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Effect of Illegal Refining on industrial Cooling water System-Case Study of Notore Ammonia Plant

Owhondah Anthony Nhoma, Harry Humphrey Donald
[1,2]*MSc Student, Department of Petroleum and Gas Engineering, University of Port Harcourt, Rivers State, Nigeria. Field Operator, Notore Chemical Industries Plc, Onne, Rivers State, Nigeria.*
PhD Student, Emerald Energy institute, University of Port Harcourt, Rivers State, Nigeria. Field Operator, Notore chemical Industries Plc

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ABSTRACT: Illegal refining of petroleum product has become a serious menace eating deep into the fabrics of the existence of residents in the Niger Delta region of Nigeria. The effect of these illegal refining is enormous. It has resulted in loss of revenue for both government and the oil companies, Destruction of life and properties of those who engage in this vice, massive pollution of the environment in this communities, and loss of livelihood as many locals have reported damaged farmlands and livestock. Even more, health care professional have warned of the effect of the soot generated from this illegal activity on the lives of residents of surrounding communities. Research has shown that black soot from illegal refining can cause respiratory track cancer.However, many are unaware of the impact of this illegal refining on the process plants in this Niger Delta region. Hence, this paper aims to investigate the impact black soot generated from illegal refining has on local process plants. It uses as a case study, the Notore ammonia production plant, situated in Onne, Rivers State, Nigeria. Using production data from this plant, it shows the impact of illegal refining on ammonia production and suggests possible solution to the production losses occasioned by fouled cooling water exchangers and equipment.

KEYWORDS: Illegal Refining, Cooling Tower, Cooling water Exchangers, Notore, Soots, Pollution, Crude oil.

I. INTRODUCTION

Illegal refining of crude oil has become a menace in the Niger Delta region of Nigeria. Apart from the deleterious effect it hason the environment, it has also resulted in heightened insecurity, loss of revenue, and loss of human lives-mostly young persons in their prime. Much has been written and said about the effect these illegal refining has had on the environment. However, the impact of black soot from illegal refining (locally referred to as "Kpofire") on industrial processes has received little to no attention. Therefore, this paper aims to investigate the impact of black soot generated from illegal refining on the industries operating in this region. We will use an ammonia production plant in Onne, Rivers State, Nigeria as a case study.

Currently, Rivers State has two of the three ammonia production plants in Nigeria. Ammonia produced in this plant is used as a feedstock for urea synthesis, which is subsequently blended to give NPK fertilizers. Therefore, any factor that impacts negatively on the ammonia production process is likely to increase the cost of fertilizer production. This increased production cost will affect the company's revenue, making it difficult to meet its obligations to employees and shareholders. Hence, the need to examine the effect black soot from illegal refining is having on the production of anhydrous ammonia.

Different methods of ammonia production exist in the literatures. However, the ammonia production plants in Nigeria uses natural gas as feedstock to produce ammonia. The raw material for this process is readily available. The Niger Delta region of Nigeria is a major gas province. Nigeria has more than 186 trillion cubic feet of recoverable gas reserve[1]. According to data from the US Geological Survey World Energy Report[2], this region is ranked 12th richest in petroleum resources. It is home to about 2.2% of the worlds discovered oil, and 1.4% of the world's discovered natural gas. These figures are impressive considering that most of these natural gas discoveries are accidental[3] as they were discovered while prospecting for crude oil. The implication is that the potentials for growing the gas reserve in this region is enormous. Moreover, Natural Gas from this region is sweet. It has very little to no sulphur content. Its calorific value is excellent[1]. Thus, with the availability of raw material and the granting of a free trade zone status to companies operating in this region, there isincreased incentive for investing in ammonia and other process plants, hence an even greater need to pay attention to the problem of black soot from illegal refining.

