# Overview of Environmental Management in Petroleum Refineries: Case Study of $S0_x$ and $N0_x$ Air Pollutants

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**Abstract:-The fluid catalytic cracking unit (FCCU) generates the highest air pollutants of all petroleum refining processes. Flue gas DeS0x and DeN0x are vital to maintain air quality standard. BioDeS0x and BioDeN0x processes are potential means of maintaining air quality standards in areas of FCCU operations in Nigeria. This is because BioDeS0x and BioDeN0x processes offer definite advantages over traditional DeS0x and DeN0x processes available world over. These advantages are: low carbon emission, no risks of secondary pollutants generated, production of biological elemental sulphur and nitrogen with economic benefits, and efficiency of process greater than 98% as compared to traditional DeS0x methods which have process efficiency greater than 90%. Therefore, Nigerian Government, air standards monitoring and enforcement agencies must make deliberate decision to enact policies and regulations that abates release of air pollutants and one way to do so is through enforcing FCCU operating refineries to deploy BioDeS0x and BioDeN0x processes to clean the flue gas generated from the FCCU.**

## I. INTRODUCTION

Crude oil (petroleum); a naturally occurring liquid undergoes series of physical and chemical refining processes to produce wide range of petroleum products (David et al, 2006). Five major steps are recognized in refining crude oil into lighter valuable hydrocarbon and these include: separation processes which takes advantage of boiling points of different petroleum fractions in an atmospheric distillation column, conversion processes which changes or breaks down heavy long chain molecules into smaller ones by either heating or catalyst activity, treating processes which are deployed to remove impurities and other non-desired components from a petroleum product, blending or combination processes are used to make mixture of a final product by adding two or more petroleum fractions together, auxiliary processes which are processes on which the main petroleum refining processes depend upon for ease of operations (South and Southwest Outreach Program, 2003). The auxiliary process could be in the form of utility or waste treatment plants (Guidebook, 2016). In petroleum refining operations, various sub-units do exist depending on the targeted product(s). These sub-units are: Atmospheric distillation, Vacuum distillation, Naphtha hydro-treating, Kero hydro-treating, catalytic reforming, Isomerization, Alkylation and Fluid catalytic cracking among many other units. The fluid catalytic cracking (FCC) unit is one most important refining process deployed to get transportation, industrial, domestic fuels and other chemicals (Moulijn et al, 2001). This secondary conversion process converts high-boiling, high-molecular weight petroleum fractions into more valuable petroleum products such as gasoline, olefin gases, heavy cycle oil, light cycle oil and other products (Gary et al, 2001). Crude oil is not only a collection of carbon and hydrogen compounds but are also present in it varying proportions of sulphur compounds, nitrogen compounds as well as other metallic trace. The conversion of these high boiling, high-molecular weight hydrocarbon (crude oil) does not only results in production of light valuable products, but also the emission of gases such as sulphur dioxides $S0_x$ ($S0_2/S0_3$), nitrous oxides, $N0_x$ ($N0$ and $N0_2$), carbon monoxide $C0$, carbon dioxide $C0_2$ and particulate matter (dust) which pollutes the environment (Yakubu et al, 2017). Recent growing concerns in the environmental impact of petroleum refining are alarming (Cuadros et al, 2012), this among others has led international and local environmental protection bodies to come up with laws governing the emission of these gases to the environment of which oil refineries are not exempted culprits (World Bank Group, 2016). In the oil refinery, the fluid catalytic cracking (FCC) process is a major source of air pollutants (Ragothaman et al, 2017). Therefore, the objective of this work is to identify major air pollutants ($S0_x$, $N0_x$, $C0$, $C0_2$ and particulate matter) from the FCC process, narrowing on oxides of sulphur ($S0_x$), their effects and control in the environment.

### ➢ *Description of FCC Process*

The FCC process can be viewed from two main fronts namely: chemical (Catalytic section) where the feed reacts with the catalysts resulting in structural changes of the feed and the physical (fractionation section) where the products of reaction are separated by distillation, absorption and treatment. The FCC process uses a micro-spheroidal catalyst (zeolite based) which behaves like a liquid when properly aerated by gas.

