Research Article

SO_2 and NO_x Analysis from Low Pressure Flares in South Pars Gas Field in Iran

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Abstract

Gas flares have always been one of the major sources of producing gases such as CO, SO_2, NO_x and CO_2. Therefore, the appropriate management of the input gas of flares has always been very important. The dispersion of these gases into the environment has harmful effects on the environment and human health. Therefore, in this study the harmful effects of SO_2 and CO_2 emission by low pressure flares in the 1-10 phases of Assaluyeh on the workers' and the locals' health. In the end by considering the acquired data from the refineries in relation to the input substance of the flares, it was calculated that 666916 tons of NO_2 gas and 1.7 tons of SO_2 are dispersed into the environment annually. As observed the effects of NO_2 gas are considerably higher than SO_2 gas. The emission rate based on the Risk Poll model causes an overall damage of 958000 dollars to human health. According to the results the most damage is caused by death, chronic bronchitis and fatigue during the day. As there are many flares active in this region (some permanently and some temporarily) a solution has to be discovered to reduce the rate of flaring or its harmful effects in this region.

Introduction

One of the most important industrial wastes in refinery plants are gases which are sent to flares. Flares are high chimneys in which gas burns and there are two types of them, open and closed and they also come in three pressures, low, intermediate and high. Gas flares have 3 benefits in the refinery industry: 1- absorbing shock from the system 2- repairing the refinery 3- burning harmful gases.

The main purpose of burning gas in gas units is to protect the tanks and pipes against the increasing pressure caused by unexpected movements and is the main cause of energy waste in refineries. The highest amount of pollutants is dispersed into the environment through this system. Among the most important gases created as a result of the input gas of flares burning are SO_x and NO_x. These two pollutants each have harmful effects on human health and on society. Both these pollutants are potentially harmful to human health and can cause problems such as olfactory dysfunction, nasal discomfort, dyspnea and respiratory problems, nervous system problems, pulmonary edema and even death. They can also be harmful to plants. This study aimed to display the equivalent financial cost of damages caused by the pollutants which result from flares.

In this study the Risk poll model was used to estimate the amount of financial damage caused. This model is a consistent program for analyzing human health and the environmental effects and costs related to the production of greenhouse gases in the atmosphere from constant sources. The World Bank reported that in 2008 approximately 150 billion meters cubed of natural gas is burnt across the world which annually add 400 million tons of greenhouse gas to the world. The leading countries in burning gas in descending order are: Nigeria, Russia, Iran, Algeria, Mexico, Venezuela, Indonesia and USA and based on presented data Iran ranks third in the world in extracting and burning renewable gas and first in the middle east [1]. The largest flaring sites in the world are in Russia and the Caspian Sea (approximately 60 billion cubic meters), Middle East and North Africa (45 billion cubic meters), African desert (35 billion cubic meters) and Latin America (12 billion cubic meters). In recent years the amount of gas burnt in

various countries has oscillated and some of them have increased and some decreased. Researches show that across the world burning gas by humans only creates 1 percent carbon dioxide and 4 percent methane [2]. Some organizations and the national oil industry associations have measured the amount of flared gas on a global scale [3, 4]. Some organizations introduced the OPG device to measure the amount of flared gas [5].

Indonesia's oil industry in 1950, burnt 95% of the gas in flares, then by using certain strategies they lowered the flared gas percentage by 28% in 1987 [6]. Some researchers recycled the gas sent to flares in Shahid Hashemi refinery which resulted in Sm^3/h of acidic gases being recycled when a Sulphur unit was turned off and 7000 sm^3/h of the gas sent to flares under normal conditions had suitable economic potential [7].

Methods and Materials

Study Area

Assaluyeh (figure 1) is south of Dehno village, east of Nakhl-e-Taghi and west of Nayband national park.

Figure1: Assaluyeh region in Iran.

The comparison of the amount of low pressure designs in phase 1 to phase 10 refineries is shown in (Table 1).

The comparison of the amount of low pressure designs in phase 1 to phase 10 refineries is shown in (figure 2).

