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Determine the Extent and Emission Factors of SO_2, NO_x, CO, NO_2 Diffused From Gas Refinery Processes Located in the South Pars Gas Field

Abstract: In this study, the sources of pollution have been first identified and then emission monitoring system has been studied in order to calculate the emission factor. In the next stage, volumetric concentration of gaseous pollutants released has been measured for phases 6, 7 and 8 of the refinery in four seasons in 2013 and three times of full load in each season in terms of ppm and according to the working hours of the units per year, the actual emission factor for CO, SO_2, NO_2, NO_x gases have been calculated in terms of ($\mu gr/m^3$) as well as the total amount of pollution released from each phase of the refinery. According to the thermodynamic relations governing the gases and mass balance of combustion products, the concentration of these gases has been processed and output of this process involving the mass concentration of the combustion gases, the emission rate and factor for each of these gases has been determined.

The results have shown that CO and NO_x pollutants have the highest rate of emission factors of the gas refinery, while SO_2, NO_2 pollutants have the lowest rate of diffusion coefficients. Therefore, according to the determination of the diffusion coefficient of highest and lowest emissions, the exact contribution of air pollutant index can be calculated in industrial areas such as South Pars. The calculations may be used to manage air pollution and current and future needs, monitoring and control systems of pollutants, damage to the urban area and environment, etc.

Keywords emission factor, gas refinery, air pollution, pollutants, environment

Introduction

Assaluyeh is one of the cities of Bushehr province in south of Iran. The capital of the city, port of Assaluyeh is considered as a huge industrial area. The fourth refinery of south pars gas is located in South Pars in the southeastern of Bushehr province in Assaloyeh and in geographical location of $52^0\ 30'$ to $52^0\ 55'$ of east longitude and $27^0\ 20'$ to $27^0\ 37'$of north latitude. It is limited to Shirino village at the westernmost point, from the east to Chahmobarak village, from the north to the foothills of the Zagros Mountains and from the south to the Persian Gulf (SPGC 2012). The refinery consists of two phases of sea and land and has been designed in three phases with harvesting and processing capacity of 110 million cubic meters and 36.7 million cubic meters for each phase. According to the design, the everyday products of the refinery contain 104 million cubic meters of dry sour gas, 170 thousand barrels of gas condensate and 5,000 tons of liquefied petroleum gas (LPG propane and butane).

Air pollution is one of the challenges facing Assaluyeh and control of air pollution in the region is the most important policies of the Environmental Protection Agency (EPA). The first step to better and more effectively control and reduce of air pollutants is to determine the amount of emissions in this industrial area. In this study, emission factor and combustion gases have been presented in terms of mass of the pollutant produced and the amount of product or used thermal energy respectively.

According to investigations carried out in Iran, Atefeh Ghanavati and colleagues have examined the diffusion coefficient and rate of SO_2, NO_x, O_2, CO_2, CO, NO, NO_2 gases in Fanavaran Petrochemical in 2009 (Ghanavati Hormozi, Nadafi et al. 2009). Torkian has done a study as the qualitative and quantitative evaluation of atmospheric pollutants in Bandar Imam and Razi Petrochemical Complex in 2000(Torkian 2001). Saeed Nazari and colleagues have determined the emission factor of combustion gases discharged from fossil fuel power plants of the country and compared its results with North America in 2009 (Nazari, Sohrabi Kashani et al. 2009). Jen Chen and colleagues have calculated emission factors of air pollutants for fixed sources at a petrochemical plant located in the industrial park of Kaohsiung in Taiwan) (Shui, Ju Kai et al. 1977). Study of air emissions in the industrial city of Cochin in India has been done by Gargava and colleagues in 1996 that indicates CO emission has the largest share in the transport sector (Gargava and Aggarwal 1999). James Lents and colleagues have done a research to study emissions from 42 gasoline vehicles in the city of Istanbul in Turkey in 2007 and concluded that nitrogen oxide has the largest contribution to air pollution of the city (Lents, Unal et al. 2007).