The FCC feed is a mixture of heavy vacuum gas oil (HVGO), light vacuum gas oil (LVGO) and the heavy atmospheric gas oil (HAGO) usually feed to the FCC surge drum from the atmospheric distillation process at temperatures between 70-80$^0$C. The mixture in the surge drum is pumped through series of heaters (heat exchangers so as to raise the temperature of the mixture to about 230-240$^0$C before channeling the mixture to a feed preheater (usually a fired heater). The feed preheater which could be cylindrical, rectangular or cathedral in shape is fitted with fuel gas burners and pilot burners. It could work on natural or force draft adjusted by manual stack damper. The manual stack damper is manually used to adjust the flow of combustion air. The feed preheater is also designed to have convection and radiation zones. The feed from the series of heaters enters the convection zone of the preheater then flows to the radiation zone of the preheater and then fed through the transfer line to the riser. Thermocouples are usually installed in the preheater to measure feed inlet and outlet temperatures in each coil, coil skin temperature, firebox temperature, convection zone temperature and the stack temperature. Draft gauges are also installed in the combustion chamber and the convection zone to monitor the draft. The most important operating variable is the transfer line temperature (fired heater outlet temperature) which value directly influences catalyst circulation and cracking reactions. Feed exits the preheating furnace through sets of nozzles into the riser and can be enriched by recycling heavy cycle oil or slurry. Feed and recycles are atomized by dispersion steam to increase intimacy of feed with catalyst. In the riser, the mixture (feed and recycle) meets the hot regenerated catalyst. The hot regenerated catalyst vaporizes the mixture, rising its temperature to reaction values (about 350$^0$C), thereby promoting cracking reactions. The riser is designed to provide housing and residence time for 90% of all cracking reactions. Cracked products, having higher volume than feed increases the fluidization of the catalyst and supply the lifting energy to carry cracked products and the catalyst to the dis-engager. Catalyst fed to the riser is fluidized by lateral and vertical steam to assist in lifting the feed and catalyst along the riser. The mixture of cracked hydrocarbon and catalyst flows from vertical riser to dis-engager through a horizontal crossover into two parallel rough-cut cyclones. In the dis-engager, cracking reaction is completed and separation of cracked hydrocarbon with spent catalyst is accomplished. The rough-cut cyclones decrease the velocity of the incoming mixture and starts separation. Cracked hydrocarbon from the top of the dis-engager flows to the fractionator while trapped catalyst is returned to the dis-engager lower part through cyclone dip-legs. Dome steam is usually injected to the upper part of the dis-engager to prevent coke formation. Spent catalyst from the dis-engager flows to the catalyst regenerator along a down-comer pipe and aeration steam is injected to the down-comer pipe to fluidize the catalyst. Spent catalyst rich in oil and coke flows down to the lower part of the dis-engager called dis-engager stripper. Equipped to the dis-engager stripper are series of baffles which increase contact between catalyst and steam to allow for stripping of hydrocarbon contained in the catalyst. Stripping steam flow rate is an important operating parameter because more or less oil in the catalyst can affect the heat balance of the regenerator. Catalyst level in the dis-engager is also an important parameter because its weight supplies the pressure needed to overcome the regenerator high pressure and allows catalyst circulation down to the stripper and then to the regenerator. The regenerator is a vessel where coke deposit on the catalyst surface is burnt; the catalyst activity is restored and the combustion heat is used to raise the catalyst temperature and sustain the cracking reaction. Hot regenerated catalyst is sent back to the riser where cracking reaction takes place. In the regenerator, combustion of coke is usually not complete; the coke is burnt to C0 instead of $C0_2$. The reason for the partial combustion is to avoid regenerator overheating, afterburning in cyclones and subsequent equipment damage. The complete combustion (C0 to $CO_2$) is done in the CO boiler where heat of combustion is used to generate high pressure steam. In the initial start-up of the FCC process, the catalyst is supplied from catalyst hoppers to the riser through a catalyst feeder that measures the quantity of catalyst loaded, ensuring a constant flow. In the fractionator, separation of cracked hydrocarbon fractions is performed. The fractionator works on the principle of repeated contact and separation of a rising vapor stream and a down coming liquid stream. Contact between the two streams takes place in a column equipped with series of trays which promotes intimate mixing of vapor and liquid phases. Cracked hydrocarbons to be distilled enter the fractionator at a very high temperature of about 500$^0$C, and have to be quenched and cooled to about 350$^0$C before separation. The fractionator bottom cooling is achieved by recycling high amount of cold bottom liquid. After fractionation, the products obtained are fuel gas, liquefied petroleum gas (LPG) and gasoline at the top of the fractionator which when cooled and compressed are sent to the vapor recovery unit (VRU) to be recovered and further separated. At the bottom of the fractionator are heavy naphtha, light cycle oil, heavy cycle oil, and bottom slurry. The bottom slurry when stripped is used as decant oil for carbon black process. The main reason for the VRU is to maximize the recovery of fuel gas, LPG and light gasoline from the main fractionator overhead system. The LPG and gasoline mixture from the VRU goes through series of distillation (separation) process in other smaller distillation columns (absorber column, stripping column and the debutanizer column). After separation with LPG, gasoline is sent to the MEROX treatment that is removal of oxides of sulphur, nitrogen and other metallic oxides. The whole FCC process is continuous and repeated again (David et al, 2006; John, 2018 and Moulijn et al, 2001).