Flare height m	C gas temperature	kg/hr Flow speed	Phase
93	58.1	1.966225	1
65	221	49.043	2, 3
25	221	65.644	4, 5
95	151	282.513	6, 7, 8
20	43.9	50.493	9, 10

Figure 2 and Table 1: Composition and percentage of output gas.

Risk Poll Model

Risk poll (Jan 2004 version 1.05) is a suitable software to analyze the various effects and damages of dispersion of pollutants such as SO_2, NO_2, CO and PM10 on health and environment. Also, the effects of heavy metals which exist in the atmosphere such as Pb, As, Ni, Mg, Cr, Cd. In this program the effect of pollutants will be analyzed on the following sources: human health, farming products and construction materials. Also, these effects will be studied in two group of physical effects and environmental damage. The emphasis of the Risk poll software is to obtain an accurate and logical estimate of the effects with consideration of simplifications. Therefore, this software requires little information to operate and it can even be said that Risk poll requires the least data to operate compared to similar software's and models. For example, to analyze a certain health risk the user needs the pollutant emission rate, location information and population density. With more accurate data the accuracy of the output of the software increases. This software has to be calibrated to be used in different countries. The calibration coefficient is the value of human life in a country compared to the European Union and the method of calculation has been brought below. It has to be considered that the aim of this software is to calculate the total effect not a section of the area being studied. The study area of Risk poll at maximum is a circle with a radius of 500km from the polluting source.

Calibration Coefficient

The calibration coefficient is calculated using this formula:

$$\text{Value of each unit in Europe} \times PPPGNP \frac{country\ being\ studeid\ PPPGNP}{Europe\ PPPGNP}$$
= value of each unit in the country being studied.

PPPGNP: power per capita equivalent to gross national product in dollar terms.

According to the most recent data from Iran's central bank in 2011 PPPGNP was 13053 dollars. Whereas this value in Europe is 31607 dollars.
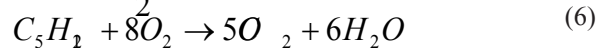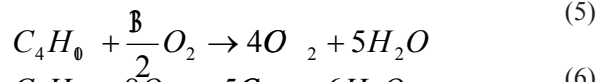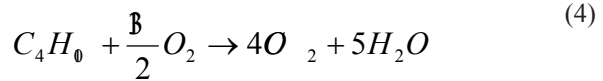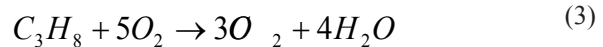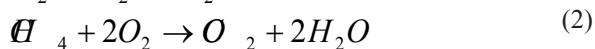
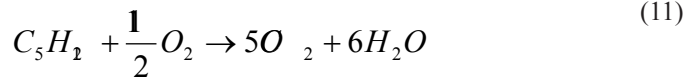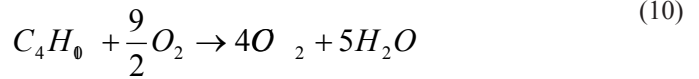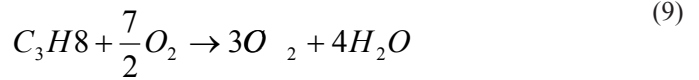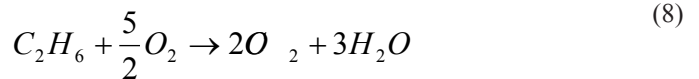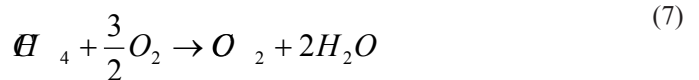$$\frac{PPPGNP\ Iran}{PPPGNP\ Europe} = 0.413$$

Results and Discussion

In this study the emission rates of SO$_x$ and NO$_x$ gases were acquired based on the collected data from the chosen flares in phases 1 to 10 in South Pars field. Then the risk of damage to human health was analyzed using the Risk poll software. In this section the method which was used is discussed. Based on the collected data from South Pars field including the amount of input gas and efficiency the reactions for complete and incomplete burning of gases are obtained. With consideration of the input flow rate and output gases the balanced equations are achieved.

