



ENHANCED AIR QUALITY IMPACTS OF PETROLEUM REFINING FOR PETROCHEMICAL INDUSTRIES

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Abstract: Though refineries and petrochemical industries meet society's energy demands and produce a range of useful chemicals, they can also affect air quality. The World Health Organization (WHO) has identified polluted air as the single largest environmental risk, and hence it is necessary to strive for and maintain good air quality. To manage potential health impacts, it is important to implement proper air quality management by understanding the link between specific pollutant sources and resulting population exposures. These industries release pollutants such as Volatile Organic Compounds, greenhouse gases and particulate matter, from various parts of their operations. Air quality should be monitored and controlled more meticulously in developing nations where increased energy demands, industrialization and overpopulation have led to more emissions and lower air quality. This paper presents a review of findings and highlights from various studies on air quality impacts of petroleum refining and petrochemical plants in many regions in the world.

IndexTerms - Refinery, Air quality management, Air, Air pollution

I. INTRODUCTION Air pollution and air quality impacts have been studied for many years now, and there are significant concerns around the world to varying degrees. This has led to the creation of Air Quality Indices (AQI), which are used to analyze the severity of air pollution and the level of risk to health, arising from particulate and gaseous air pollution. A variety of indices have been in use in various regions around the world. For instance, the Pollutant Standards Index (PSI) established by the United States Environmental Protection Agency (US EPA), the Common Air Quality Index in European countries, and the Air Quality Health Index in Canada, to name a few [1]. Outdoor pollution is persistent enough to penetrate into the indoor environment and cause sustained, high exposures of occupants to some pollutants [3]. It is therefore crucial to understand the link between specific pollutant sources and the resulting population exposures in order to have proper air quality management [4].

Refineries and petrochemical industries are one of the contributing sources to the degradation of air quality. Though these industries meet the energy needs and growing demand for various products generated from them, they can also contribute to air quality concerns [5]. Exposure to pollution causes many health impacts and has been identified as the world's largest single environmental health risk, contributing to numerous deaths [6] and therefore lowering air pollution levels can lead to a significant improvement in health outcomes. In the same analysis done by the World Health Organization (WHO), it was estimated that pollution contributed to the death of 7 million people in 2012. Of these deaths, 40% related to outdoor pollution were due to ischaemic heart disease, 40% from stroke, 11% from Chronic Obstructive Pulmonary Disease (COPD), 6% from lung cancer, and 3% due to acute lower respiratory infection (in children). Similar effects were linked to indoor air pollution, with 34% of the deaths due to stroke, 26% from ischaemic heart disease, 22% from COPD, 12% from acute lower respiratory infection (in children), and 6% from lung cancer. Since industrial activities contribute to a decrease in air quality, it is important to address this issue, and identify new ways to improve the situation. As refineries and petrochemical industries release a number of pollutants into the surrounding air, we need to understand the sources of pollution in these industries and the nature of the pollutants, in order

to develop effective control strategies. Among the pollutants released by these sites, the main ones are Volatile Organic Compounds (VOCs), particulate matter and greenhouse gases. VOCs found in the ambient air near petrochemical sites are both of aromatic and aliphatic types [7]. Pollutants are released in various areas and sources in the petroleum refining and petrochemical industries, starting from process emissions to storage and handling emissions. It arises from the production process, pipelines, flanges, valves, storage tanks, and waste zones. Pollutants are released even during non-routine operations like maintenance and shutdown [8,9], and the release of pollutants can vary seasonally [10]

3.0 Various Sources of Air Pollution from the Petroleum Industry.

There are various sources of emissions in the petroleum refining and petrochemical industries,

3.1. Process Emissions

In petroleum refining and petrochemical industries, the typical processes that take place include separations, conversions, and treating processes like cracking, reforming, isomerization, to name a few. The emissions arising from these processes are termed as process emissions, and are typically released from process vents, sampling points, safety valve releases, and similar items.

3.2. Combustion Emissions

Combustion emissions are generated from the burning of fuels, which is done for production and transportation purposes. The nature and quantity of emissions depends upon the kind of fuel being used.

3.3. Fugitive Emissions

Fugitive emissions include sudden leaks of vapors from equipment or pipelines, as well as continuous small leaks from seals on equipment. These emissions are not released from vents and flares, but may occur at any location within a facility. Sources of fugitive emissions are mostly valves, pump and compressor, and piping flanges. Fugitive emissions are a source of growing concern, as their effective control requires good process safety mechanisms for mitigation, as well as ongoing leak detection and repair (LDAR) programs. They can be minimized by proper design, and procedure alterations.

3.4. Storage and Handling Emissions

These emissions are released from the storing and handling natural gas, oil, and its derivatives. This is a potential problem in every petroleum refining and petrochemical industry, including any product distribution sites. Handling mainly includes loading and unloading operations for shipping products to customers. There might be emissions during material transfer to these vehicles. These facilities have tanks for storage at the production sites and terminals for transportation, and air pollution here arises from the boil off or evaporation losses. Breathing losses also contribute to the air emissions, as the air within the tanks expands and contracts with daily temperature changes. Likewise, when there is an increase in the liquid volume in a tank, there is a corresponding decrease in the vapor phase volume as VOC saturated air is pushed out.