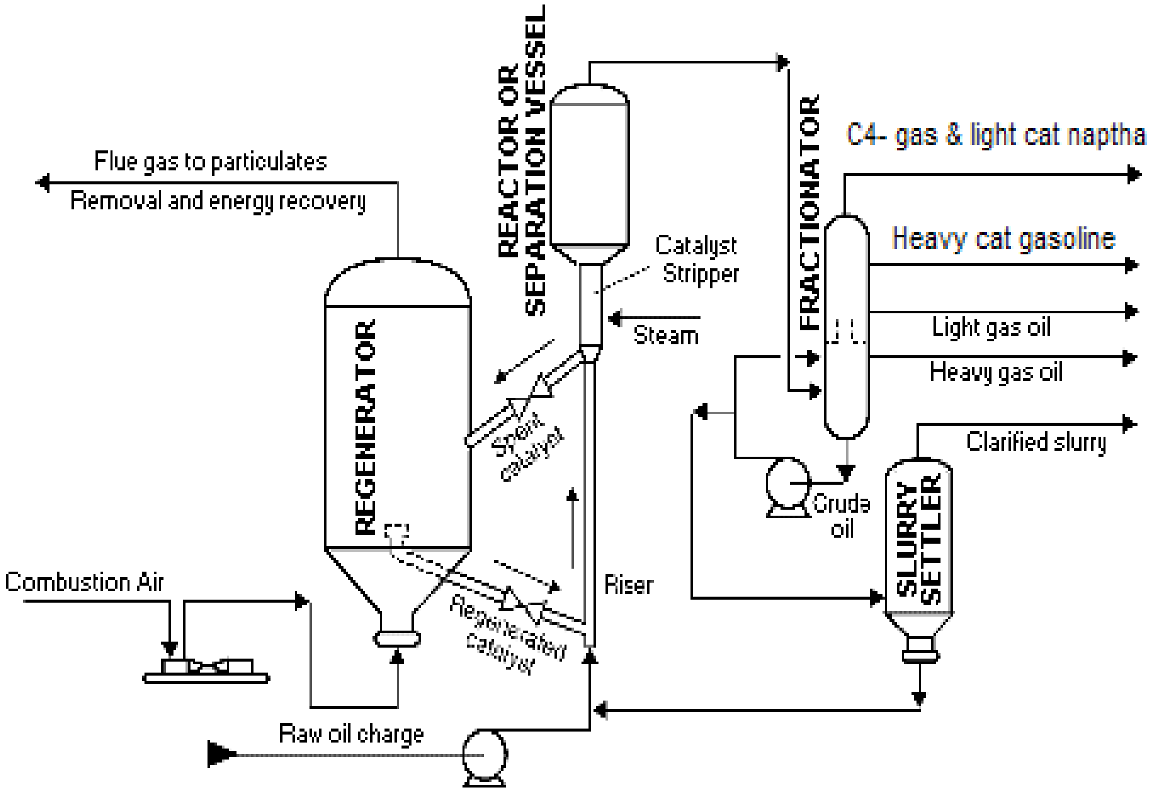

Fig 1:- Process flow diagram of FCC process (John, 2018).

