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# Best Available Technology to Reduce Emissions of Pollutants from Oil Refining Industry

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## Abstract

*This paper presents a typical analysis concerning the reduction of pollutants emissions into the air from oil refining industry by using the Best Available Technology procedure. The pollutants ejected in atmosphere as $SO_2$,, $NO_x$ and volatile organic compounds (VOC) were studied and their reduction was related with investment and operating costs, with efficiency of the cleaning process and with other unit' impacts.*

**Key words:** *BAT, pollutant, fuel, air, emissions*

## Introduction

The term "Best Available Technology" (BAT) is taken to mean the latest stage of development (state of the art) of processes, of facilities or of methods of operation which indicate the practical suitability of a particular measure for limiting discharges [1].

In determining whether a set of processes, facilities and methods of operation constitute the best available technology in general or individual cases, special consideration should be given to:

- comparable processes, facilities or methods of operation which have been recently successfully tried out;
- technological advances and changes in scientific knowledge and understanding;
- the economic feasibility of such technology;
- time limits for application;
- the nature and volume of the effluents concerned;
- the precautionary principle, i.e. action should be taken when there is reason to assume that certain damage or harmful effects on the living resources of the sea are likely to be caused by discharged substances, even where there is no scientific evidence to prove a causal link between discharges and effects caused by substances.

In a previous paper we have presented a case study concerning the Best Available Technology applied into a Fluid Catalytic Cracking in order to reduce the emissions of pollutants in atmosphere [2]. It was also presented the legislative system and emissions limits for $SO_2$, $NO_x$ and particulates.

## BAT Applied to Refining Industry

Best Available Technology in the refining industry is different in function of methodological approaches like:

- to consider refinery as a whole (black box = bubble) and identify global emissions limits no referring explicit to any given technology;
- to make a breakdown of the refinery in various elementary units or functions (group of units) and then to identify the BAT for these units/functions and decide emissions units for each one.

Both approaches have their advantages and disadvantages (table 1):

**Table 1.** Comparison of the methodological approaches [3]*

| Approach | Advantage | Disadvantage | References |
|---|---|---|---|
| GLOBAL (Bubble) | a. Simple<br>b. Easy to crate a standard | a. Not precise<br>b. Not too explicit for technological analysis | Many directives from EC |
| FUNCTION | a. Not too complex<br>b. Rigorous<br>c. Systematic | Global emissions not taken into account | Other technical notes |
| UNIT | a. Systematic<br>b. Rigorous | a. Very complex<br>b. "Old-fashioned" when new process appear | Choice made in USA |

** In certain case the "unit/function" approach is most rigorous and is used in UE member states. In the other cases, global (bubble) approach is more flexible and gives industry the choice on how to implement technologies to achieve emissions limits. It is used in several member states, especially for establishing $SO_2$ emissions limits.*

The functions which may lead to noticeable emissions are:

- Sulfur recovery (SRU);
- Fluid catalytic cracking (FCC);
- Coking and other thermal conversion processes;
- Storage and loading.

Many of other processes of the refinery are carried-out in closed systems and have insignificant emission under normal conditions. One exception is the excess gas produced in the case of a unit malfunctioning. This gas is collected into the flare gas system. This flare gas system will be analyzed together with the refinery fuel system.

To make an assessment of the inter-functional aspects of managing a refinery with a view to air emissions, the most important aspects are:

- Fuel management;
- Catalyst management;
- Operational control and design measures.

This assessment includes a general review of the "state of the art" together with possible Best Available Technologies that may be used for reducing emissions. This approach has led to the identification of the technologies which are listed in the table 2 and will be analyzed in detail in following sections.

## BAT Analysis for Sulfur Recovery Unit (SRU)

The chemical reactions in Sulfur recovery unit are:

a. In the combustion furnace:

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$$

b. In reactors (2 or 3 stages)

$$SO_2 + 2\ H_2S \rightarrow 3/2\ S + 2\ H_2O$$

Global yield in terms of sulfur recovery can be calculated with the following relation:

*YIELD (% mass) = 100 x (Sulfur production) / (Sulfur content in the sour gas)* (1)

A typical yield of 2 stage SRU = 94 – 96 %. When the gas flow is lower than specified design parameters the yield decreases rapidly, and in this situation sulfur emissions may increase.

