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Best Available Technology to Reduce Emissions of Pollutants into Fluid Catalytic Cracking Unit

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Abstract

The aim of this paper is to present a case study regarding the Best Available Technology analysis in order to reduce emissions of pollutants in Fluid Catalytic Cracking unit. The pollutants ejected in atmosphere as SO_2, NO_x and particulates (catalyst fine) were studied and their reduction was associated with investment and operating costs, with efficiency of removing and with other unit impacts.

Key words: *BAT, pollutant, FCC, efficiency.*

Introduction

Fluid catalytic cracking is considered the primary conversion process in an integrated refinery. For many refineries FCC unit is the key to profitability in that the successful operation of the process can determine whether or not a refiner can stay in business and remain competitive in today's market. Withal the new environmental protection restrictions could affect the refinery financial balance by higher cost of clean production. It is obviously a new direction of investment effort in order to respect new specifications for products and to reduce the pollution under the legislation limits.

Best Available Technology (BAT) is a spare no expense doctrine which prescribes the acquisition of the best technology available, without regard for traditional cost – benefit analyses [1]. This can be result of a future-oriented business strategy, or reflect concern for other factors, such as environmental impact.

This paper presents a BAT study to reduce emissions of pollutants into the air from Fluid Catalytic Cracking Unit (FCCU).

Pollutants Emitted by FCCU

A. Main pollutants and sources (Annex II of Directive 84/360/EEC)

- o SO_2 and other sulphur compounds;
- o NO_x and other nitrogen compounds;
- o CO (depends on the combustion process, but the catalyst regeneration is the major source of CO) ;

- Organic compounds (VOC) – in particular hydrocarbons (excluding Methane);
- Particulates.

B. Other possible pollutants are:

- CO_2 – the CO_2 emissions are high, but they are outside the scope of this research;
- H_2S – are controlled, their impact on the environment is hardly measurable.

Environmental Protection Actions

The European Community and different international agencies created a legislative system in order to assure a higher environmental protection, as follows:

1. Directives 89/779/EEC to set air quality standards for SO_2 and particulates.
2. Directives 85/203/EEC to set air quality standards for NO_x.
3. These 2 directives were later completed by Directive 84/360/EEC requiring adoption of "Best Available Technology not Entailing Excessive Costs" and by the Large Combustion Plants Directive 88/609/EEC.

The specifications for SO_2, NO_x and particulates (dust) established by Directive 88/609/EEC are presented in tables 1-3.

Table 1. Emissions limit value for SO_2 for new plants

Type of fuel	Limit value (mg/Nm^3)
Gaseous fuels in general	35
Liquefied gas	5
Low calorific gases from gasification of refining residues, coke oven gas, blast furnace gas	800
Liquid fuel: 50 to 300 MWth / 300 to 500 MWth / more than 500 MWth	1700 / 1700 to 400 / 400

Table 2. Emissions limit value for NO_x for new plants

Type of fuel	Limit value (mg/Nm^3)
Gaseous	350
Liquid	450
Solid with less than 10% volatile compound	1300
Solid in general	650

Table 3. Emission limit values for dust for new plants

Type of fuel	Thermal capacity (MWh)	Limit value (mg/Nm^3)
Solid	>500 / <50	50 / 100
Liquid	All plants	50
Gaseous	All plants	5 / 10[1)] / 50[2)]

[1)] - for blast furnace gas
[2)] - for gaseous produced by steel industry

Other relevant regulation:

1. Regulation on the sulphur content and other quality constraints of refined products (Clean Air Act Amendment).

2. Directive 501/82/EEC, the so called SEVESO Directive, concerning hazards outside the limits of the plant for neighbouring population.
3. Regulation concerning waste management and disposal of hazardous material.
4. Draft regulations concerning the emissions of VOC.

Technologies to Prevent/Reduce Emissions

SO_2 Emissions

The total emissions and SO_2 concentration in flue gases are related mainly to the amount of coke formed, its sulphur content and the concentration of sulphur in the feedstock. Catalyst regeneration provides a flue gas with a high content of pollutants as: SO_2, NO_x and CO.

