Atmospheric Concentration Saturated and Aromatic Hydrocarbons Around Dura Refinery

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Abstract. The process of oil reproducing in the refinery considered as one of the largest industrial facilities responsible for the emission of many pollutants into the air and works to pollute the air surrounding the refinery. Hydrocarbons are among the most important pollutants emitted into the air from oil recycling operations and should be studied to reduce the proportions of hazardous pollutants. As the pollution caused by the burning of fuel in the chimneys of the refinery Dura is a dangerous contaminant to the environment, where the exposure of substances and pollutants that lead to disruption of the balance of the natural elements of the atmosphere and thus harmful to human and sustainability. The aim of this study is to study the concentration of hydrocarbon contaminants that cause air pollution caused by stacks of fireplaces in Doura refinery. The rates of the most dangerous contaminants on the human respiratory system, which cause dry cough, bronchitis, chest pain and shortness of breath, were studied as a study of carbon, sulfur and nitrogen oxides. In this research, a large number of analyzes, tests and certification were carried out on periodic tests provided by the Doura refinery after repeated field visits to examine concentrations of contaminants present in the atmosphere. Where the maximum distance of pollutant concentration from the source was found, as well as a comprehensive study of an integrated set of weather conditions such as wind speed and climate effects to preserve and sustain the environment.

Keywords: Sulphur dioxide; Hydrocarbons; pollution; refinery; Chimney; wind, Doura refinery, Air pollution.

1. Introduction

Atmospheric sulfur dioxide is related to many important processes in the atmosphere: global warming, pollution of air, and precipitation of acids. Sulfur dioxide has natural, as well as anthropogenic origins. Since industrialisation, anthropogenic emissions were increased dramatically where the main origin of Sulfur dioxide is the burning of coal and oil. Thanks to adaptation of newer technologies and stricter regulatory requirements, sulphur dioxide emissions were substantially reduced in Europe over the last 30 years [1].
Emissions in Finland in comparison to other parts of Europe were fairly low but there were nevertheless no apparent reduction in atmospheric concentrations[2]. Sulphur dioxide levels in Finland peaked in the 1980s at 600 kilograms of gross pollution. So far the overall emission of sulfur dioxide have been dropped dramatically to 100 kilotons[3]. Oil refinement and other operations that lead, like benzene and 1,3-butadiene, to low levels of emissions of substances with possible carcinogenic content. The petroleum sectors have been shown to have high mortality from multiple cancers[4]. If proximity to pollutants may trigger cancer overmortality by petroleum industry staff, it is reasonable to assume that air pollution from petroleum industries could also cause cancer over-mortality among residents of communities subjected to those pollutants, especially for pulmonary cancer. Just a limited studies have also documented the correlation between air pollution in petroleum and local communities' cancer risk[5]. The oil and petrochemical sectors are known as Taiwan's main cause of industrial air pollution[6]. Taiwan has increased rates of severe irritative symptoms in people, upper respiration symptoms and asthma in school children[7] as a result of sensitivity to petrochemical air pollution. Furthermore, studies have found that the incidence of liver cancer in men and woman lung cancer will increase with residential petrochemical air pollution[8]. More petrochemical air emission was correlated with modified birth sex ratios and an increased chance of kid delivery at term[9]. In the last decade the threats of family planning caused by air pollution[10] have become increasingly concerned.

In the environment with volatile organic materials, the hydrocarbons constitute the leading factor in the troposphere's physical-chemical process (atmosphere that leads significantly to ozone production and other optical oxidizing agents) [11]. For comparison, hydrocarbons like benzene, toluene, and xylenes are extremely toxic or cancerous. Hydrocarbons typically present in urban regions as well as in the industrial environment as a due to human operations, primarily due to exhaust of motor vehicles and several other combustion operations which use and distribute fossil fuels, as well as solvents[12].