**Table 2**. Technologies to be analyzed for pollutant emissions reduction [4]

| Pollutant | SPECIFIC FUNCTIONS | | INTER-FUNCTIONAL ASPECTS | | |
|---|---|---|---|---|---|
| | **Sulfur recovery** | **Storage/ Loading** | **Fuel** | **Operational design** | **Waste water treatment** |
| $SO_2$ | -3-rd reactor<br>-new design<br>- tail gas clean-up unit | – | - Flue gas desulphurization<br>-$SO_2$management<br>-Use of low sulfur fuels | – | – |
| $NO_x$ | – | – | -Low $NO_x$ burner<br>- Selective catalytic reduction<br>-Thermal de-$NO_x$ | – | – |
| VOC | – | -Floating roof or cover<br>-Vapor recuperation system | | - Monitoring<br>-Maintenance | - Float cover<br>- Drums |
| Particulates | – | | - Cyclone<br>- Multi-cyclones<br>-Electrostatic precipitator<br>-Wet scrubber | – | – |

Most of refineries have 2 or more SR units installed. Normally they operate under shared load. If one unit is shut down for any reason the majority of its load can be switched to the other running unit minimizing the increase in emissions. If required, changes can then be made to the main process units to reduce the quantity of $H_2S$ produced.

Emissions limits for a SRU should then take into account the 2 parameters: yield and availability, in addition to its capacity.

With the exception of $CO_2$ arising from the combustion furnaces there are no other notable emissions from the SRU other than $SO_2$.

## Technologies to Prevent/Reduce Emissions

Tail gas from a SRU contains $SO_2$ and $H_2S$ totaling 5% of total sulfur intake for a plant with a yield of 95%. For a production of 30 000 tons of S/year, sulfur emissions are 1580 tons (or 3160 of $SO_2$).

Improvement of the yield and consequently reduction of sulfur emissions can be obtained through for principal technologies and/or a combination of them:

- addition of a third reactor;
- improvement of the performance of reactors through new design (new units);
- addition of a tail gas clean-up unit (TGCU).

These technologies are widely considered as the best available to prevent/reduce $SO_2$ emissions. For instance, the addition of a TGCU to a three stage SRU achieves at design conditions yields in the range of 98 – 99,9%. But it is important to know that the efficiency of SRU may fall of at flows below design. The BAT analysis regarding $SO_2$ emission control for Sulfur recovery unit is shown in table 3.

**Table 3.** Analysis of BAT regarding $SO_2$ emission control (SRU)
***Capacity of the unit: 30 000 t/yr of Sulfur production (yield = 94 - 96%, 2 stages)***
***Initial pollutant concentration: 34 000 mg $SO_x/Nm^3$; Total $SO_2$ quantity: 2000 t/yr***

| Name of technology | 3-rd Reactor | 3-rd Reactor *Improved Reactor Design *Improved catalyst | Tail gas clean-up unit |
|---|---|---|---|
| Overall eficiency | 97 % | 98 – 99 % | 98 – 99,9 % |
| Investment cost | 2 Million Euro | 2,5 Million Euro | 3 – 10 Million Euro |
| Operating cost | 0,1 Million Euro/yr | 0,1 Million Euro/yr | 0,1 – 0,5 Million Euro/yr |
| Other impacts | Negligible | Negligible | Increased energy consumption |

## BAT Analysis for Storage and Loading

Crude oil, other feedstock and petroleum products are stored in various tanks and supplied to and shipped from refineries by:

- pipelines;
- tank trucks;
- rail tank cars;
- barges;
- sea-going vessels.

There are two major sources of VOC emissions from storage and loading as:

- breathing losses (in tanks);
- working losses (displacement and withdrawal).

### Control of Emissions from Storage

The bulk storage of volatile products takes place in the following tanks:

- floating roof tanks with efficient seals or fixed roof tanks incorporating an internal floating roof with high efficiently seals;
- fixed roof tanks which, for a given product or intermediate, have balancing lines or other means for vapor recovery (absorption etc.)

### Control of Emissions from Loading/Unloading

***A. Vessels and barges***: displaced vapor containing air/gas recycled or routed through a vapor recovery unit or incinerator unit;

***B. Rail tanks/road trucks***: for loading/unloading of rail tanks or road trucks there are two alternatives:

1. ***Bottom loading***: the loading/unloading pipe is flange connected to a nozzle situated at the lowest point of the tank. A vent pipe on top of the tank is connected to a gas balancing line;
2. ***Top loading***: a flexible joint pipe is introduced into the tank through the upper tank opening. The tank opening should be closed by means of a flexible, elastic cone fixed to the filling pipe or by other means. The displaced air/gas is collected by a second line and treated as described above.

The available technologies for emissions decreasing are:

- Incineration of vented products in process heaters, special combustors or flares;
- Vapors recovery units, by:
  - a gas collecting or balancing system;
  - a recovery system utilizing adsorption, absorption, condensation or incineration of VOC.