Fig 1 is the process flow diagram of the fluid catalytic cracking process showing all inter-relationship between components, energy and material flow.

## II. MATERIALS AND METHODS

This work obtains data from past and present studies, government and non- government bodies and existing literature. The study relies on secondary data, and these data were obtained from World Bank Reports, United Nations Environmental Protection Programme, Published materials, Books, Conferences, Seminar Papers, Journals and the internet. The obtained data would be analyzed and descriptive method would be used to logical present and interpret results.

## III. ATMOSPHERIC CONTAMINANTS ASSOCIATED WITH FCC PROCESS-ORIGIN

The FCC process is associated with certain environmentally harmful atmospheric contaminants; these emissions have tendencies of inhibiting the survival of living organisms through direct inhalation and indirectly because of the damage done by these emissions to the environment to which the organisms depend. These air contaminants have their origin in the FCC's catalyst regenerator. They are either chemically formed during the regeneration combustion process or physically, from the carryover of catalyst particles entrained in the regenerator flue gas.

- *Oxides of Sulphur (S0x)*

Oxides of sulphur such as sulphur dioxide and sulphur trioxide are among the gases identified as major sources of environmental pollution. The largest proportion of sulphur oxide pollutants emitted into the environment is in form of sulphur dioxide (Yateem, 2011). During combustion process of fuels, sulphur dioxide ($S0_2$) is formed alongside small quantity of sulphur trioxide ($S0_3$). In the FCCU regenerator, $S0_2$ is formed from the oxidation of the sulphur content of the fuel. Studies show that sunlight initiates oxidation of $S0_2$ to $S0_3$. The small quantity of $S0_3$ formed during combustion of fuels and the portion of $S0_3$ formed as a result of oxidation of $S0_2$ to $S0_3$ gets hydrolyzed in the atmosphere to produce sulphuric acid mist which reduces visibility. The sulphuric acid mist particle size formed after the hydrolysis of $S0_3$ is a function of water vapour present in the atmosphere and the particle size ranges between 0.5 to 0.6□□(Nelson et al, 2012).

- *Oxides of Carbon (C0x)*

Carbon has two main air polluting oxides (carbon monoxide C0 and carbon dioxide C02). Carbon monoxide is a colourless, odourless, non-irritating, and tasteless gas that arises from both natural and anthropogenic sources. It is produced as a primary pollutant during the incomplete combustion of fossil fuels and biomass. In the regenerator, C0 is formed from incomplete combustion of the carbon content of the coke on catalyst. The EPA standard for C0 release to the atmosphere is 500 ppm; therefore, this effluent must be regulated within the EPA limit. For this reason, a C0 boiler is installed in the FCC unit to process the flue gas C0 from the regenerator to within the limit of acceptability. Auxiliary fuel is needed to power the C0 boiler because of small heating value of the flue gas. The heat generated by the C0 boiler process is useful for steam generation (Kunz, 2009). Petroleum refineries contribute about 2.7% of world's carbon dioxide ($C0_2$) emissions. The Fluid catalytic cracking unit (FCCU) being the heart of the refining industry, contributes about 20% of the refinery $C0_2$ emissions (Digne et al, 2014).

- *Oxides of Nitrogen (N0x)*

Nitrogen oxides are gaseous mixtures of two primary elements namely nitrogen and oxygen. The two main oxides of nitrogen generated in the FCC process are nitric oxide (N0) and nitrogen dioxide ($N0_2$) and are major contributors in polluting the lower atmosphere (tropopause and troposphere). Across the globe, nitrogen oxides emissions by human sources are estimated to be about 50 million metric tons (World Bank Group, 1998). Once in the atmosphere, nitrogen oxides undergo rapid chemical reactions to form other pollutants such as ozone and aerosols. $N0_2$ and N0 cause poor visibility due to smog, poor air quality.

- *Particulate Matter*

Particulate matter is a collection of large and small particles of different sources and chemical composition; they are finely divided solid or liquid particles which could be reactive or non-reactive and ranging between 0.0002 to 500 microns in size (Khan et al, 2014).

