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Vapor Loss of Volatile Organic Compounds (VOCs) from the Shipping Port of Abadan Petroleum Refinery

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ABSTRACT: Hydrocarbon storage tanks, the major source of volatile organic compounds (VOCs) emission, have unfavorable effects on atmospheric chemistry and human health. The present study aims at calculating the amount of VOCs' loss with an emphasis on benzene, toluene, ethylbenzene, and xylene (BTEX). It has been performed by means of TANKs 4.0.9d and WATER9 Software Programs, as well as field measurement for validation. It, then, provides control strategies to reduce the amounts of VOCs in the shipping port area. Emission sources include 32 internal and external floating roof storage tanks, 7 pump houses, and one wastewater treatment pool. Field sampling has been done, using SKC sampling pump and activated carbon adsorption tube according to NIOSH 1501 standard. The obtained samples have been analyzed with FID and GC-MS. Results show that the total emission of VOCs has been equal to 933.25 tons/year, the majority of which (881.74 tons/year) comes from storage tanks, followed by pump houses and wastewater treatment pool (47.88 and 3.63 tons/year, respectively). BTEX emission includes 1.49 tons/year of benzene, 3.2 tons/year of toluene, 0.57 tons/year of ethylbenzene, and 1.53 tons/year of xylenes. In order to reduce the emission of VOCs from the storage tanks, the paper proposes to change the design of tanks' roof and sealing. As a result, the total emission of VOCs could be reduced by 18.27%, equivalent to 158.16 tons/year. The total cost of the oil vapors loss is estimated at 253'000 $/year, part of which (i.e., up to 43'000 $/year) could be saved by applying the proposed control strategies.

Keywords: Emission rate, VOCs, TANKs 4.0.9d, WATER9.

INTRODUCTION

Among the main emission sources of Volatile Organic Compounds (VOCs) that exist in an oil shipping port, storage tanks, pump houses, piping fittings (including the valves, the flanges, etc.), and the wastewater treatment pool are of higher account. Light hydrocarbons are vaporized during the transportation, storage, and embarking procedures of petroleum products. Vaporization of the petroleum products should receive more attention from economic and environmental viewpoints, as its mismanagement does bring irrecoverable damages. Not only does this problem result in a loss of valuable hydrocarbon products, but also it is considered an important air pollution

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source with volatile organic compounds. The current study evaluates the amount of VOCs' emission, with an emphasis on BTEX from the storage tanks in the shipping port of Abadan petroleum refinery Co. in Mahshahr. For so doing, it uses TANKs 4.09d Software Program. The amount of these compounds' emission from the wastewater treatment pool are calculated, using WATER9 Software Program. And as for evaluating emission rates from pump houses and piping fittings, emission factors and related equations from EPA- Protocol for Equipment Leak Emission have been implemented.

TANKs 4.0.9d is designed to estimate the emission of organic liquids from storage tanks to the atmosphere. In this software, such information as storage tank characteristics (e.g. diameter, buildings, etc.), properties of liquid inside the storage tank (e.g. chemical composition, temperature, etc.), and location of storage tank (e.g. ambient temperature, proximity to the urban area, etc.) must be entered to get a report on emission to the atmosphere. The report provides a monthly, annual, or part of a year estimate of emission for each material, reserved in the storage tanks, or a combination of them.

Cunningham (1996) studied the available methods and software programs, used for calculating the emission amounts of VOCs, in different industrial fields and concluded that the results obtained from TANKs 4.0.9d are accurate and well-founded enough to meet the measurement and control requirement.

Jackson (2006) performed a case study on Dar-Es-Salaam City in Tanzania. He determined VOCs' emission from organic liquid storage tanks of eight different companies and prepared the dispersion patterns, using CALPUFF Model.

Karbassi et al. (2007) analyzed the conventional methods for calculation of emission from storage tanks and, using TANKs 4.0.9d, obtained the emission of petroleum products from an Iranian oil storage company.

EPA, Ch.1 AP-42 (2006) proposed a model to estimate the emission from organic petroleum storage tank. It presented details of different types of storage tanks like internal and external floating roof.