The VOC emission control by BAT analysis for storage and loading unit is presented in table 4.

**Table 4.** Analysis of BAT regarding VOC emission control (Storage and loading)
***Storage emissions = 0,19% of throughput of volatile products with fixed roof tanks***
***Loading emissions = 0,05% of throughput of volatile products without vapor recovery***

| Name of technology | Floating roof tanks | Fixed roof internal cover tanks | Secondary seals for gasoline storage | Vapor recovery for fixed tanks | Vapour recovery systems (for loading) | |
|---|---|---|---|---|---|---|
| | | | | | Single stage | Double stage |
| Efficiency | 95 % (0,009% on throughput) | 90 % (0,02% on throughput) | 98 % | 93-99% (down to 10 g/Nm$^3$) | 93-99% (down to 10 g/Nm$^3$) | Near 100% (down to 150 mg/Nm$^3$) |
| Investment cost | 0,26 Million Euro per tank (D = 20 m) | 0,2 Million Euro per tank (D = 20 m) | 140 Euro/ linear meter | 1 Million Euro for 4 tanks (D = 20m) | 1,3 Million Euro for 4 tanks (D = 20 m) | 1,8 Million Euro for 4 tanks (D = 20m) |
| Operating cost | No operating costs Products savings give opportunity benefits | | | 0,05 Million Euro/yr | 0,05 Million Euro/yr | 0,12 Million Euro/yr |
| Other impacts | - | - | - | Recovery of products | Recovery of products | Recovery of products |

# Fuel Management

Fuel management has a primary objective of optimizing refinery operating costs and in this BAT context it involves the effective utilization of refinery hydrocarbon streams for the production of process heat and utilities (steam and/or power) while minimizing the impact of the environment.

The following factors may impose major constraints of the fuel system:

- refinery configuration and crude oil type (sulfur content);
- fuel requirements in relation to quantity and quality of available fuels;
- safety and environmental restrictions;
- climate and/or local conditions;
- operational flexibility or limitations with reference system;
- complexity with respect to number of units and their various interdependent operational constraints;
- age of the various units and technology restrictions;

- high degree of process and energy integration of various units.

The structure of refinery fuels is quite simple. There are three types of fuels: gas, liquid and solid. The gas fuel source is assured by the refinery light gas fraction and by natural gas from the external producers. The liquid fuel is a mixture of liquid residues from crude oil distillation, thermal processes, catalytic cracking and other heavy fractions without other utilization.

## Aspects of $NO_x$ Emissions of Refining Fuels

Fuel gas composition, burner design, furnace design and operating conditions determine $NO_x$ from gas firing (Table 5)

**Table 5**. $NO_x$ emissions ranges for existing and new equipments ($NO_x$ as $NO_2$)

**A. Existing (mg/Nm$^3$)**

| Equipment type | Gas (Natural + refinery) | Liquid refinery fuel (Atmospheric and Vacuum residue) | Particulates (fuel oil firing) |
|---|---|---|---|
| Process furnaces | 160 – 1300 | 280 – 1000 | 500 - 1000 |
| Boilers | 280 - 1100 | 500 - 1000 | 200 - 250 |

**Gas turbines (g/ GJ)**

| Fuel gas type | Without steam injection | With steam injection |
|---|---|---|
| Cat cracker off gas | 320 - 350 | 125 – 140 |
| Natural gas | 240 -700 | 100 - 120 |

**B. Expected $NO_x$ for new furnaces with optimal burner and furnace design**

| Process furnaces | Gas (Natural + refinery) | Liquid refinery fuel (Atmospheric and Vacuum residue) | Particulates (fuel oil firing) |
|---|---|---|---|
| Process furnaces (mg/Nm$^3$) | 100 - 120 | About 250 | About 500 |
| Boilers (mg/Nm$^3$) | 60 - 120 | About 250 | About 500 |
| Gas turbine (g/GJ) | 65 - 120 | N.A. (not applicable) | N.A. |

Regarding liquid refinery fuels this is composed by a mixture of:

- Atmospheric Residue;
- Vacuum Residue;
- Thermal and Catalytic Cracking Residue;
- Hydroconversion Residue.

The liquid refinery fuels have different sulfur content as a function of crude oil source (table 6).