Air pollution has several effects spanning from health, environmental and economic effects. With respect to health, polluted air from the FCCU causes diseases such respiratory infections, heart disease, and lung cancer, according to the World health organization. On the environment, it leads to the formation of ground level ozone which destroys plants, animals and farms. These pollutants also contaminate water bodies making them harmful for man and animals. The effect of these pollutants on the economy is indirect, the economy progresses when people are healthy. If people are not healthy, money is channeled to health and healthcare facilities. These pollutants also destroy farm produce leading to food shortage.

According to an analysis performed by PricewaterhouseCoopers Limited in 2017, (from three point view that is downside, base case and upside), the downside scenario assumes that if Dangote refinery a 650,000 bpd starts operations by 2019, operating at 50% utilization, existing refineries of total existing capacity 445,000 bpd operates at 15% utilization and modular refineries having total installed capacity of 100,000 bpd also come on-stream in 2019, operating at 90% utilization summing up to 70%, 20% and 90% respectively by 2030, the net effect would be that Nigeria by 2019 becomes Africa's 3rd largest refiner of petroleum products. Considering the base case scenario, if Dangote refinery operates at 50% utilization, existing refineries operates at 20% utilization and modular refineries of combined capacity of 200,000 bpd also come on-stream in 2019, operating at 90% utilization summing up to 90%, 30% and 90% respectively by 2030, the net effect is that Nigeria becomes the largest producer of refined products by 2019. Considering also the upside scenario, if Dangote refinery operates at 60% utilization in the same 2019, existing refineries operates at 20% utilization and modular refineries of combined capacity of 300,000 bpd also come on-stream in 2019, operates at 90% utilization summing up to 90%, 70% and 90% respectively by 2030, the net effect is that getting to the beginning of next decade, Nigeria assumes the first position in among producers of refined products in Africa (PriceWaterHouseCoopers, 2017). Considering any of the view points, Nigeria will be at least third largest refiner of petroleum products as such; it should adopt laws that abate damage to the environment.

## IV. FLUE GAS CLEANING PROCESSES

These processes aim at removing already formed sulphur, Nitrogen and carbon oxides and are considered as secondary measures. In the traditional methods of flue gas cleaning, chemicals are used to either $DeS0_x$ or $DeN0_x$ the flue gas. These methods have two draw-backs: firstly is the high cost of chemicals because of the need to constantly add the chemicals to the cleaning process which raises operating costs and secondly is the formation of products such as di-sodium sulfate which are normally is difficult to dispose (Van Groenestijn et al 2005). Alternative to the traditional method of desulphurizing flue gas is the use of biological method known as BioDeS0x or BioDeN0x processes (Zhang P, 2018). These processes are based and rooted biological Sulphur and Nitrogen cycle theory. The desulphurization process which forms the core of this work is divided into three distinct but connected steps. Firstly, the hot flue gas is cooled and dissolved in water or the absorption tower where the S0x in the flue gas is converted to sulphite ($S0_3^{2-}$) or sulphate ($S0_4^{2-}$). Secondly, the sulphate reducing microbes (usually bacteria reduces the sulphate or sulphite to sulphide ($S^{2-}$) in an anaerobic reactor and external carbon supply. Thirdly, in the aerobic reactor, sulphur reducing bacteria converts sulphide into elemental sulphur. The elemental sulphur thus produces can be purified and used for making of fertilizer and other purposes. Another advantage of the BioDeS0x process is that no secondary pollutants are produces as in the case of the traditional DeS0x methods (Zhang P, 2018).

- *$S0_x$ and $N0_x$ removal from flue gases*

The process involves passing the hot flue gas through an absorber in the form of a reverse jet wet scrubber where particulates and $S0_x$ are absorbed. Important reactions identified during the absorption process are:

$\boldsymbol{S0_2+NaHC0_3\rightarrow NaHS0_3+C0_2}$ …………. **(1)**
(Van Groenestijn et al 2005)

$\boldsymbol{NaHS0_3+\frac{1}{2}0_2+Na0H\rightarrow Na_2S0_4+H_20}$… **(2)**
(Zhang P, 2018)

Equation (2) consumes only a portion of $NaHS0_3$ produced in equation (1).