Doura refinery considers as one of the largest and oldest refineries in Iraq. Its establishment in 1953 was a real beginning for the advancement of the modern oil industry. It is a transformative refinery that aims to obtain the maximum benefit from crude oil, benzene, liquefied petroleum gas, jet fuel, gas oil, diesel, crude oil, grease, wax, asphalt, etc., It also contains a sophisticated laboratory for the manufacture of plastic cans for the packaging of oil produced, producing about 80 thousand packs per month. The unit consists of several units such as distillation unit, oil production unit, light oil unit, refining unit and power unit. It is noteworthy that all these units have chimneys that transmit fuel combustion products to the outside air[9].
In 2014, concerns emerged about the impact of the liquidator on the population, because, when the refinery was built at the end of the 1950s, the Dora area was not inhabited. Therefore, the Committee called for the health and environment of the Iraqi parliament to "implement the decision to transfer the refinery to another place according to environmental and international regulations that prevent the establishment of refineries within the communities. Hence, the need to conduct a research regarding the evaluation of the air quality surrounding the refinery of the course is required. This is what the research indicates, using the data provided by the Doura refinery and inserting them into a program of air dispersion modelling and testing.[13]
Figure 4. the site of the Doura refinery from Google Earth

Figure 5. Air dispersion modeling examination program,

The objective of this research is to study the causes of environmental pollution and to work according to the scientific methodological bases to determine the sizes of the air pollution problem in the Doura refinery and to determine the risks caused by flue combustion products by calculating their emissions. Besides, the study aims to measure the concentrations of these pollutants by the program of air dispersion sampling and modelling. Moreover, study a full range of weather conditions, including all categories of stability and wind speed to find the maximum effects of pollution to work on reducing them and maintaining a sustainable environment.[14]

2. Theoretical part 2

2.1. Main Refining Units in Dawrah
Each operational unit of the refinery contains several chimneys. The total number of chimneys (44-50) [6] each of which emits fuel combustion products into the atmosphere, the most important of which are sulfur oxides, nitrogen and carbon. These units include the refining unit, Hydrogenation, Fat Unit, Air Distillation Unit and other units like generating unit and light oils unit.
These units perform several necessary operations. For example, the refining unit treats raw oil and extracts the many desired compounds and converts them into products suitable for consumption because it is not possible to use crude oil in the form that is found in the ground. Refining means breaking crude oil into its original components and molecules and rearrange them to be different from those found in crude oil, i.e., manufactured into final usable products (10). Energy unit dealing with several types of fuel such as fossil fuels, which includes oil, coal and gas, which has been used extensively since the last
century and is still being used with the same extravagance as its prices rise day by day, with severe damage to the environment. Furthermore, like the oil of shale, it is like oil that is mixed with sand as in Figure 6. For the Hydrogenation Unit, there are five Hydrogenation Units in the Refinery, which are designed to improve the properties of light and medium oil derivatives and reduce their content of sulfur, nitrogen, oxygen and other impurities through the process of media hydrogenation.[14] The fat unit is a part of the production process includes the essential oils of all kinds involved in the production of all kinds of ready-made oils, and after adding the necessary chemical enhancers, as well as the wax in addition to the oxidized solvent asphalt, which is processed in the form of pellets, pellets and also grease of all kinds. In the air, the distillation unit distil the crude oil into fractions. [15] The fat unit includes the essential oils of all types involved in the production of all kinds of ready-made oils. Moreover, after the addition of the necessary chemical enhancers, wax as well as the oxidized solvent asphalt, the providing process cried out in the form of droplets in pelvic cars. And also grease of all kinds. It is produced in the air distillation unit by distilling crude oil into fractions. Besides, there are other refining units, such as the generating unit and the light oils unit, where all the combustion products are sent to the air. Not only the stacks of these units cause air pollution in the refinery, but the torch system also has the effect of adding pollutants to the air.[16]

2.2. Burning system
The burning system operated by air pressure and used to burn gases of any quantity. Also, it is used in oil and natural gas production and processing, in refineries and chemical processing plants of all kinds. The burning system is essential in these units and it's usually receiving free gases from safety valves, blowdown valves and gas discharge lines that cannot be discharged into the atmosphere due to their environmental impacts, so they are burned in this system. Moreover, this system can be considered a safe way to burn the vapors produced from these units after the isolation of liquids through a controlled burning to maintain the safety of workers and equipment (10). Note that, the type of Burning system located in the Doura refinery is one of the most common and most straightforward of such systems. It provides sufficient and safe burning of gases at different degrees of flame. Also, steam injection methods can be used in this system, as shown in Figure 6. Finally, burning toxic gases is the best solution for discharging high concentration gases in oil and natural gas processing units, especially hydrogen sulfide gas.