**Table 6.** Sulfur content in liquid refinery components

| Crude oil source | Sulfur content, mass % | | |
|---|---|---|---|
| | Atmospheric Residue | Vacuum Residue | Cracked Residue |
| North Sea | 0,6 – 1,1 | 1,1 – 1,8 | 3,5 – 6,5 |
| Middle East | 2,3 – 4,4 | 3,6 – 6,1 | 6,5 – 11,4 |

The BAT analysis regarding $SO_2$ emissions control is presented in table 7 and of $NO_x$ emissions control is presented in table 8. This case study is made for a power unit of 500 MW where 3 M tons/year of gaseous and liquid fuel is burned. The volume of flue gas is 1680· $10^6$ $Nm^3$/yr and initial pollutant concentration of $SO_2$ is a function of sulfur content of fuels. For $NO_x$, the initial concentration is variable and the final pollutant concentration is a function of the cleaning process.

**Table 7.** Analysis of BAT regarding $SO_2$ emission control
***Capacity of the process = 3 Mt/yr (120000 t/yr liquid fuels + 180000 t/yr gaseous fuel)***
***Volume of flue gas = 1680·$10^6$$Nm^3$/yr***
***Initial pollutant concentration: 5000 mg $SO_x$/$Nm^3$ (for liquid fuels with 3% S) ;***
***Total $SO_2$ quantity: 8400 t/yr***

| **Name of technology** | **Flue gas desulfuri-zation** | **Regenerative catalytic flue gas desulfurization** | **Refining $SO_2$ management operation** | **Liquid fuel desulfuri-zation** | **Gasification of liquid fuel** |
|---|---|---|---|---|---|
| Efficiency | 90 % (500 mg/$Nm^3$) | Up to 95-98 % (100 – 250 mg/$Nm^3$) | Global | Up to 85 % (down to 750 mg/$Nm^3$) | Replacement of most liquid fuels by gaseous fuel with 0,01 S% |
| Investment cost | 30 – 50 Million Euro | 50 – 80 Million Euro | 0 | 100 – 300 Million Euro | 200 – 400 Million Euro |
| Operating cost | 5 Million Euro/yr | Variable | Variable | 20 – 50 Million Euro/yr | 20 – 40 Million Euro/yr |
| Other impacts | -Increased energy consumption; -By product; -Raw material handing. | -Increased energy consumption; -Possible bottlenecking of $H_2S$ handing facilities. | - | -Increased energy consumption; -Catalyst disposal; -Marketing low sulfur fuel oil. | -Increased energy consumption; -Possible difficulties in burning low calorific value gas. |

**Table 8.** Analysis of BAT regarding $NO_x$ emission control
***Capacity of the process = 3 Mt/yr (120000 t/yr liquid fuels + 180000 t/yr gaseous fuel)***
***Volume of flue gas =1680·$10^6$$Nm^3$/yr***
***Initial pollutant concentration: variable***

| **Name of technology** | **Low $NO_x$ burners** | **Thermal De-$NO_x$** | **Selective catalytic reduction** |
|---|---|---|---|
| Efficiency | 10 – 50 % (150 – 300 mg/$Nm^3$) | 60 – 80 % (200 mg/$Nm^3$) | 85 % (50 mg/$Nm^3$) |
| Investment cost | 0,5 – 1,0 Million Euro | 3 – 5 Million Euro | 15 – 20 Million Euro |
| Operating cost | N.A. | 0,2 – 1 Million Euro/yr | 2 Million Euro/yr |
| Other impacts | -Increased particulate emissions with liquid fuels. | -Energy to produce $NH_3$; - Risk of $NH_3$ emissions. | -Energy to produce $NH_3$; - Risk of $NH_3$ emissions; - Catalyst disposal. |

The technology applied for the reduction of $NO_x$ emission control must be chosen by balancing of all the parameters: efficiency, investment cost, operating cost and other impacts.

## Conclusions

In the last time there are many environmental actions in order to reduce atmospheric pollution. The legislative forums discuss about new limits for pollutants emissions with very restrictive specifications for CO, $SO_x$ and $NO_x$.

These new rules ask greater investments and greater operating costs in order to meet new specifications for atmospheric emissions. In this case, BAT could be a very useful tool when the upgrading of the unit is recommended or when new limitations are imposed to pollutants emissions.

Using Best Available Technology analysis it is possible to obtain a correct image about the advantages and disadvantages of each technology regarding oil refinery pollutant emissions.

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# Cea mai bună tehnologie disponibilă pentru a reduce emisiile poluante din industria de rafinare a țițeiului

## Rezumat

*Această lucrare prezintă o analiză tipică referitoare la reducerea emisiilor de poluanți din aer în cazul industriei de rafinare a țițeiului folosind procedurile celei mai bune tehnologii posibile. S-au studiat po - luanții eliminați în atmosferă ca : $SO_2$, $NO_x$ și compuși organici volatili (COV), iar reducerea lor a fost corelată cu costurile de investiție și de operare, cu eficiența procesului de curățare și cu impactul asupra instalației.*