By knowing the amount of gas entering the flares and an efficiency of 90%, the burning reaction for each gas can be written based on the intended gas and this can be repeated for complete or incomplete burning reactions. Also by considering the entering gases, the rate of emission for gases in each phase can be acquired by using the amount designed gases and the real rate of emission. The percentage of output gases with the mentioned efficiency is obtained in terms of mol/hour based on this data.

The reactions for complete burning of output gases from flares have been stated below:

$$H_2S + O_2 \rightarrow H_2O + SO \tag{1}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{2}$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{3}$$

$$C_4H_{10} + \frac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O \tag{4}$$

$$C_4H_{10} + \frac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O \tag{5}$$

$$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O \tag{6}$$

The reactions for incomplete burning of output gases from flares:

$$CH_4 + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \tag{7}$$

$$C_2H_6 + \frac{5}{2}O_2 \rightarrow 2CO_2 + 3H_2O \tag{8}$$

$$C_3H8 + \frac{7}{2}O_2 \rightarrow 3CO_2 + 4H_2O \tag{9}$$

$$C_4H_{10} + \frac{9}{2}O_2 \rightarrow 4CO_2 + 5H_2O \tag{10}$$

$$C_5H_{12} + \frac{1}{2}O_2 \rightarrow 5CO_2 + 6H_2O \tag{11}$$

The amount of carbon dioxide is equal to:

$$CO_2 : 0.9*821.7 + 0.9*2*6.6 + 0.9*3*2.8 + 0.9*4*9.2 + 0.9*5*253.2 = 2140.434 (mol/h)$$

The amount of H$_2$O produced in complete reactions:

$$H_2O = 3207.231 (mol/h)$$

The amount of H$_2$O produced in incomplete reactions: $H_2O = 356.359 (mol/h)$

The amount of CO$_2$ produced in complete reactions: $CO_2 = 237.8 (mol/h)$

The amount of O$_2$ produced in complete reactions:

$$O_2 = 3744.6 (mol/h) \text{ [Complete reaction]} + 297 (mol/h) \text{ [incomplete reaction]} = 4041.15 (mol/h)$$

$$N_2 = 15202.4 (mol/h)$$

The amount of N$_2$ entering because of the input O$_2$ from air:

Considering the calculations and values above, the final percentage of the output gas composition is shown in (table 2).

Percentage	(mol/h)	substance
19.7	4327.17	H$_2$O
9.8	2158.83	CO$_2$
1.80E-06	0.04	H$_2$S
1	237.82	CO
69.3	15235.43	N$_2$

Table 2: Composition and percentage of output gas.

The rate of transformation for N$_2$ and H$_2$S mols into NO$_x$ and SO$_x$ is equal to:

$$N_2 \rightarrow 2NO_X \qquad (12)$$

$$H_2S \rightarrow 2SO_x \qquad (13)$$

The rate of emission is shown in (Table 3) which is the rate of the actual amount to the designed amount in each phase.

	Designed	Actual	Rate
Phase 1	11.41	7.22	0.63
Phase 2, 3	26.66	10.56	0.4
Phase 4,5	20.62	7.47	0.36
Phase 6, 7, 8	3.78	3.43	0.91
Phase 9, 10	10.42	7.01	0.67

Table 3: Rate of Emissions.

The flared gases (low pressure) in south pars field in Table 3 for the designed amount and actual amount have been reported in terms of kilogram/hours and in this table the height of each flare has been documented for each phase. The difference between the designed amount and actual amount in terms of kilogram/hours can be seen in the table. Considering the analysis of (Table 4), the total designed amount is less that the actual amount.