SO_2 emissions will be significantly lower when cat cracker feedstock is hydrotreated. Hydrotreating of the FCC feed reduces SO_2 and NO_x emissions from the regenerator flue gas, but a number of refineries cannot justify the high capital cost of this process.

In the FCC itself, SO_2 can be reduced using a de-SO_x additive which is added in small quantities to the normal cracking catalyst. Some metal oxides contained in the catalyst matrix such as aluminium, magnesium or calcium are able to sulphated and act as an SO_x absorber in the regenerator. Once returned to the reactor the sulphate is reduced to H_2S and released in the riser or stripper and subsequently recovered in Sulphur Recovery Unit (SRU). This gives some additional load of the downstream equipment and may require debottlenecking of the gas recovery and H_2S scrubbing sections. With de-SO_x catalyst a desulphurisation of 30-70 wt% is possible [2].

A de-SO_x agent can be used in combination with an oxidation promoter as described above in a complete combustion regenerator. As a consequence NO_x formation is promoted to a greater extent than in a conventional regenerator in a CO_2/CO environment. Operating conditions of the regenerator, especially partial versus full combustion and excess oxygen level, will greatly influence the additive's effectiveness [3].

A third option is flue gas scrubbing (desulphurisation) where three main processes are available (Exxon Wet Gas Scrubber, Haldor Topsoe's WSA and united Engineers' Mgo), but due consideration has to be given to the handling of effluent [4]. Table 4 presents a BAT analysis regarding the SO_2 emission control using different technologies.

Particulate (Catalyst Fine) Emissions

Control of particulate emissions can be achieved by different means such as: operating parameters and secondary emission control equipment.

A number of possibilities for recovery of catalyst particles from regeneration flue gas are available. The most applied techniques are:

- tertiary cyclones: conventional cyclones fitted externally to the regenerator but operating on the same principle. They are high velocity devices and recovered catalyst is returned to a dust hopper;
- multi-cyclones: gas stream is distributed over a number of parallel multi-cyclones. They were developed to protect power recovery expanders by removing catalyst particles about 10 μm [3];
- electrostatic precipitators: typically installed downstream of the flue gas recovery (prior to atmospheric discharge) to minimise the particulate concentration;
- wet flue gas scrubbing together with feed desulphurisation, presented above.

BAT analysis of particulates emissions control is presented in Table 5.

Table 4. Analysis of BAT regarding SO_2 emission control (case study)

Capacity of the unit: 1,5 Mt/yr
Feedstock source: W. Texas virgin gas oil [1-pag 57]
Feedstock sulphur content: 1,75 wt%; Volume of gas: 1050 x 10^6 Nm^3/yr; Initial pollutant concentration: 2800 mg SO_x/Nm^3

Name of technology	**De- SO_x additive catalyst**	**Distillate feedstock desulphurisation**	**Residue feedstock desulphurisation**	**Flue Gas desulphurisation**	**Regenerative flue gas desulphurisation**	**Wet gas scrubber (Caustic scrubbing)**
Efficiency	25 -75 % (700- 2100 mg/Nm^3)	Up to 90 % depending of the feedstock (down to 300 mg/Nm^3)	Around of 85 % depending of the feedstock (down to 400 mg/Nm^3)	90 % (280 mg/Nm^3)	95 – 98 % (60 – 140 mg/Nm^3)	Up to 85 % depending of the feedstock (down to 400 mg/Nm^3)
Investment cost	0 (in some cases Amine treatment capacity will have to be increased)	45 – 50 Million Euro (excluding H_2 production and H_2S handling facilities)	200 – 300 Million Euro	15 – 20 Million Euro	24 – 28 Million Euro	10 Million Euro
Operating cost	0,1 Million Euro/year	4 – 9 Million Euro/year	30 – 50 Million Euro/year	2 – 3 Million Euro/year	1,5 Million Euro/year	2 – 5 Million Euro/year
Other impacts	- increased energy consumption; - possible bottlenecking of H_2S handling facilities.	- increased energy consumption; - production of low sulphur fuels; - FCC catalyst protection.	- increased energy consumption; - production of low sulphur fuels; - FCC catalyst protection.	- increased energy consumption; - raw material supply and handling	- increased energy consumption; - possible bottlenecking of H_2S handling facilities.	- waste water production; - reduced particulate emissions.