3.5. Auxiliary Emissions

Auxiliary emissions originate from units like cooling towers, boilers, sulfur recovery units, and wastewater treatment units. Atmospheric emissions from cooling towers mainly include gases, which are stripped when the water phase comes into contact with air during the cooling process. In wastewater treatment units, emissions may arise by stripping of the VOCs from contaminated wastewater in the pond, pits, drains or aeration basins.

4.0 POLLUTANTS OF CONCERN

4.1 Volatile Organic Compounds

Hydrocarbons, both aliphatic and aromatic, are the main VOCs (Volatile Organic Compounds) that are generated from the petroleum industry. Regulated emissions and leaks both contribute to the VOCs concentration. Aromatic VOCs are mainly comprised of Benzene, Toluene, Ethylbenzene, and Xylene (BTEX), and benzene is of particular concern since it is carcinogenic. Short term exposure to VOCs may cause dizziness, fatigue, nausea and depression. Exposure to certain VOCs may even result in mutations and cancers, and others may cause damage to the central nervous system, kidneys and liver.

The detection of VOCs in air typically follows one of two strategies, active and passive sampling. In active sampling, a pump draws air from the sample location through an adsorbent substrate at a specific flow rate, or into a collection container, or to an in-situ continuous sensor, depending on the type of VOC and concentration to be measured. It is important to know the atmospheric lifetime of VOCs to gain an understanding of the distances they might travel in air. A higher atmospheric lifetime indicates that the

VOC can travel a greater distance in the atmosphere, possibly leading to impacts much farther away from the emission source.

4.0 Greenhouse Gases

The greenhouse gases associated with the petroleum refining and petrochemical industries are mainly methane, carbon dioxide and nitrous oxide. In 2006, it was noted that equipment leakage and venting of CH₄ and CO₂ from petroleum and natural gas industries contributed to 317 million metric tons of CO₂ equivalent (MMTCO_{2e}). Out of this, 261 MMTCO_{2e} of CH₄ and 28.50 MMTCO_{2e} of CO₂ were emitted from the natural gas industry, whereas 27.74 MMTCO_{2e} of CH₄ and 0.29 MMTCO_{2e} of CO₂ were emitted from the petroleum industry. Many refineries meet their heat and electricity needs by producing it themselves from gas, Fluid Catalytic Cracking coke and fuel oil. In this case, the fuel requirement, and hence the greenhouse gases emissions, are higher than they are for the refineries which procure these utilities from elsewhere. The greenhouse gas emissions are also linked to the complexity of the refineries, where in general the more-complex refineries emit more such gases. Even during the production stage, greenhouse gas emissions are significant. In 2013, the carbon dioxide emissions during oil production and processing were estimated to be 130 kg CO₂ per Ton of Oil (TOE). For each ton of hydrocarbon production, there would be release of 1 kg of methane, and 0.4 kg of nitrogen oxides. The count of wells and the production rate from each well have an important effect on the greenhouse gases emissions.

Particulate Matter

Particulate matter (PM) is of increasing concern in recent years as studies have shown links with a variety of health impacts such as respiratory and cardiovascular morbidity, and even lung cancer. According to the International Commission on Radiological Protection (ICRP) Publication 30, particulate matter that is larger in size (over 10 µm) is intercepted by the nasal, tracheal mucus and is concentrated mainly in the naso-pharyngeal region. Particulate matter of very small diameter is considered to be the most problematic as it penetrates deep into the lungs, thereby depositing in the bronchioles and alveoli in the pulmonary parenchyma region. Therefore, in many regions the focus of measurement and regulation is on particulate matter with a size of less than 2.5 µm (PM_{2.5}).

According to World Health Organization (WHO) guidelines, the annual arithmetic mean concentration of PM_{2.5} should not exceed 10 µg/m³, while the 24-h mean concentration of PM_{2.5} should be below 25 µg/m³. Particulate matter in air is sampled using integrated sampling systems, typically for a period of 24 h. Filter substrates in the system capture PM, from which it is possible to measure the mass concentration using gravimetry. Captured PM can also then be analyzed for its chemical components where desired. Based on the formation mechanism, particulate matter can be classified into two types, namely primary and secondary particulate matter.