OVERVIEW OF AMMONIA PRODUCTION PROCESSES

Natural gas is supplied to Notore Chemicals via Nigeria Gas Company (NGC) pipeline and arrives the ammonia plant at about 41.2Kg/cm2. The gas is preheated to a temperature of about 399^0C in a fuel gas preheat coil. The preheated Gas is then sent to the hydrotreater and Zinc Oxide Guard Chamber (desulphurization Unit) where the natural gas is cleaned of all impurities. The purified Natural gas is then mixed with steam in a ratio of 3.5:1.0 and preheated to about 510^0C[4]. The fuel-gas and steam mixture is sent to the primary reformer where it undergoes reforming reaction to yield an effluent comprising of carbon dioxide, carbon monoxide, and hydrogen. The methane slip out of the primary reformer is about 9.8mol%. The Process gas is then taken to the secondary reformer via a transfer line where further reforming reaction takes place.

Equation of reaction

$$CH_4 + H_2O = CO_2 + CO + H_2O$$

In the secondary reforming unit, the unreacted methane (about 9.8mol%) is reformed to increase the yield of carbon dioxide, carbon monoxide, and hydrogen. A four-stage centrifugal compressor is used to compress air from the atmosphere to about 35Kg/cm2. This air is preheated to about 482^0C (Ref4) and sent to the secondary reformer. The air supplies the Nitrogen needed for ammonia synthesis. This reaction is endothermic. The heat needed for this reaction is supplied by the exothermic reaction of hydrogen from the process gas and oxygen from air (about 21%) to produce steam. The process gas out of the secondary reformer comprises mainly of Hydrogen, Nitrogen, Carbon monoxide, and Carbon dioxide.

Equation of reaction

$$H_2 + O_2 = H_2O \qquad \Delta H = +ve$$

$$CH_4 + H_2O = CO_2 + CO + H_2O$$

This Process stream is cooled via waste heat boilers to about 399^oC. It is then sent to the shift converters (high temperature shift converter and low temperature shift converter) where the carbon monoxide reacts with steam to form carbon dioxide.

Equation of reaction

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H = +ve$$

The produced carbon dioxide is sent to the Benfield unit where a solution of Potassium trioxocarbonate (iv) is used to selectively absorb the carbon dioxide (CO_2). The absorbed (CO_2) is then sent to urea where it is compressed and made to react with ammonia to produce ammonium carbamate, the precursor to urea.

The process gas out of the Benfield unit now comprises predominantly of Hydrogen and Nitrogen, with traces of CO_2. which must be kept at the barest minimum since they are poisonous to the synthesis gas converter catalyst. This is achieved by passing it through a methanator. The methanation reaction is simply the reverse of the reforming reaction. It is exothermic. The equation of the reaction is shown below.

$$CO_2 + H_2 = CH_4 + O_2$$

The process gas consisting of Hydrogen and Nitrogen in the ratio of 3:1 is then sent to the synthesis gas compressor which compresses it to about 150Kg/cm^2. The synthesis gas converter is loaded with promoted iron catalyst and operates at about 450^0C[4]. These conditions favour the formation of ammonia. The produced ammonia is chilled using ammonia in a flash drum. The refrigerant compressor handles the vapour generated from the chillers and flash drum. The produced ammonia is then sent to the urea synthesis unit for urea production.

Equation of reaction

$$N_2 + 3H_2 = 2NH_3 \qquad \Delta H = +ve$$

Overview of cooling water system in ammonia plant

Cooling water is very important in every process plant. It is the lifeblood of the process industry. Apart from taking out the heat generated due to the mechanical components of turbines, pumps, and compressors; it is also used to control the temperature of process streams and to maintain turbine vacuum systems. A cooling water temperature difference of one degree Celsius (1^oC) can have significant impact on the ammonia production process. Below is a process flow diagram of ammonia cooling water system as designed by Kellog and Brown[4].