Table 5. Analysis of BAT regarding particulates emission control (case study)

Capacity of the unit: 1,5 Mt/yr; Volume of gas: 1050 x 10^6 Nm^3/yr;
Initial pollutant concentration: 450 mg/Nm^3 (Total quantity: 475 t/yr)

Name of technology	**Tertiary cyclones**	**Multi-cyclones**	**Electrostatic precipitator**	**Wet gas scrubber**
Efficiency	30 – 90 % (60 – 150 mg/Nm^3)	70 – 80% (40 – 100 mg/Nm^3)	85 - 95% (< 50 mg/Nm^3)	85 - 95% (< 50 mg/Nm^3)
Investment cost	0,5 – 1,5 Million Euro	1 – 2 Million Euro	3 – 5 Million Euro	10 Million Euro
Operating cost	0,1 Million Euro/year	0,1 Million Euro/year	0,25 – 0,5 Million Euro/year	2 - 5 Million Euro/year
Other impacts	Possible energy consumption reduction (power from the turbo expander).	Possible energy consumption reduction (Power from the turbo expander).	Increased energy (electricity) consumption.	-waste water (Na_2SO_4); -reduced SO_2 emission; -increased energy consumption.

NO_x and CO Emissions

NO_x is formed in the regenerator from the nitrogen contained in the coke deposed on catalyst. In the same time, a fraction of carbon is partially oxidised to CO. The concentration of NO_x depends by the process type, the operating conditions and the utilisation of the unit. In a complete combustion the NO_x concentration in flue gas increases and CO concentration decreases, compared to a CO_2/CO type regenerator, where a downstream CO boiler is used [3].

Considering the options available to control NO_x emissions, the linkage of NO_x and CO concentrations should be considered.

Dosage of the promoter and adjustment of the excess air should be balanced in order to obtain minimum CO and NO_x emissions. Table 6 presents the BAT analysis regarding CO/NO_x emissions control.

Table 6. Analysis of BAT regarding NO_x and CO emission control (case study)

Capacity of the unit: 1,5 Mt/yr
Coke: 75 000 t/yr; Volume of gas: 1050 x 10^6 Nm^3/yr;
Initial pollutant concentration: variable (function of the crude oil type)

Name of technology	**Thermal De-NO_x**	**Selective catalytic reduction**	**CO/NO_x optimisation**
Efficiency	60 – 80 % (about 200–400 mg/Nm^3)	85% (about 150 mg/Nm^3)	30% (700 mg/Nm^3)
Investment cost	0,35 – 1,5 Million Euro	1 – 3 Million Euro	-
Operating cost	0,05 Million Euro/year	0,1 – 0,4 Million Euro/year	0,5 Million Euro/year
Other impacts	-energy consumption to produce NH_3; -risk of NH_3 emissions.	-energy consumption to produce NH_3; -catalyst disposal ; -risk of NH_3 emissions.	-

The restrictive limits imposed for FCC emissions by national and international environmental protection agencies could be respected by an optimum design of the unit, conjugated with the quality of the feedstock, operating conditions, catalyst type and the mechanical conditions of the unit.

Conclusions

The new rules and specifications on environmental protection lead to major investments and greater operating costs in that unit where pollutants as SO_x, NO_x or particulates are ejected in the atmosphere.

Applying Best Available Technology analysis, it is possible to have a correct image about the advantages and disadvantages of each technology regarding FCC unit. In the same time, BAT is a very useful tool when the upgrading of the unit is recommended. By using it, the refiner is able to choose that technology which assures the optimum between pollutants reduction and total costs.

References

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Rezumat

Scopul acestei lucrări este de a prezenta un studiu de caz privind folosirea analizei BAT în vederea reducerii emisiilor poluante din instalația de cracare catalitică în strat fluidizat. Poluanții eliminați în atmosferă ca SO_2, NO_x şi particule (catalizator fin divizat) au fost studiați şi reducerea lor a fost asociată cu costurile de investiție şi de operare, cu eficiența îndepărtării, precum şi cu alte impacturi asupra instalației.