WATER9 Model was designed to calculate the emission rate of VOCs and other toxic compounds via surface evaporation from wastewater gathering, storage, and removal equipment. This software program evaluates the emission rates of each compound in wastewater individually according to its properties and concentration.

Pandya et al. (2006) investigated the emission of total VOCs and their individual compounds as well as hydrocarbons at an oil refinery. They performed VOCs sampling, using activated charcoal sampling tube, and analyzed their samples via gas chromatography–mass spectrometry (GC-MS). Their results indicated that the 8 h average concentration of benzene, toluene, ethylbenzene, and xylene was 23.48-113.05, 18.7-72.54, 2.91-9.80, and 5.83-27.64 μg/m^3, respectively.

Rattanajongjitrakorn and Prueksasit (2014) measured the concentration profile of BTEX around a gasoline station in the borderline of Bangkok-Nonthaburi in Thailand, using activated charcoal sampling tubes and a sampling pump with GC/FID analysis. Total BTEX at the center was 12.8 and 22.9 times higher than at the vicinity of the gasoline station road and at the backside gasoline station, respectively.

Howari (2015) evaluated the evaporation loss of VOCs in an area, consisted of fixed and floating roof storage tanks in UAE-Sharjah, using Gaussian dispersion model. He included total loss, breathing loss, vapor pressure, product molecular weight, tank diameter, daily temperature, paint factor, tank capacity, and number of material circulation in the tanks in his calculation. The Gaussian model showed that the concentration of VOC exceeded 19’800 ppm.

Wei et al. (2016) applied an inverse-dispersion calculation method (IDM) to estimate the emission rate of VOCs for the complicated industrial area sources, through a case study on a petroleum refinery in Northern China. Their results showed that the monthly VOCs emission from this refinery was 183.5 ± 89.0 ton in March and 538.3 ± 281.0 ton in June.

Correa et al. (2012) studied the effects of BTEX emission on health quality deterioration for people, living and working in the regions around gasoline stations. In this study, they selected 11 gasoline stations in Rio de Janeiro, Brazil, gathering 49 samples from the area in the vicinity of these gasoline stations, up to a radius of 250 m. Their results indicated an emiision of 29.7 $\mu g/m^3$ for benzene, 7.47 $\mu g/m^3$ for toluene, 23.3 $\mu g/m^3$ for ethyl benzene, 9.46 $\mu g/m^3$ for p-xylene and m-xylene, and 14.3 $\mu g/m^3$ for o-xylene.

Ceron Berton et al. (2017) studied the characteristics and sources of BTEX hydrocarbons in the atmosphere of two different locations at Yucatan, Mexico. They measured the concentrations of benzene, toluene, ethyl benzene, o-xylene, O3, NOx, CO, and PM2.5, along with meteorological parameters between 2016 and 2017. Samples were gathered three times a day, with each one requiring 1.5 h to be performed. Afterwards, the samples got analyzed by GC and flame ionization detector (FID). Maximum concentration of BTEX was observed at noon and afternoon in both spring and summer. Bivariate and multivariate analyses were performed to correlate the BTEX concentration with probable sources of air pollution.

Allen (2016) investigated gas emission from oil and gas operations as well as their implications on air quality in the United States. Increased oil and gas production, especially from shale resources that use horizontal drilling and hydraulic fracturing, places this country as the largest oil and gas producer in the world in 2014. Allen’s research evaluated the air quality, especially greenhouse gases as an indicator of air pollution and emission of toxic gases to the atmosphere in oil and gas production operations. National Emission Inventories (NEI) shows that VOCs and NOx emitted from oil and gas supply chain have increased considerably, while the sources of greenhouse gases have decreased remarkably over the last decade. This study show that both energy production and consumption must be performed with the consequence evaluation of the air quality in energy infrastructures.

Zhang et al. (2018) performed an observation and analysis on the VOCs in the atmosphere of a petrochemical zone in Yangtze River delta, China. The amounts of VOCs were measured in the second industrial area of China from 5 Nov. 2013 to 6 Jan. 2014. Results indicated 41.8% for alkanes, 20.1% for aromatics, 17.9% for alkenes, and 12.5% for halo hydrocarbons.