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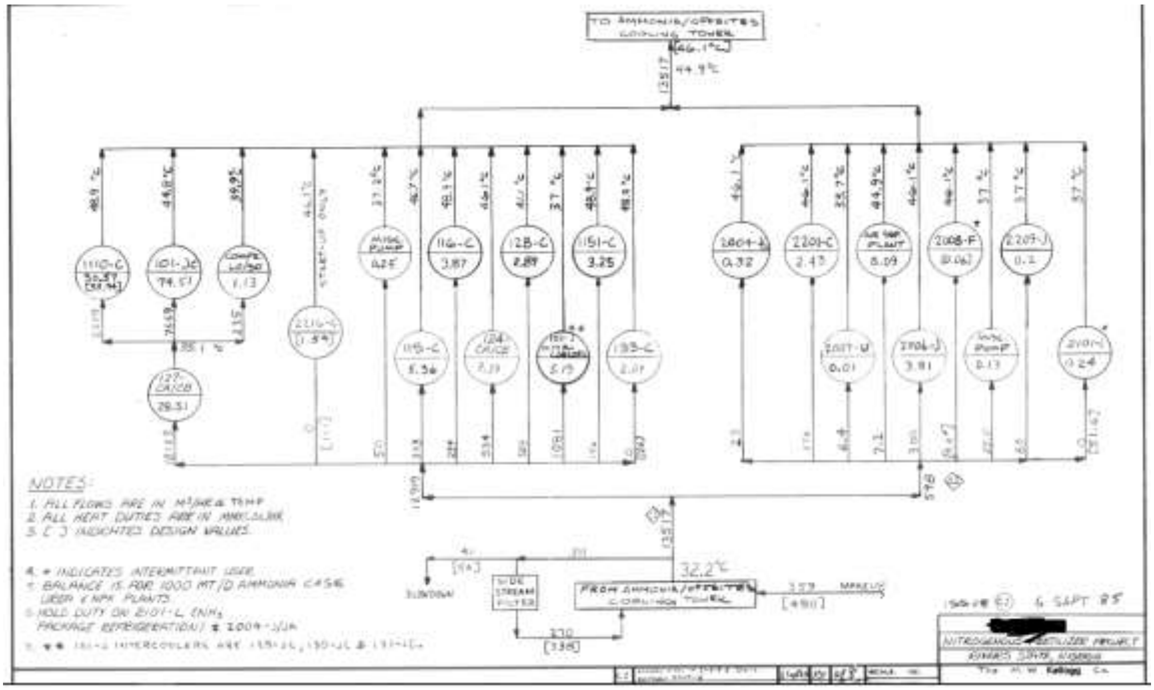

Fig.1; Ammonia cooling water system,
Source: Ammonia operation manual, M.W. Kellog Kellog[5]

The Ammonia unit cooling tower is a six-cell unit with adjustable pitch induced draft fans, designed to provide 32.2°C cooling water at a design ambient wet bulb temperature of 25 °C, with a maximum hot water return design temperature of 46.1°C. The design circulation rate of the cooling water system is for a maximum of 16,895 M3/hr[4].

The primary source of cooling water is raw water from the raw water storage basin, pre-treated with calcium hypochlorite for control of bacteria and algae. The cooling water make up rate is dependent on losses due to evaporation, drift, and blowdown.

Chemical injection systems are provided to control PH and inhibit corrosion and biological growth. Caustic injection system is provided to raise the PH of the cooling water system, to reduce the natural corrosiveness of the recirculating water. The normal PH is 7.5, with a range between 7.0 and 7.8.

A phosphate-based corrosion inhibitor is injected into the cooling tower basin for corrosion protection and scale inhibition.

A dispersant injection system is also provided for scale and fouling control in the cooling water and heat exchangers. A phosphate type dispersant is injected into the chemical distribution header. The dispersant solution will improve the effectiveness of the biocides by loosening the slime masses and preventing organisms and suspended solids from settling on heat exchanger surfaces.

A gas chlorination injection or bio detergent system is also provided for control of microbial growth in the cooling water system. The chemical injection rates are determined by laboratory analysis of the recirculating cooling water.

A side stream filter is provided to remove suspended solids from the recirculating cooling water. The filter is designed to filter 2% of the circulating water. The filter is backwashed at intervals. The backwash cycle is activated at a pre-set pressure differential.

The blowdown rate is normally controlled to maintain eight cycles of concentration in the circulating cooling water. Blowdown consists of removing a portion of the concentrated circulating cooling water and replacing it with fresh makeup water, which will lower the concentration. The concentration must be within the safe limits to prevent scale formation. The Blowdown rate is set to maintain the hardness level below 250 ppm of calcium carbonate.