OZONE

Ozone is a secondary pollutant that is formed from the reaction between VOCs, oxides of nitrogen, and sunlight. Hence, ozone production depends on the amount of VOCs, NO_x, and also the ratio of VOC/NO_x. The petrochemical industry can be a significant source of hydrocarbons (VOCs) and NO_x, and hence it contributes to a favorable atmosphere for the formation of ozone. In the case of ozone resulting from coal-fired power plant emissions, hydrocarbons have to be provided from the surrounding region, and the power plant location relative to sources of reactive hydrocarbons is important in determining the impact on ozone formation. The effects can be worse in summer when temperatures and ozone production rates are higher. Other factors such as vehicular emissions also increase ozone formation by contributing to high levels of ozone precursors. Hence the urban zones/ traffic prone regions near petrochemical sites are at high risk of ozone formation. The presence of ground level ozone and airborne particles is a characteristic of photochemical smog, which is characterized by haze and reduced visibility. Topography and meteorology such as inversions also influence smog retention by trapping the pollutants. Smog can cause respiratory problems, coughing, irritation, reduced lung function, asthma, lung inflammation and damage to the lung lining.

6.1 Air Pollution Control Methods Used at Refineries for Control of Gaseous Emissions

The air pollution control methods used in refineries are based on the same principles and (lie same unit processes used in other industries. Their features are unique only in the technical details of application and design. Removal of vapor-phase objectionable components from gas streams generally falls into one of the following four categories:

- (1) Absorption into a liquid.
- (2) Adsorption on a solid.
- (3) Chemical conversion to another compound.
- (4) Incineration

Oxides of Sulfur

There are no commercially developed processes which can economically recover sulfur or sulfur dioxide from stack gases normally produced in combustion operations. There has been a tremendous amount of research and development activity on power plant flue gases. Refinery flue gases contain sulfur dioxide in low concentrations and there are no satisfactory methods for further reductions. Special methods have been applied to gas streams which contain higher concentrations of SO₂ than the refinery flue gases. Briefly, these methods all consist of absorption of the sulfur dioxide in solutions of lime water, ammonia, sulfuric acid, ammonia or sodium sulfite.

Hydrocarbons

Probably the largest single source of hydrocarbon emissions in a refinery is gasoline storage. There are several types of tanks and tank modifications that can be used to control evaporation losses. Each type of tank is designed for specific storage requirements and the type selected should be based on actual storage conditions. Tanks and equipment to control evaporation loss are recommended by the API. API informational bulletins are available on the use of plastic foam, low-pressure tanks, and floating roof tanks. Internal floating covers, vapor balancing systems or vapor recovery systems can be installed on fixed roof tanks. Pump gland losses can be reduced by the use of mechanical seals on pumps handling gasoline or lighter material. Preventive maintenance programs help to keep hydrocarbon leakage to a minimum. Evaporation from sewers and oil-water separators is a minor source of loss but it can be minimized by liquid sewer seals and covered separators. On unit shutdowns, vessels are depressured to the fuel gas system, to the vapor recovery system, or to the field flare. Emissions during loading of tank trucks and tank cars are greatly reduced by submerged loading techniques. Evaporation loss calculation methods for loading operations have been developed by the API's Evaporation Loss Committee. Vapor recovery or incineration systems have been developed for additional vapor control at loading facilities. However, use of them has proved too costly and burdensome to economically justify recovery of the small additional amount of vapor being lost. They are being used where unusually restrictive control has been implemented.

Oxides of Nitrogen

Refinery stack gas streams have very low concentrations of nitrogen oxides and are not a serious problem under normal conditions. Commercial processes for dealing with such gas streams

have very poor removal efficiencies. Studies are being made on the catalytic decomposition of nitric oxide and engineers claim gains for the use of catalytic oxidation in chemical plant gases as a means of simultaneous removal by two-stage combustion and tangential firing systems.

Air Pollution Control Methods Used at Refineries for Control of Particulate Emissions

Since catalyst fines, clays, and fly ash are solid materials with similar characteristics, the methods and equipment to remove them from gas streams are similar. Procedures commonly used are classified as dry collectors and wet collectors. Dry collectors in common

use are:

- (a) Filters
- (b) Gravity-settling chambers
- (c) Cyclone separators
- (d) Mechanical centrifugal separators
- (e) Electrostatic precipitators
- (f) Sonic agglomerator

Wet collectors utilize a liquid, usually water, to remove the particles from a gas stream. Spray chambers and the Venturi scrubber are most commonly used. The most up-to-date reports on removal of particulate matter from gaseous streams are based on research studies sponsored by the API's Committee on the Disposal of Refinery Wastes.

CONCLUSION

Exposure to poor air quality appears to contribute to health conditions and deaths from COPD (Chronic Obstructive Pulmonary Disease), respiratory infection, lung cancer, and heart damage. The direct contribution of refining and petrochemical emissions to health effects cannot be determined for certain, as many other factors such as population lifestyle and habits, and other emission sources also need to be considered before drawing any firm conclusions. This needs more research and extensive studies before we can infer more from any associations between specific emissions and health effects, but it is clear that any positive impacts on air quality can be beneficial. To maximize the benefits of new legislation and policies to improve air quality, it is desirable to carry out policy analysis using statistical modeling. Such statistical modeling enables the analysis of the distributional consequence of different scenarios for emission reduction. This could thereby make it easier to conclude whether certain emission reduction policies could lead to minor or significant

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