Aklilu et al. (2018) studied the sources of VOCs during the enhancement of hydrocarbons concentration in the vicinity of heavy oil extraction zone in Alberta, Canada. VOCs had higher concentrations in summer which may be due to atmospheric chemistry and also increased vaporization during summer’s months.

Hadidi et al. (2016) showed that an oil refinery in Saudi Arabia emitted large amounts of contaminants like NOx, SOx, and VOCs to the atmosphere. An optimization model was developed to identify the best technology for pollution control with minimum investment.

Ashrafi et al. (2012) determined the evaporative loss of stored liquids from tanks of an oil company in Asalouyeh zone, Iran, using storage tank emissions calculation software (TANKS 4.0.9d) and VOCs emission dispersion from liquid storage tanks via AERMOD dispersion model.

Syimir Fizal et al. (2018) stated that the BTEX, present in petrol, is simultaneously released to the environment in the form of liquid spills or vapor losses. Petrol brand 1 has the highest average benzene concentration at 32842.87 mg/l. On the other hand, petrol brand 5 has the highest average TEX concentrations of about 21685.68 mg/l toluene, 13310.39 mg/l xylene, and 17799.77 mg/l ethylbenzene.

Wenkatram et al. (2009) used the AERMOD Model for mobile sources and modeled the organic volatile compounds of VOC benzene, butadiene 1 and 3, as well as toluene released into the open air in a large way in North Carolina. Their results showed that AERMOD formulation was suitable to estimate the concentration associated with the release of associated materials near roads.

Malakar and Das Saha (2015) estimated the VOC emission rate inside an oil refinery and carried out a factor analysis through the measured VOC emission rate. Based on the flow rate of sewage and VOC in wastewater flows, the rate of VOC emission was estimated through the WATER9 program.

Dumanoglu et al. (2014) collected 160 samples from ambient air, using inactive sampling in four seasons between 2009 and 2010 from 40 different sites in Aliaga, Turkey, to determine seasonal and potential sources of VOCs. VOC concentrations were higher in summer than in winter, probably due to increased evaporation from their sources at higher ambient temperatures.

Somarin and Peyghambarzadeh (2020) measured the concentrations of some hazardous pollutants such as CO, CO_2, H_2S, SO_2, NOx, and CxHy from six petrochemical incinerators. They then implemented AERMOD to evaluate these components' dispersion in an industrial area along with the residential areas around it.

Masih et al. (2018) performed BTX sampling, using a SKC Model with 220 low-volume sampling pumps, equipped with activated pipes, made of coconut wood, with a flow rate of 250 ml/min for 20-24 hours. Their analysis was performed according to NIOSH 1501 Method. They showed that the mean concentration of BTEX was the highest during the winter (39.3µg/m^3), while that of summer was 25.1 µg/m^3 .

The present study calculates the amount of VOCs in the location for storage tanks at the shipping port's foreshore, having an area of 2 km^2 with 40 emission sources during 12 months of 2017. WATER9 and TANKs 4.0.9d software programs have helped calculating the emission from the wastewater treatment pool and storage tanks, respectively. Emission factors are implemented to calculate the emission from piping and pump houses. Field measurements have also been performed for the sake of comparison and validation of the models. In the end, some strategies are suggested to reduce VOCs emission from the shipping port of Abadan petroleum refinery Co. in Mahshahr. Therefore, this paper has attempted to find some suitable control strategies to reduce the emissions and evaluate the economic benefits of this reduction.

MATERIALS AND METHODS

Mahshahr oil shipping port is located 11 km east of Bandar-e-Imam Khomeini, to the north of Persian Gulf (30° 27′ N, 49° 20′ E) in Mahshahr, Khuzestan Province, southwest of Iran. This port has an 85-year history of petroleum product export and import. With the port located 130 km from Abadan refinery, different types of refinery products should be transported to its storage tanks in Mashahr via pipelines. There, the materials are stored and exported, later.

In the coastal region of this port, forty VOCs emission sources exist. They include 32 storage tanks of both external and internal floating roof types, 7 pump houses for high octane gasoline, kerosene, gas oil, light and heavy naphtha, gas condensates, and MTBE and DPG transportation, and one wastewater pool. Storage tanks with oil vapors in the port are consisted of 28 external floating roof and 4 internal floating roof tanks.

