAT for Desalting
- BAT for the Energy System
- BAT for Etherification



- BAT for the Gas Separation Processes
- BAT for Hydrogen consuming Processes
- BAT for Hydrogen Production
- BAT for Integrated Refinery Management
- BAT for Isomerisation
- BAT for Natural Gas Plants
- BAT for Polymerisation
- BAT for Primary Distillation Units
- BAT for Product Treatments
- BAT for Storage and Handling of refinery materials
- BAT for Visbreaking
- BAT for Waste Gas Treatments
- BAT for Waste Water Treatments
- BAT for Solid Waste management



Emerging Techniques

- Emerging tecnique is understood as a novel technique that not yet been applied in any industrial sector on a commercial basis.

References

 Integrated Pollution Prevention and Control (IPPC).
Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries - February 2003.