Low pressure flared gases in south pars zone				
	Designed amount (kg/hr)	height (m)	Rate (Actual/ Design)	Actual amount (kg.hr)
Phase 1	196625	93	0.63	124420.03
Phase 2, 3	40439	65	0.4	16017.85
Phase 4, 5	69818	54	0.36	25292.94
Phase 6, 7, 8	80650	95	0.91	73182.41
Phase 9, 10	54930	95	0.67	36953.87
Total	442462			275867.09

Table 4: low pressure flared gases.

According to (Table 5) the acquired rate in each phase is based on the actual amount and designed amount. The values presented in the table below have been collected from south pars field phases and also the calculated rate in this table is the rate of operational coefficients in 2011 in relation to designed coefficients for the gases mentioned in Table 5. The gases in this table can be compared to the calculated rate in terms of mol/hour, as a result of which the highest rate belongs to N$_2$ and the lowest rate belongs to H$_2$S.

	Rate of actual/designed	Gases (mol/hr)		
		H$_2$O	H$_2$S	N$_2$
Phase 1	0.63	24511	498	86223
Phase 2, 3	0.4	3156	64	11100
Phase 4, 5	0.36	4983	101	17528
Phase 6, 7, 8	0.91	14417	293	50715
Phase 9, 10	0.67	7280	148	25609
Total		54346	1103	191176
Rate (%)		19.7	0	69.3

Table 5: The output gases in each phase based on the emission rate.

The amount of output gas for each phase has been reported as ton/year for phases 1-10 in Table 6, and this amount has been reported based on the input gases of each phase. For example, the highest output of NO$_x$ can be seen in phases 4 and 5 and least is in phases 2 and 3 and by analyzing the table below these rates can be stated for each gas in each phase. The output gases have been reported in terms of ton/year and the variation in the amount of output of these gases depends and their input.

Flare output (ton/year)				
	NO$_x$	So$_x$	H$_2$S	N$_2$
Phase 1	3774332.5	21549.549	497.6801	86223.08
Phase 2, 3	485908	2774.2914	64.07139	11100.37
Phase 4, 5	767271.75	4380.7375	101.1718	17528.01
Phase 6, 7, 8	2220018.3	12675.193	292.7296	50715.41
Phase 9, 10	1121010.7	6400.4099	147.8155	25609.03
Total	8368541.2	47780.18	1103.468	191175.9

Table 6: flared output gases.

The results of (Tables 7 and 8) show the damage caused in each phase by nitrate and sulfate.

			Cost of damage (dollar/year)				
		Exposure response function	Phase 1	Phase 2, 3	Phase 4, 5	Phase 6, 7, 8	Phase 9, 10
Sulfates	1	Death	7.43E+05	9.56E+04	1.51E+05	4.37E+05	2.21E+05
	2	Chronic bronchitis	3.25E+05	4.18E+04	6.60E+04	1.91E+05	9.65E+04
	3	Limited actions	1.12E+05	1.45E+04	2.28E+04	6.61E+04	3.34E+04
	4	Hospitalized due to respiratory problems	4.60E+02	5.92E+01	9.34E+01	2.70E+02	1.37E+02
	5	Children's chronic cough	5.10E+03	6.57E+02	1.04E+03	3.00E+03	1.52E+03
	6	Congestive heart failure in elderly	4.34E+02	5.59E+01	8.82E+01	2.55E+02	1.29E+02
	7	Asthmatic cough	2.16E+04	2.78E+03	4.39E+03	1.27E+04	6.41E+03
	8	Bronchodilation (asthmatics)	9.35E+03	1.20E+03	1.90E+03	5.50E+03	2.78E+03
	9	Lower respiratory system symptoms (asthmatics)	6.96E+02	8.96E+01	1.42E+02	4.10E+02	2.07E+02
	10	Bronchodilation (children with asthma)	4.30E+03	5.54E+02	8.75E+02	2.53E+03	1.28E+03
	11	Children with asthmatic cough	1.11E+03	1.43E+02	2.26E+02	6.54E+02	3.30E+02
	12	Lower respiratory system symptoms (children's asthma)	2.95E+02	3.80E+01	6.00E+01	1.74E+02	8.77E+01
Total			1.22E+06	1.57E+05	2.49E+05	7.19E+05	3.63E+05

Table 7: The Cost of Damages caused for each illness based on dollar/year for SO$_x$.