Materials and Methods

- **Calculate the emissions from stacks**

Emission factors are an important tool for estimating emissions in the atmosphere. This factor can be expressed based on mass of pollutant produced or energy consumption on the product or raw material (a unit of weight, volume, distance, produced energy or emission time) or other desired activity profiles (USEPA 2012). According to the standard rules of clean air, the study of the pollutants emission from industries is one of the ways to identify and determine the air quality. For this purpose, the emission factor has been calculated and evaluated and this is a useful and essential tool for managers to control the air quality. There are several methods including continuous monitoring, material balance method, modeling and a few other methods to calculate the emission factor. Continuous monitoring is the best method for calculating the emission factor and determines the rate and mode of emission, but the cost involved is high. By measuring the concentration of gases from the flue and calculating the flow rate of the exhaust gas, the mass of output pollutants can be determined per unit of time.

Using the balance method has a lower administrative cost and higher reliability than continuous monitoring and it is widely applied in industries and areas that make measurement impossible. In this research, monitoring and balancing methods have been used to calculate the emission factor.

In general, emission estimation equation is as follows (USEPA 2012):

$$E = A \times EF \times (1\text{-}ER / 100), (1)$$

In which, E = emission rate (mass of pollutant), A = rate (rate of production of industrial unit), EF = emission factor (mass of pollutant emitted for the production or activity rate), ER = total percentage of emission; the amount will be zero if emission reduction systems have not been used.

In this study, the sources of pollution have been first identified and then emission monitoring system has been studied in order to calculate the emission factor. Testo 350 XL device has been used for a sampling of combustion gases. The device has the capability to measure emissions of SO_2, NO_x, CO, NO_2 by electrochemical sensor. The probe of the device can withstand temperatures up to 1100 Cand calculates combustion efficiency according to the ambient temperature, flue temperature and type of fuel. The flow and rate of the exhaust gas is measured by the device. After identifying the type of fuel consumed in the device and for measuring gases in each stack, the probe is inserted through the Sampling Point and placed in various parts of stack cross section in measuring on-site. When all parameters analyzed reached a sustainable stability, the information is stored. Since the emission factors show the production rate and emissions in normal conditions of a process, sampling has been done in normal operating conditions of the system and avoided in abnormal conditions such as repairs or out of service equipment that affect the performance of the process (Method 1997). In each season, days of sampling have been also determined based on the maximum activity of the refinery in that day. The sampling time of the stacks and their number in each sample are presented Table 1.

Table 1 Date of sampling and the number of stacks

Number Stacks	Date of sampling	Sampling frequencies
16	Spring 2013(May)	3 Days
16	Summer 2013(July)	3 Days
16	Fall 2013(Oct)	3 Days
25	Winter 2013(Dec)	3 Days

The volumetric concentration of gaseous pollutants released has been measured for phases 6, 7 and 8 of the refinery in four seasons in 2013 and three times of full load in each season in terms of ppm and according to the working hours of the units per year, the actual emission factor for CO, SO_2, NO_2, NO_x gases have been calculated in terms of ($\mu g/m^3$) as well as the total amount of pollution released from each phase of the refinery. According to the thermodynamic relations governing the gases and mass balance of combustion products, the concentration of these gases has been processed in the EXCEL software and output of this process, involving the mass concentration of the combustion gases, the emission rate and factor for each of these gases have been determined. The stages of determination and calculation of emission factor of exhaust gases from refinery are presented in Fig 1.

In order to calculate the annual emissions of pollutants from stacks of gas refinery 4, the time of the operation and the output flow has first been calculated. Thus, a 24-hour shift has been considered to obtain the total production time per day. The total duration of activity is 12 months a year at the refinery.