The mixture from the absorber is transferred to the anaerobic reactor where sulphites and sulphates are biologically converted to sulphides by sulphate reducing microbes in the presence of an electron donor (usually $H_2$ for a large scale plant and methanol or ethanol for small scale plant). In a petroleum refining complex where the catalytic reformer unit is found, $H_2$ generated from this unit can be utilized as an electron donor since $H_2$ generation is capital intensive. The reactions involved for electron donation by $H_2$ are:

$\boldsymbol{Na_2SO_3+3H_2\rightarrow NaHS+3H_20}$………... **(3)**
(Zhang P, 2018)

$\boldsymbol{Na_2S0_4+4H_2+C0_2\rightarrow NaHS+NaHC0_3+3H_20}$
………………………...……………..…… **(4)**
(Van Groenestijn et al 2005)

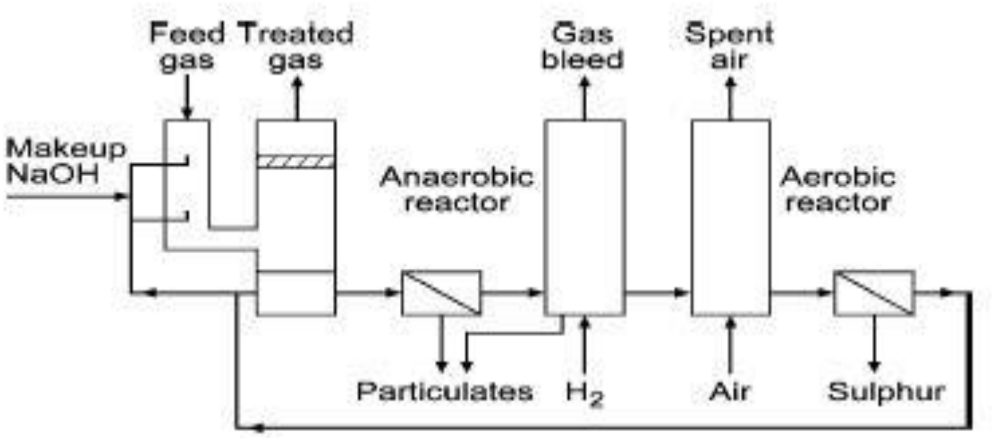

Fig 2:- Process flow diagram of a BioDeS0x Unit (Van Groenestijn et al 2005).

The inlet and outlet of the flue gas is referred to as feed gas and treated gas respectively. This technology can be extended to DeN0x the flue gas; the challenge with BioDeN0x of flue gas by this technology is that 95% of N0x is N0 which is a gas with poor solubility in water. To get rid of the solubility challenge, Fe(II)EDTA is used in the bio-scrubber liquid to react with N0, thus a nitrosyl complex $Fe(II)[EDTA]N0^{2-}$ is formed. The scrubber liquid (containing nitrosyl complex and absorbed $N0_2$) is transferred to an anoxic bio-scrubber where biological denitrification reaction happens using an electron donor such as ethanol, to yield dinitrogen gas ($N_2$) Van Groenestijn et al, (2005) and Van Groenestijn, (2019) . According to Van Groenestijn et al (2005), there is the possibility of simultaneous removal of $S0_2$ and $N0_2$ using this process; by simple modification making use of two bio-scrubbers attached to a wet limestone gypsum plant. They further stated that operational costs are lower compared to the traditional caustic soda process while capital costs are higher. On payback period, they deduced 2 years even on high sulphur loads. Studies by Zhang P, (2018) shows some of the advantages of BioDesS0x over traditional DeS0x methods and they are: low carbon emission, no risks of secondary pollutants generated, production of biological elemental sulphur with economic benefits and efficiency of process greater than 98% as compared to traditional DeS0x methods which have process efficiency greater than 90%. These advantages can be extended to BioDeN0x over traditional DeN0x because of similarity of the two processes.

## V. CONCLUSION

The fluid catalytic cracking unit is the highest air pollutants source among the petroleum refining process units as such; measures must be put in place to check the release of these pollutants into the environment so as to minimize the health challenges associated with these pollutants. Measures to be adopted by Nigeria to minimize the release of these air pollutants from the FCCU include:

- ➢ With Nigeria about to become the largest refiner of crude oil, Government and pollution control agencies must make deliberate attempt to have a detailed knowledge of the health effects of air pollution, this way, sound policies and regulations that states maximum permissible air pollutants emission from the FCC units can be enacted to prevent or control air pollution.