As can be seen in Fig. 1, the shipping port of Abadan petroleum refinery Co. in Mahshahr is in the south-west of Iran in Khoor-e-Moosa region. Fig. 2 demonstrates the storage tanks arrangement with numbers within the port area. As previously stated, there are 32 product storage tanks with oil vapors. For external floating roof tanks, some data is required for TANKs 4.0.9d software program, like tank diameter, tank volume, annual number of charge and discharge of each tank, internal surface condition of the tank, surface paint and its quality, roof paint, tank building, elementary and secondary sealings, and the content of the storage tank. For internal floating roof tanks, other extra information should be prepared for TANKs 4.0.9d such as the number of supports, effective diameter of the supports, deck type, deck fittings type, etc. (EPA, TANKs 4.09d, 1999; Cunningham, 1996; Jacson, 2006; Karbassi et al., 2007; Pandya et al., 2006). Table 1 shows the characteristics of all active oil product storage tanks in the foreshore part of the shipping port of Abadan oil refinery Co. in Mahshahr.

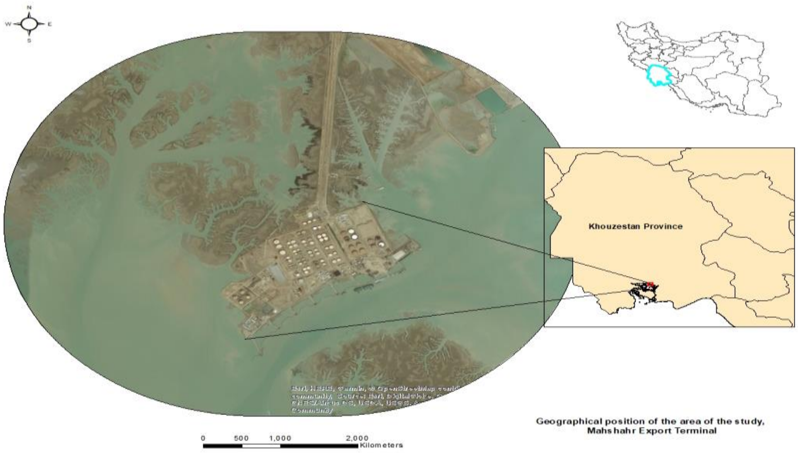

Fig. 1. Position of the studied area in the country and a view of the position of Mahshahr shipping port in the Persian Gulf

Fig. 2. Location of storage tanks in Mahshahr shipping port

Table 1. Number of tanks and type of stored products along with physical properties of the products

#	Type of product	No. of tanks	Vapor pressure (psia)	Density at 25 °C (kg/m^3)
1	Jet naphtha	6	0.01	775-840
2	Condensate (I)	3	2.5	915
3	Heavy naphtha	4	3.9	715-780
4	MTBE	4	5.2	740
5	Euro-4 gasoline	10	8.8	749
6	Condensate (II)	1	9.8	925
7	Light naphtha	8	10.8	740

In this study, meteorological information, for the duration of 5 years (2012-2017), was used for the area of study. To calculate solar radiation coefficient, the following procedure was performed:

a) According to the longitude and latitude of the studied area, the solar height characteristics for sunny hours of the day as well as cloudy fraction of that time got calculated for a 5-year statistical interval.

b) The zenith angle was calculated using the arithmetic average of the solar height at each time and at the last hour as follows:

$$\phi = \left[\frac{\varphi(tp) + \varphi(t)}{2} \right] \quad (1)$$

where φ is the solar height and ϕ, the zenith angle.

The clear sky solar radiation was determined, using Eq. (2) as follows:

$$R_0 = 990(\sin \phi) - 30 \quad (2)$$

where R_0 is the clear sky solar radiation.