Annual operating time (seconds) = 365 days . 24 hours . 60 minutes . 60 seconds = 31536000

Then, concentration of emissions, which is in ppm, is converted into mg/m^3 according to equation (2). In this equation, M is the molecular mass of the desired pollutant.

$$mg/m^3=(ppm\times1000\times M)/24.5 \text{ , (2)}$$

Flow rate or outlet flow of a stack must be calculated separately according to equations (3) and (4) in addition to concentration and the total work hours.

$$Q_e=A \ \ V \text{ , (3)}$$

$$A=\pi D^2/4 \text{ , (4)}$$

Q_e: The output of the flue gas flow rate (m^3/s)
A: Cross sectional area of stack (m^2)
V: the velocity of flue outlet gas (m/s)
D: internal diameter of the stack (m)

According to Equation (5), diffusion rate is:

== C , (5)

C: concentration of the desired pollutant (mg/s)
Q: flow rate of the flue gas outlet (m^3/s)

$E_{year}=E_D$ aaaaa rrrrrr riiggiii(((eec) , (6)

E_{year}: Annual diffusion rate of pollutant (g)

EF = E_{year} / (amount of annual production), (7) Similarly, this amount is calculated separately for each pollutant and stack and the sum of emission factors is considered according to equation (8) to calculate total emission factor.

$$EF\ (g/ton) = (EF\ of\ stack\ 1) + (EF\ of\ stack\ 2) + \ldots + (EF\ of\ stack\ n), \quad (8)$$

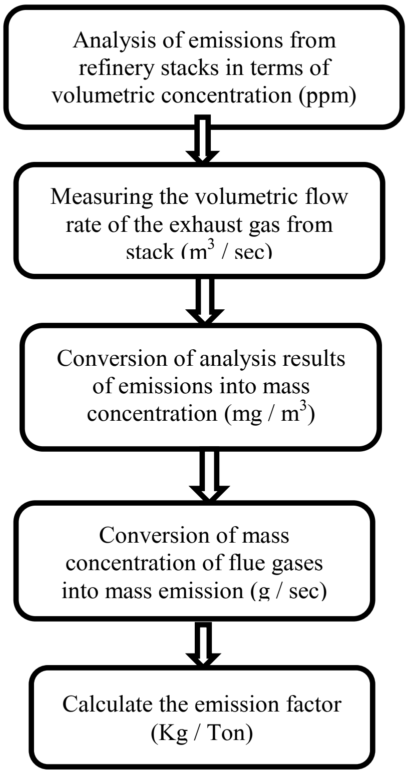

Fig 1 Stages of calculation of emission factor of exhaust gases from refinery

- **Calculate emissions from Flares**

Flaring system is one of the most energy consuming sectors and most pollution mainly comes from this area. In refinery units, low quality gases and gases discharged from the units are led to flaring system at the time of emergency situation through the main pipeline of flare where the gases are burned. Main goal of designing flare is to create safety and security for process units and staff against the dangers of increased pressure and ignition of high-pressure gases. Instead, this system releases environmental pollutants into the atmosphere. The most important compounds of the associated gas contain methane, ethane, propane, butane, hydrogen sulfide. When these gases are burned in flare environmental pollutant emissions such as NO_x, SO_2, CO and CO_2 are created. Eight flares are at work in refinery 4 of south pars. Thus, in order to calculate emissions through flare system, net heat value is first calculated and then the emission method is used.

- **Calculation of net heat value**

The net heat value (NHV) is first calculated (equation (9)) and so, MEKLER method has been used for this purpose. In this method, first the molecular weight of the gas flow (MW) and then the specific gravity of gas (SP.GR) (equation (10)) calculated are calculated (Ghadyanlou 2010). Calculation procedure is as follows:

$$NHV=155+1425*SP.G \quad , (9)$$

$$SP.GR=\frac{MW_{(gas)}}{MW_{(air)}} \quad , (10)$$

$$MW(gas)=\sum_{i=1}^{n} MW_i * Wt\%=19/01 \quad , (11)$$

$$SP.GR=\frac{19/01}{29}=0/655 \quad , (12)$$

$$NHV=155+(1425*0/655)=1089(\frac{BTU}{SCF}) \quad , (13)$$

Results and Discussion

Calculation and precise determination of the contribution to air pollution index of industrial areas has been as essential to decision-making in relation to pollution management programs in order to prevent degradation of the environment. Fig 2 shows the comparison chart of diffusion coefficient values obtained from direct measurement method and the method of calculation of the total emissions from stacks and flares of the refinery according to the seasons of the year. As it has been shown in Fig 2, the values of emission factors obtained from direct measurement are higher than the values of emission factors obtained by computational methods. Since, the actual values of emission have been obtained from the normal operation of the refinery in the method of measuring the accuracy of the results is high. Evaluation of the charts shows that CO and NO_x pollutants and SO_2 and NO_2 pollutants have the highest and lowest amount of the emission factors in the desired gas refinery respectively. In the selected gas refinery of the study, NO_x emission sources assign to two main sources including combustion process at high temperature of 1500 Cand emissions from vehicles formed by the combination of NO and NO_2. In general, the amount of NO_x in the flow of exhaust gas from the stacks of gas refinery rises with increasing combustion temperature which its main component is NO, oxidized to NO_2 at room temperature and in the presence of oxygen. NO and NO_2 emissions are highest in winter. Since the main source of the pollutant is power plants and heating installations, increasing pollutant concentrations may be due to greater activity of the installations in cold seasons. In addition, calm winds that reduce the effective loss of air pollutants, happen in cold seasons more than summer. The average of emission factor for NO_x, SO_2, NO_2 and CO gases from the gas refinery has been estimated 5430.25 Kg/ton, 1.54 Kg/ton, 1.71 Kg/ton and 75.09 Kg/ton respectively by the use of measuring method (Table 2). The average of emission factor for NO_x , SO_2, NO_2 and CO gases from the gas refinery is obtained 1435.1 Kg/ton, 0.53 Kg/ton, 0.14 Kg/ton and 17.41 Kg/ton respectively by the use of computational method (Table 3). The emission factors are greatly reduced by the use of continuous monitoring and reduce emissions systems from refinery stack.