		Exposure Response Function	Cost of damages (dollar/year)				
			Phase 1	Phase 2,	Phase 4, 5	Phase6, 7, 8	Phase 9, 10
Nitrates	1	Death	3.91E+06	5.03E+06	7.94E+06	2.30E+07	1.16E+07
	2	Chronic bronchitis	1.79E+06	2.30E+06	3.63E+06	1.05E+07	5.31E+06
	3	Limited actions	5.86E+05	7.54E+05	1.19E+06	3.45E+06	1.74E+06
	4	Hospitalized due to respiratory problems	2.42E+03	3.12E+03	4.92E+03	1.42E+04	7.19E+03
	5	Children's chronic cough	2.68E+04	3.45E+04	5.44E+04	1.57E+05	7.95E+04
	6	Congestive heart failure in elderly	2.28E+03	2.94E+03	4.64E+03	1.34E+04	6.78E+03
	7	Asthmatic cough	1.14E+05	1.46E+05	2.31E+05	6.69E+05	3.38E+05
	8	Bronchodilation (asthmatics)	4.91E+04	6.32E+04	9.99E+04	2.89E+05	1.46E+05
	9	Lower respiratory system symptoms (asthmatics)	3.65E+03	4.70E+03	7.43E+03	2.15E+04	1.09E+04
	10	Bronchodilation (children with asthma)	2.26E+04	2.91E+04	4.60E+04	1.33E+05	6.72E+04
	11	Children with asthmatic cough	5.84E+03	7.52E+03	1.19E+04	3.43E+04	1.73E+04
	12	Lower respiratory system symptoms (children's asthma)	1.55E+03	2.00E+03	3.15E+03	9.12E+03	4.61E+03
		total	6.51E+06	8.38E+06	1.32E+07	3.83E+07	1.93E+07

Table 8: The Cost of damages caused for each illness based on dollar/year for NO_x.

According to the analysis carried out on Table 7 and Table 8 a pie chart was drawn for sulfates which is presented below which shows that the most damage inflicted is related to death and after that its bronchitis in adults. The first three destructive effects in Table 9 are: death, chronic bronchitis and daily fatigue which cause more damage compared to other effects. However, it should have considered that the destructive effects of sulfates on the workers' and locals' health is negligible compared to nitrates' effects.

As shown in the table above the destructive effects caused by the emission of NO_x by the flare being studied are significant and costly. The majority of these effects involve death, chronic bronchitis and daily fatigue. The overall cost of these damages add up to 951000 dollars annually, 60% of which is due to death as a result of NO_x emission. The amount of damage caused by each gas is shown in (Table 9).

Total damage	Cost of damages	Lowest cost	Highest cost
SO_x	8.121452	2.2	29.306897
NO_x	950639.9	269259.27	342106.4

Table 9: Comparison of damages caused by NO_x and SO_x.