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BLACK SOOT- SOURCE, COMPOSITION AND CHEMICAL ANALYSIS

Black soot, sometimes referred to as lampblack or carbon black, is a fine black or brown powder that can be slightly sticky and is a product of incomplete combustion of fueled carbon[6]. A major component of soot is black carbon. It consists of agglomerated nanoparticles with diameters between 6 and 30nm. The soot particles can be mixed with metal oxides and with minerals and can be coated with sulfuric acid.

Soot is the common term for a type of particle pollution called PM 2.5: particulate matter that is 2.5 micrometers in diameter or smaller. Such fine particles are even smaller than dust and mold particles, or approximately 1/30 of the size of a human hair.

A mature soot particle is typically composed of a stack of layers, each of them having a graphite-like hexagonal structure. Not all layers are arranged in a parallel fashion. In addition to carbon, soot contains remnants of other elements present in the original fuel.

Soot as an airborne contaminant in the environment has many different sources, they include soot from coal burning, internal-combustion engines, power-plant boilers, hog-fuel boilers, ship boilers, central steam-heat boilers, waste incineration, local field burning, house fires, forest fires, fireplaces, and furnaces. These exterior sources also contribute to the indoor environment sources such as smoking of plant matter, cooking, oil lamps, candles, quartz/halogen bulbs with settled dust, fireplaces, exhaust emissions from vehicles, and defective furnaces. Soot in very low concentrations can darken surfaces or makethem appear black. Hence the term black soot. Soot is the primary cause of "ghosting", the discoloration of walls and ceilings or flooring where they meet.

The formation of soot depends strongly on the fuel composition. The rank ordering of sooting tendency of fuel components is:

Naphthalenes → Benzenes → Aliphatics

However, the order of sooting tendencies of the aliphatics (alkanes, alkenes, and alkynes) varies dramatically depending on the flame type. The difference between the sooting tendencies of aliphatics and aromatics is thought to result mainly from the different routes of formation. Aliphatics appear to first form acetylene and poly-acetylenes, which is a slow process; aromatics can form soot both by this route and by a more direct pathway involving ring condensation or polymerization reactions, building on the existing aromatic structure[6].

THE ANATOMY OF SOOT

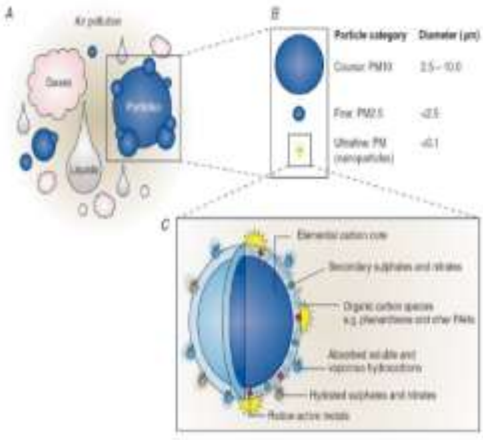

Fig.2 the anatomy of black soot showing the elemental carbon core[6]

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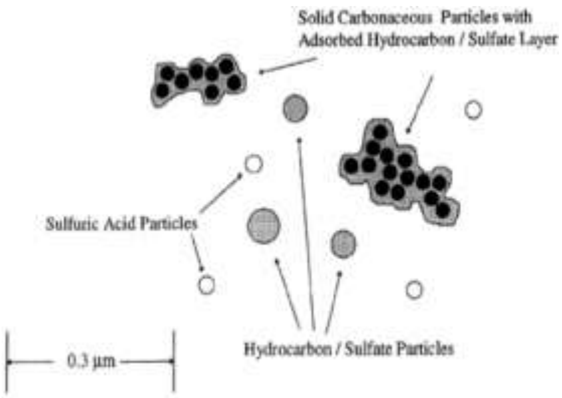


Fig.3 Soot nucleation and growth.