Table 2 The average emission factors obtained from direct measurement method

Pollutant	CO	NO_2	NO_x	SO_2
Average emission factor	75.09	1.71	5430.25	1.54

Table 3 The average emission factors obtained from computational method

Pollutant	CO	NO_2	NO_x	SO_2
Average emission factor	17.41	0.14	1435.1	0.53

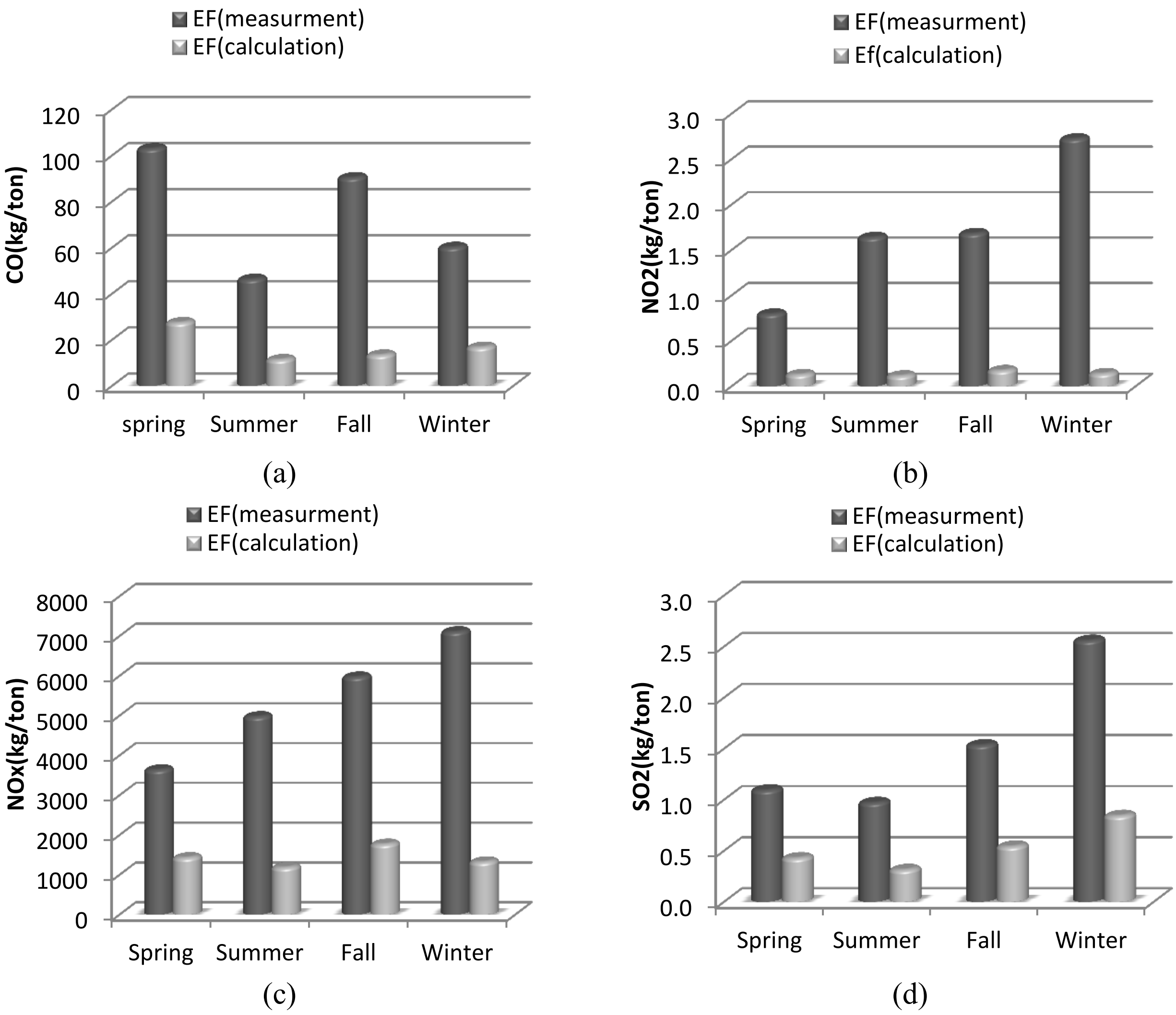

Fig 2 Emission factor values obtained by direct measurement and calculation methods (a)-CO, (b)- NO_2, (c)- NO_x, (d)- SO_2

Conclusion

Basically, increasing the flow rate of the exhaust gas is one of the ways that industries can apply not to observe emission standards and that's why America Environmental Protection Agency states the emission standards in terms of gram per product (g/ton) (U.S.EPA 2013), which is more relatively accurate and equitable standard to control industrial units and industries. In order to evaluate the diffusion rate of these units accurately, daily and annual emissions and most importantly, their diffusion coefficient have been also calculated. Other factors such as production methods, machinery, raw materials and fuel and so on determine the diffusion rate in industries. Environmental risks that threaten the region, is the chance of rain that will be the heaviest acid rain with the weather of the region and this is very dangerous for the residents of South Pars. Due to the prevailing wind direction that is from northwest to southeast, more pollution will be released towards the south east. SO_2 emission factor has been less than all gases due to the use of natural gas and less production of SO_2 is obtained due to having minimum sulfur. NO_x emission factor is higher than other pollutants. So, we can say that the dominant form of nitrogen dioxide is thermal NO_x in this process and the main factor affecting on the rate of its formation is air_fuel ratio. Therefore, the extra air should be considered to burners to ensure complete combustion of gas. Finally, it can be concluded that calculation and precise determination of the contribution to air pollution index of industrial areas has been as essential to decision-making in relation to pollution management programs in order to prevent degradation of the environment.

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