(Figure 3) has been used to better show the comparison between the damages caused by the two pollutants under study and as it is shown the damages caused by SO_x are negligible compared to those caused by NO_x.
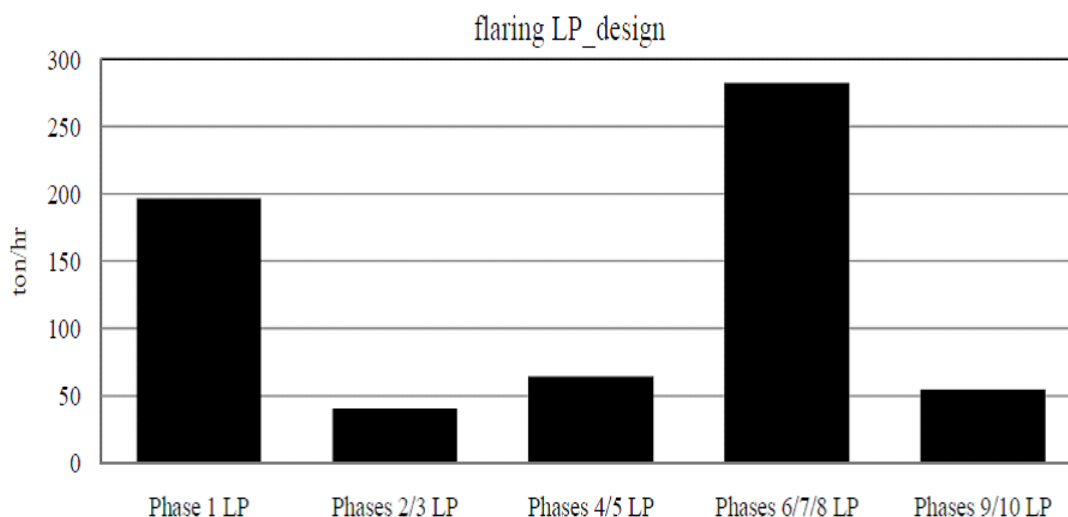
Figure 3: Comparison of damages caused by NO$_x$ and SO$_x$.

Finally, the cost of damages inflicted in terms of million dollars per year for nitrate and sulfate gases in each phase are presented in (Table 10). Based on the statistical analysis of the data in this table, the cost of damages caused by nitrate gases in each phase was noticeably higher than sulfate gases. The total cost of damages caused by nitrate and sulfate gases is shown at the bottom which was 85.70 million dollars per year for nitrate and 2.71 million dollars per year for sulfate.

Cost of damages (million dollar/year)		
	Nitrates	Sulfates
Phase 1	6.51	1.22
Phase 2, 3	8.38	0.16
Phase 4, 5	13.23	0.25
Phase 6, 7, 8	38.27	0.72
Phase 9, 10	19.32	0.36
Total	85.7	2.71

Table 10: Cost of damages inflicted.

Conclusion

Flares of gas refinery plants are one of the major producers of gases such as CO$_2$, NO$_x$, SO$_x$, CO and etc. Therefore, proper management of the input gas of flares is very important. The dispersion of these gases in the surrounding environment has detrimental effects on the environment and human health. In this study the damage caused by the negative effects of SO$_x$ and NO$_x$ emission from phase 1 to 10 flares in Assaluyeh on the health of workers and locals was analyzed. The area studied was a circle with a radius of 50km. Based on the data collected from the refinery in regard to the composition of the input of the flares, annually 666916 tons of NO$_x$ gas and 1.7tons of SO$_x$ gas are dispersed into the environment. As shown above the effects of NO$_x$ are much more significant than the effects of SO$_x$. Based on the Risk poll model this emission rate causes a damage of 958000 dollars to human health. The majority of these damages are death, chronic bronchitis and daily fatigue. Considering that most flares in this region are active (some permanently and some temporarily) a strategy has to be devised to reduce the rate of flaring or reduce their negative and damaging effects in this region.

References

1. Rodriguez JA, Hrbek J (1999) Interaction of sulfur with well-defined metal and oxide surfaces: Unraveling the mysteries behind catalyst poisoning and desulfurization. Accounts of chemical research 32: 719-728.

2. Pharr DM, Huber SC, Sox HN (1985) Leaf carbohydrate status and enzymes of translocate synthesis in fruiting and vegetative plants of *Cucumis sativus* L. Plant physiology 77: 104-108.

3. Stern DI, Koufmann RK. Annual Estimates of Global Anthropogenic Methane Emissions: 1860-1994.

4. Greenhous Gas Emisions-Emission and Action Plants. The Australian Petroleum Exploration and Production Industry Association. August 1997.

5. OGP Report No.2 66/216 (Sep 1994) Methods for Estimating from E and Operation.

6. Barns DW, Edmonds JA (1990) An Evalution of the Relationship between the Production Industry Association, August 1997.

7. Attar A (1978) Chemistry, thermodynamics and kinetics of reactions of Sulphur in coal-gas reactions: A review. Fuel 57: 201-212.