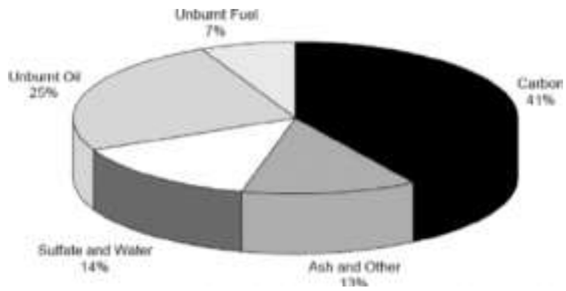


Fig.4 Soot composition

Source: Research Gate Photos

The Intergovernmental Panel on Climate Change (IPCC) adopted the description of soot particles given in the glossary of Charlson and Heintzenberg (1995)[7], "Particles formed during the quenching of gases at the outer edge of flames of organic vapours, consisting predominantly of carbon, with lesser amounts of oxygen and hydrogen present as carboxyl and phenolic groups, and exhibiting an imperfect graphitic structure.

Formation of soot is a complex process, an evolution of matter in which several molecules undergo many chemical and physical reactions within a few milliseconds. Soot is a powder-like form of amorphous carbon. Gas-phase soot contains polycyclic aromatic hydrocarbons (PAHs). The PAHs in soot are known mutagens and are classified as a "known human carcinogen" by the International Agency for Research on Cancer (IARC)[7].

In February 2017, the Rivers State Ministry of Environment declared the soot an "emergency situation". In the same month, Nyesom Wike, the Governor of Rivers State, established a committee to probe the cause of the soot and suggest ways forward.

The report revealed that there were two major causes of the soot; the activities of illegal oil thieves who employ crude and primitive techniques and the inappropriate burning of these illegal refineries by security operatives during their trail and raid on the criminals.

The effect of the black soot on the health of the residents of Port Harcourt and its environs in Rivers State are well documented by various researchers and committee reports as the microscopic particles can penetrate deep into the lungs which is linked to a wide range of serious health effects, including premature death, heart attacks, and strokes, as well as acute bronchitis and aggravated asthma among children[8].

However, the technological consequences and its attended effect on industries, asset losses, reduced machinery availability, increased operational complexities and cost cannot be overlooked.

This paper reviews the effect of the black soot on the ammonia cooling water operation and the cascading effect on the Ammonia production at Notore Chemical Industries. It x-rays the increased frequency of chemical dosing, clogging of side-stream filters, reduced heat transfer efficiency, increased downtime for maintenance and heat exchanger cleaning, increased blowdown rate and reduced production.

Effect of soot on ammonia cooling water system

The prevalence of black soot has affected the ammonia cooling water system negatively. The exact extent of this impact may not be quantifiable in the short term. This is because the frequent shutdown occasioned by frequent exchanger fouling will have long term effect on other process equipment not directly involved with the cooling water system. Take for example, The primary reformer. It is made up of 368 catalyst tubes (material of construction loaded with promoted Nickel Oxide catalyst. These tubes are made of high-grade alloys that have been heat treated. However, temperature cycling due to frequent start-up and shutdown reduces the useful life.

The effect of cooling water on ammonia processes is most pronounced in the ammonia refrigeration system and the turbine vacuum system.

THE AMMONIA REFRIGERANT SYSTEM

The ammonia refrigerant system consists of the following:

1. The Refrigerant Compressor
2. The Refrigerant Cooler
3. The Flash Tanks
4. The Level Control valves.

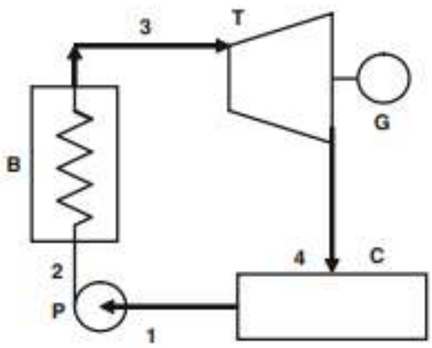
The ammonia refrigerant compressor compresses vapours from the various ammonia chillers and flash tanks to a discharge pressure of about 16.7Kg/cm2 and a discharge temperature of about 136^{o}C. This compressed vapour is then cooled in the refrigerant cooler to about 42.2 ^{o}C. Fouling of the exchangers results in poor heat transfer coefficient. The result is that the ammonia refrigerant condensers are not able to sufficiently condense the compressed ammonia vapour. This results in less liquid ammonia available for chilling the ammonia in the synthesis loop of the ammonia production process. Inefficient chilling results in produced ammonia entering the synthesis gas converter, where they serve as inerts, recycling the converter, thus reducing the quantity of ammonia produced.