2.3. Combustion Operations in The Refinery and The Resulting gases
According to the biological theory of oil formation, oil is a viscous, and dense oil tends to be black mainly consists of several aromatic hydrocarbons or activated as well. Many mineral elements, such as
elemental sulfur and iron. The burning of oil contributes to the production of the most important hydrocarbons that pollute the air, e.g. the pollution and release of natural gas which is produced from various chemicals, including methane, ethanyl, propane, butane and other gases. Where experts in environmental and public health research have alerted the consequences of burning oil fields and that gases like sulfur oxides, nitrogen and methane that, in addition to their environmental or economic consequences, are extremely toxic to the respiratory system.

2.4. Types of gaseous pollutants from refineries
In this paper, we focus on the most dangerous emissions because of their adverse effects on the environment when maintained at higher levels more than the permissible limits (14); these pollutants are:

- Sulfur oxides (SOx): The chemical molecule SO2 is sulfur dioxide, in specific. SO2 is produced from volcanoes and different industries. Its combustion creates sulfur oxides, as coal and petrochemical comprise sulfur compounds. The excess sulfur dioxide SO2 oxidation generally produces H2SO4 sulfuric acid, which forms acido rain in the appearance of a catalyst such as NO2. These are some of the grounds for concern regarding the environmental effects of using these oils as energy sources[15].

- The NOx (nitrogen oxide): NOx, especially nitrogen dioxide, these materials are emitted from combustion at high temperature. This type of gas can be seen in the form of domes of brown fog or pull of feathers that spread over cities. Nitrous oxide is a chemical compound referred to as NO2. It also represents one of the multiple types of oxides of nitrogen compounds. This poisonous brown-red gas has a strong, aromatic odor. Therefore, NO2 is one of the most visible air pollutants.

- Carbon dioxide (CO2) is a greenhouse gas. This gas is emitted from the combustion process, but it is a necessary gas for living organisms so that it is natural gas in the atmosphere.

| Air pollutants     | Global symbol | The sources   | Maximum allowable limits by mg/cubic meters. |
|--------------------|---------------|--------------|---------------------------------------------|
| Nitrogen oxides    | NOx           | Gaseous fuels| 350                                         |
| Sulphur oxides     | SOX           | Liquid fuel  | 500                                         |
| Carbon dioxide     | CO2           | All sources  | 500                                         |

2.5. Degrees of Air Stability
One of the essential pillars of the study of air pollution is the knowledge of the degree of stability of air because of its importance in the diffusion of pollutants. Thus, stability and instability in the atmosphere can be defined as if an air block is forced to rise under the influence of any external forces until it reaches a certain level, then the external forces are removed, we will find one of the following cases:

- Stable Atmosphere: If the ascending air goes back up to its original position.
- Neutral Atmosphere: If the rising air stays up in its place.
- Unstable Atmosphere: If the upward air continues to rise, moving away from its original position.

2.6. Environmental Impact and General Rules of Stability and Instability
The air in average weather conditions, is either in saturation or in the non-saturation state, that the unsaturated air temperature becomes lower with rising at the rate of dry thermal self-reduction which is 10°C / 1 km. So, If the dry thermal self-reduction rate of the surrounding medium is 13°C / 1 km, the rising air continues to rise to the top and does not tend to return to its original place and so that it will be in an unstable situation, and this is the condition of air instability of the unsaturated air. However, If
the temperature of the dry thermal self-reduction rate is 8°C / 1 km, the air will tend to return to its original position, and in this case, the air is in a stable state. The spread of pollutants in the unsaturated air is relatively faster than the saturated air, because of the presence of sufficient area of pollutants to be saturated in the air. Thus, in this case, the process of transporting pollutants will be more efficient, and this will adversely affect the environment.