- ➢ Government and pollution control agencies must ensure and enforce compliance to these regulations for both existing and yet to be commissioned refining plants.

- BioDeS0x and BioDeN0x technologies of stripping flue gas of oxides of Sulphur and Nitrogen should be adopted for existing and yet to be commissioned FCC units because of the advantages these technologies offer over the traditional technique of cleaning flue gas of Sulphur and nitrogen oxides.

## REFERENCES

[1]. Cuadros J.F, Melo D.C, Filho R.M, Maciel M.R.W, (2012), Fluid Catalytic Cracking Environmental Impact: Factorial Design Coupled with Genetic Algorithms to Minimize Carbon Monoxide Pollution, Journal of Chemical Engineering Transactions, Vol. 26, pp. 243-248.

[2]. David S.J and Peter R.P, (2006), Handbook of Petroleum Processing, Springer, Netherlands.

[3]. Digne R, Feugnet F and Gomez A, (2014), A Technical and Economical Evaluation of $C0_2$ Capture from Fluidized Catalytic Cracking (FCC) Flue Gas, Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 6, pp. 977-1129.

[4]. Fluid Catalytic Cracking, Encyclopedia of Earth and Life, http://www.eoearth.org/view/article/51cbf2147896bb431f6a7bea/?topic=51cbfc98f702fc2ba812eaa6, accessed 25/11/2019.

[5]. Gary, J.H and Handwerk, G.E, (2001), Petroleum Refining Technology and Economics, 4th Edition, Marcel Dekker. New York.

[6]. Guidebook, (2016), EMEP/EEA Air Pollutant Emission Inventory Guidebook, European Environment Agency.

[7]. John J, (2018), Fluidized Catalytic Cracking, Colorado School of Mines, Earth Energy and Environment.

[8]. Khan R.R and Siddiqui M.J.A, (2014), Review on effects of Particulates; Sulfur Dioxide and Nitrogen Dioxide on Human Health, International Research Journal of Environment Sciences, Vol.3, pp. 70-73.

[9]. Kunz R.G, (2009), Environmental Calculations: A Multimedia Approach, John Wiley & Sons, Inc.

[10]. Moulijn J.A, Makkee M and Diepen, A.V, (2001), Chemical Process Technology, John Wiley, UK.

[11]. Nelson H.W and Lyons C.J, (2012), Sources and Control of Sulfur-Bearing Pollutants, Journal of the Air Pollution Control Association, Vol. 7, No. 3, pp. 187-193.

[12]. Price Water House Coopers, (2017), Nigerian Refining Revolution, Price Water House Coopers International Limited.

[13]. Ragothaman A and Anderson W. A**,** (2017), Air Quality Impacts of Petroleum Refining and Petrochemical Industries, MDPI Journal on Environment, Vol.4, pp. 1-16.

[14]. South & Southwest Outreach Program, (2003), Environmental Impact of the Petroleum Industry, Hazardous Substance Research Centers, USA.

[15]. Van Groenestijn J.W, Kraakman N.J.R, (2005), Recent Developments in Biological Waste Gas Purification in Europe, Chemical Engineering Journal 113, Elsevier, pp. 85-91.

[16]. Van Groenestijn J.W, Biotechniques for air pollution control: past, present and future trends, https://core.ac.uk/download/pdf/61908782.pdf. Accessed 12/12/2019.

[17]. World Bank Group, (1998), Handbook of Nitrogen Oxides: Pollution Prevention and Abatement Handbook, The World Bank.

[18]. World Bank Group, (2016), Environmental, Health, and Safety Guidelines Petroleum Refining, The World Bank.

[19]. Yakubu J.M, Patel R, Mujtaba I.M, (2017), Optimization of Fluidized Catalytic Cracking Unit Regenerator to Minimize $C0_2$ Emissions, Journal of Chemical Engineering Transactions, Vol. 57, Pg. 1531-1536

[20]. Yateem W, (2011), Environmental Impact of Fluid Catalytic Cracking Unit in a Petroleum Refining Complex, Loughborough University Institutional Repository, Loughborough, UK. Unpublished.

[21]. Zhang P, (2018), Application study of Bio-FGD based on environmental safety during the coal combustion, 2018 7th International Conference on Clean and Green Energy-ICCGE 2018, Earth and Environmental Science 154, IOP Publishing.