The fouling of the ammonia refrigerant condenser is manifested in high refrigerant temperature in the outlet of the ammonia refrigerant condenser, the ammonia refrigerant compressor final discharge pressure increasing above its setpoint value of 19.7Kg/cm2, and the intermittent lifting of the refrigerant receiver relieve valve.

Another area affected by increased fowling caused by black soot is in the turbine vacuum system. The turbine system is a typical example of a Rankine[10] cycle. It is a thermodynamic cycle having the following component, namely:

1. A turbine
2. A heat source (Boiler)
3. A heat sink (Condenser)
4. A pump

The figure below shows a typical Rankine cycle



P= Pump, B= Condenser, T= Turbine, and C= Boiler

Fig.5 Typical Rankine cycle

Source: Chemical Thermodynamics- An Introduction2012 (Springer Books).

The efficiency of a Rankine cycle is given as

$$\eta_t = 1 - \frac{T_C}{T_H}$$

Where T_C is temperature of the heat sink (condenser) and T_H is the temperature of the heat source or boiler.

Therefore, increasing the temperature of the cooling water will lead to a loss in vacuum, leading to increased steam consumption and possibly plant shutdown.

Fouling due to excessive black soot reduces the heat transfer coefficient of the surface condenser. This can also result in increased steam consumption to power the pumps and compressors, and in extreme cases, it has resulted to plant shutdown.

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The figure below shows a trend of the effect black soot has had on ammonia production in Notore Chemical Industry Plc. The production data was collated from December 2021 till date. It is important to note that this period coincided with the period of excessive soot accumulation in the atmosphere due to illegal refining before the effort of the state government caused the excessive soot generation to abate