The saturated air temperature decreases when it rises by the self-saturated thermal decrease of 6.5 °C / 1 km. If that rate is 8 °C / 1 km, the air continues to rise and does not tend to return to its original position, and here it is in a state of instability. While, if the rate of thermal decline of the surrounding is 4 °C / 1 km, the air, in this case, tends to return to its original place, and here the air is in a stable state. However, the diffusion of saturated air is relatively less because the air saturation ratio is relatively higher and so that it is less efficient than the unsaturated air in transporting pollutants that affect the environment.

3. Air Pollution Modeling

A program was used to model the results of air pollution obtained from the refinery in this research. One of the programs of the AIR company that specialises in environmental programs was used. The program LAKES ENVIRONMENTAL that used for testing air dispersion modeling as shown in Figure 7. This program uses information from sources and meteorological conditions to calculate how pollutants pass through the atmosphere and what the concentration of pollutants is at specific points. This program requires several data to be entered, processed and then modelled for results. These results were taken from the Doura refinery as well as the results we studied.

The data obtained from the refinery relating to the source of emissions (such as fuel combustion emissions products in the refinery), flowing gas flow rate and the chimney dimensions are entered in the program to assess emission concentrations and then assess their environmental impact as shown in Figure 8.

In order to determine the types of emissions from the combustion furnace stacks due to fuel combustion, it was assumed that combustion reactions were complete due to combustion in an open atmosphere and the sufficient amount of oxygen. It must be noted that the mass flow rate of the O₂, CO₂, SO₂ emissions that taken from the refinery is listed in Table 2.
Table 2. Mass flow rate of the O₂, CO₂, SO₂ emissions[11]

| Polluting factor | Measuring unit | Released gases | Measuring unit | Released gases |
|------------------|----------------|---------------|----------------|---------------|
| COx              | Ton / month    | 112721.5      | m³/month       | 204948.13     |
| NOx              | Ton / month    | 332.9         | m³/ month      | 641.6         |
| SOx              | Ton / month    | 2647.4        | m³/ month      | 4862.6        |

There are many operational units of the refinery, and each unit contains several chimneys. Moreover, based on the data provided by the Department of Environmental Protection in the refinery, the height of the chimneys ranges between 10 and 15 and 30 meters and the diameter between 1 - 3 meters. In this research, variable heights and diameters were taken, and the effect of each height and diameter was calculated separately in the diffusion of contaminants.

The speed of the exit gas from the chimney is 2.5 m, the speed of the exit stack gas is 25 m/s, the temperature of the exit gas stack is 450 K, and the ambient temperature is 29°C.

All the categories of stability of atmosphere were taken into account at various speeds ranging from 1 m / s to 20 m / s, which covers stable, moderate and unstable climate stability categories to study the effect of diffusion of pollutants in these different conditions and their comparison. Besides, the surrounding area of the refinery was characterized by to consider as a different terrain (simple and complex terrain), so as to study the effect of the spread of pollutants in the area when it is open free of buildings and taking into account the surrounding buildings and their height.

4. Results and Discussion

In this study, the effect of a number of factors on the concentrations of pollutants from the Doura refinery has been studied. These factors are the effect of the chimney height on pollutants concentration, the relationship between the chimney height and base and its effect on the spread of carbon dioxide, and the amount of carbon dioxide concentrations on the ground.

4.1. Effect of Chimney Height On The Concentration and The Spread of Contaminants

The height of the chimney has a significant effect on the concentration of the pollutants produced by the chimneys. Where, when the height is 10 meters, we notice an increase in concentration levels with the increment of height. Moreover, it was found that the concentration at a distance of 50 meters is 1.131 micrograms/cubic meters, and at a distance of 100 meters, the concentration will be 1.419 Micrograms / cubic meters, as shown in Figure 8. Also, when the height chimney is 15 meters, we noticed that at 100, 200 and 300 meters of chimney height, the concentration will be 2.341, 1.065 and 0.751 Micrograms / cubic meters respectively as shown in Figure 9. Besides, when the height chimney is 20 meters, it was found that at levels of 400, 500 and 700 meters, the concentration is 718.200, 583.800 and 337.100 respectively, as shown in Figure 10.