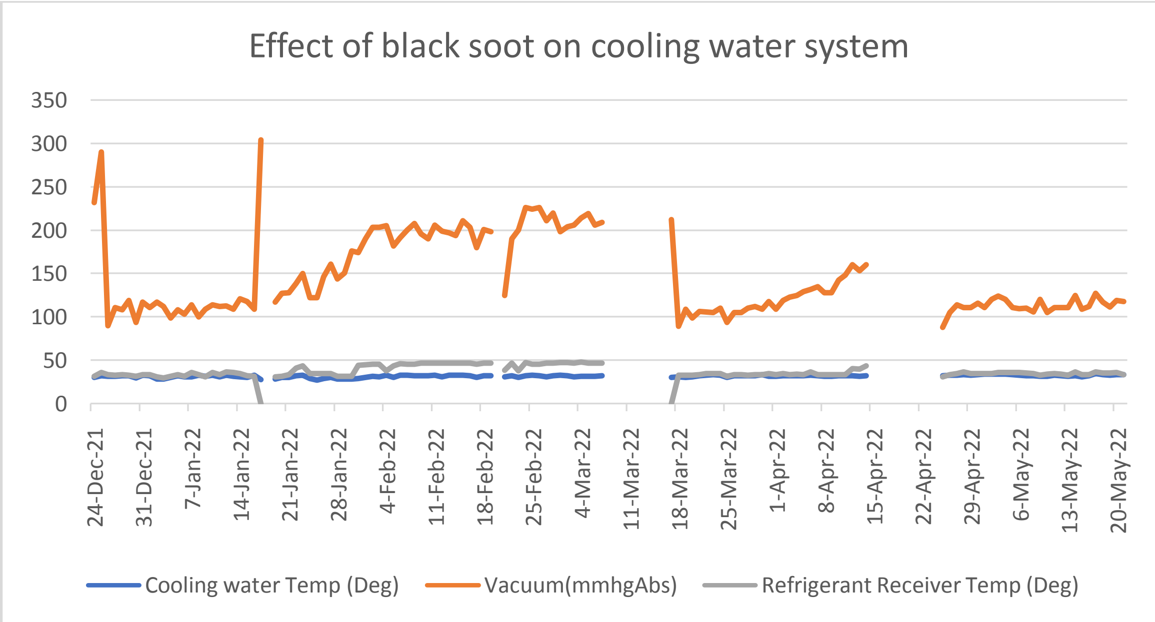

Chart 1: Effect of soot induced fouling on ammonia production. Data from ammonia production daily parameter sheet. Xxx industries plc.

It can be seen from the chart that between December 2021 to February 2022, the vacuum system was significantly bad. This period coincided with the peak period of excessive soot due to "kpofire." The chart shows a direct correlation between the amount of soot in the atmosphere and the fouling frequencies of the exchangers and hence the deterioration of turbine vacuum system.

It is also noteworthy that the break in trends observed from the chart is the shutdown period caused by excessive fouling. The data shows increased frequency of shutdown due to fouling during peak soot production period.

Moreover, the plant witnessed a drop in production as most of the process vents were left open to take the inerts (uncondensed ammonia formed which can no longer take part in the reaction in the synthesis gas converter). The net effect of these inerts is quenching of the converter, frequent lifting of pressure relieve valves, and contamination of the atmosphere.

The effect of soot is also shown in the number of shutdowns for exchanger cleaning experienced in thisperiod. From the available record, ammonia plant experienced 67% more shutdown due to fouling than during other times. Moreover, the consumption of cooling water treatment chemicals increased by 70% more than at other times. Similarly, the company spent almost twice the normal amount of money in cleaning fouled exchangers in ammonia plant. The figure below shows the effect of black soot on cost of exchanger cleaning.

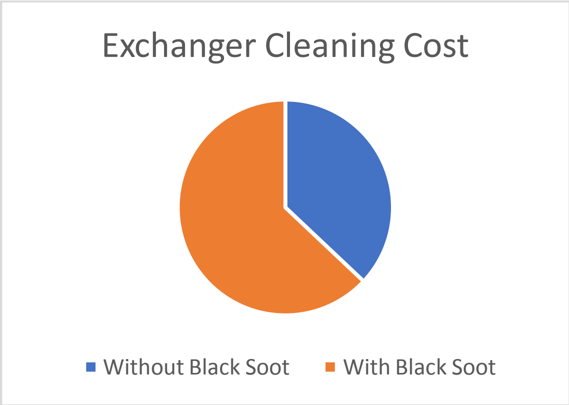

Chart3 increases cost due to soot induced fouling, Data source: Notore Chemical Industries Plc.

II. RECOMMENDATION AND CONCLUSION

The forgoing shows the impact that illegal refining of crude oil in the Niger Delta region is having on industrial processes. The impact of black soot from illegal refining goes beyond its effect on the cooling water system. It also involves the production losses caused by downtime incurred while cleaning the exchangers. It is also evident in the stress on machineries and equipment that must undergo endless cycles of start-ups and shutdowns due to fouled cooling water system. What about the stress on the employees who will have to work extra hard for additional/unplanned start-up and shutdowns? The cost is enormous.

As it is, there is little that company management can do to stop these illegal refining than hope for government to wake up to their responsibility of fighting this menace that is eating deep into the fabrics of the society. In recent times, the state government has shown increased willingness to clamp down on illegal refining. However, it is a tough battle to win. This is because some the security agencies are complicit in this illegal web of local crude refining.

However, companies operating in these regions might consider factoring this into consideration when designing future plants. The goal might be to build plants that are resistant to the effect of soot induced fouling. They could consider building cooling towers with louvres covered with rollable filters to prevent soot from coming into contact withtheir cooling water system. They can also consider chemicals that will help reduce the effect of these soot particles on the cooling water exchangers by reacting with the soot particles and possibly taking them out of solutions.

Another alternative could be to come up with an optimized program of heat exchanger cleaning that will reduce the downtime incurred during this cleaning and increase productivity.

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