Figure 11 shows that, when the height chimney is 25, the concentration at a distance of 800,900 and 1000 meters is 297000, 244400 and 208800 respectively.

Finally, at chimney height of 30 meters, the concentration at a distance of 700,7500,8000,8500 and 9000 meters, is 15790000, 14750000, 13520000, 1260000, and 1181000, respectively, as shown in Figure 12.
Figure 8. CO$_2$ Concentration from 100 meters from the chimney. (10 meters firm chimney base)

Figure 9. CO$_2$ Concentration from 300 meters from the chimney. (15 meters firm chimney base)

Figure 10. CO$_2$ Concentration from 700 meters from the chimney. (20 meters firm chimney base)
Figure 11. CO₂ Concentration from 1 kilometer from the chimney. (25 meters firm chimney base)

Figure 12. CO₂ Concentration from 10 kilometer from the chimney. (30 meters firm chimney base)

4.2. The Relationship Between Chimney Height and Base and Its Effect On the Spread of Carbon Dioxide
From the previous drawings, we conclude that the relation between the chimney height and the distance from which the contaminants spread away from the chimney and the concentration of carbon dioxide emissions is positive. The higher the rise of the chimney, the greater the spread of carbon dioxide in the air away from the chimney with a lower concentration of pollutants at the ground level.

4.3. The Relationship Between the Chimney Height and The Amount of Carbon Dioxide Concentrations On the Ground
Figure 13 shows the spread of pollutants at different chimney heights, where there is an inverse relationship between chimney height and smoke emission concentrations. The higher the chimney, the lower the concentration of a pollutant at ground level and vice versa.
4.4. Spread of Pollutants for Different Categories of Stability

It was found that pollution of CO₂ concentrations exceeds the permissible limits of Iraqi environmental legislation when the chimney height is from 20 to 30 meters. Here we will discuss the worst pollution cases by categories of air stability:

- **Class A**: The concentration of the CO₂ pollutant is the highest at the ground level because of the fluctuation of smoke due to high degree of vertical air disturbance, making the smoke circulate at a right level so that it brings pollutants to the ground. This occurs only in warm conditions at low wind speed, which is similar to the unstable class A as in Figure 14.

- **Class B**: Due to the high-speed wind (5) m/s, and the overcast or partly cloudy conditions that prevent heat radiation, the vertical motion will be discouraged; therefore, the contaminants will extend to greater wind-direction distances as in Figure 15.

- **Class C**: Contaminants are within a reflective layer, either surface reflection (occurring on net nights or at night with a light cloud cover) or upper reflection (occurs when the previous night's reflection increases during the day phase due to the warming of the earth's surface to form a roof that prevents the polluter from moving vertically). The slanted line in the left part of the figure is like a static heat tool, while the two connected lines are the ambient temperature. In general, when the polluter is dispersed within the reflection layer, the vertical motion will be blocked as in Figure 16.
5. Conclusions
By using data modelling by the program, and by depending on the data provided by the Doura refinery, it was found that; NOx, SOx, CO2 emissions from the combustion processes in the refinery were observed as a result of the presence of these substances in the raw material of the oil. Besides, carbon dioxide emissions were found to be within the limits of Iraqi environmental legislation when the chimney height was 10 meters and 15 meters. Where carbon dioxide exceeds the limits allowed by Iraqi environmental legislation when the height of the chimney is between 20 - 30 meters.
It must be noted that Gases like SOx, NOx were not drawn in the program in this research because the emission rate for both of them is meagre to almost.
Besides, in this study, it was found that, when the chimney height is high, the contaminants are spread over vast distances. Furthermore, when the wind speed is high, and the weather is overcast or partly cloudy, the pollutants will spread far from the source of pollution to the wind. Also, it is found that in hot conditions and when wind speed is low, the highest concentration of contaminants is at ground level.
Finally, we suggest using this updated modelling of this research before starting any project in the refinery, because it will give a complete predictive picture of the pollutants and their spread. Furthermore, this will contribute to improving the environment and preserving it through the design stage and thus preserving the environment sustainability.

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