Hourly solar radiation and its monthly average got calculated, using the clear sky solar radiation and the cloudy fraction according to Eq. (3):

$$R = R_0(1 - 0.75n^{3.4}) \quad (3)$$

where R is the solar radiation and n, the cloudy fraction. (Ashrafi et al., 2012)

The region's metrological data, including daily average temperature, average atmospheric pressure, average maximum and minimum daily temperature of the environment, average zenith angle, and average wind speed, were gathered and added to Tanks 4.0.9d databank. Table 2 shows some of these meteorological data on a monthly basis. Analysis and comparison of the hourly variation of the ambient temperature with the daily average temperature of the studied area shows that 3-5 p.m. is the best time interval for field measurement of the pollutions from the storage tanks, since the temperature at this interval is very close to the daily average temperature.

Table 3 shows the required data from "EPA- Protocol for Equipment Leak Emission" to calculate emission from pump houses and piping systems (EPA, Ch.1, AP-42, 2006). These data were used to calculate the amount of emission from valves, pumps, and other fittings. The amount of emission from industrial wastewater pool was calculated, using such data as density and concentration of the oil products, pH, TDS, TSS, etc. to be added to Water9 software program (EPA, WATER9, 2001; Malakar et al., 2009).

Table 2. Five-year average of the meteorological information of the shipping port

Month	Average wind speed (mph)	Radiation coefficient (Btu/ft.ft.day)	Minimum air temperature (^oF)	Maximum air temperature (^oF)
Jan.	10.3	573	55.4	68
Feb.	10.3	693	60.8	77
Mar.	10.5	797	69.8	84.2
Apr.	9.6	869	78.8	93.2
May	11.4	904	91.4	107.6
Jun.	12.1	917	96.8	114.8
Jul.	12.3	909	98.6	118.4
Aug.	9.4	861	100.4	118.4
Sep.	10.7	762	91.4	111.2
Oct.	7.4	636	82.4	100.4
Nov.	9.2	530	68	84.2
Dec.	11	509	59	71.6
Annual average	10.3	747	90.3	95.7
Atmospheric pressure (psia)	14.655			
Average temperature (^oF)	79.4			

Table 3. Average emission factor for flow passing through pipelines based on EPA (EPA, Ch.1, AP-42, 2006)

Equipment	Service	Emission factor (kg/h/source)
Valves	Gas	1.3E-05
	Light liquid	4.3E-05
Pump insulation	Gas	6.5E-05
	Light liquid	5.4E-04
Other equipment (compressor, …)	Gas	1.2E-04
	Light liquid	1.3E-04
Fittings (flanges, …)	Gas	4.2E-05
	Light liquid	8.0E-06

Field measurement was performed via sampling at VOCs emission points of 10 different storage tanks, using sampling pump SKC-PCXR8 and activated charcoal sampling tube during an hour (Rattanajongjitrakorn and Prueksasit, 2014; Syimir Fizal et al., 2018). The samples were then analyzed with GC-MS (Masih et al., 2018; Ceron Berton et al., 2017; Correa et al., 2012), with the results compared with those obtained from TANKs 4.0.9d. It is worth mentioning that it involves high operational and safety risks for workers to ascend the tanks and perform measurements while they are in service or to cover the roof outlets. Therefore, 10 sample tanks were selected. They had a low capacity and contained all the petroleum products stored in the shipping port to represent the 32 external floating roof tanks in the field measurement. Basically, the importance of using TANKs 4.0.9d for calculation of tank vapors' emission is the reduced potential risks during the operation. For internal floating roof tanks, field measurement was not possible due to the presence of MTBE.

Results of TANKs 4.0.9d show that the most important parts of the emission occurred from the rim seal and deck fitting of the storage tanks. For the sake of validation, the amounts of emission from rim seal section were measured in the field for each tank. As for the measurement, a plastic cover was used to cover the distance between the body of the tank and its roof. Fig. 3 illustrates this procedure. After 3 h of accumulating the exit gas under the cover, the volume of the exit gas from a hole on the plastic cover got measured over time. This gas was also analyzed, using a sampling tube and SKC pump for an hour.

In order to measure the emission from roof fittings or deck fitting section, all the openings on the supports, valves, and vents above the roof were temporarily closed for 3 h, with the exception of those required for the measurement of exit pollutants. Afterwards, the volume of the exit gases from the limited openings and its VOCs content was measured using sampling tube and suction pump for an hour.

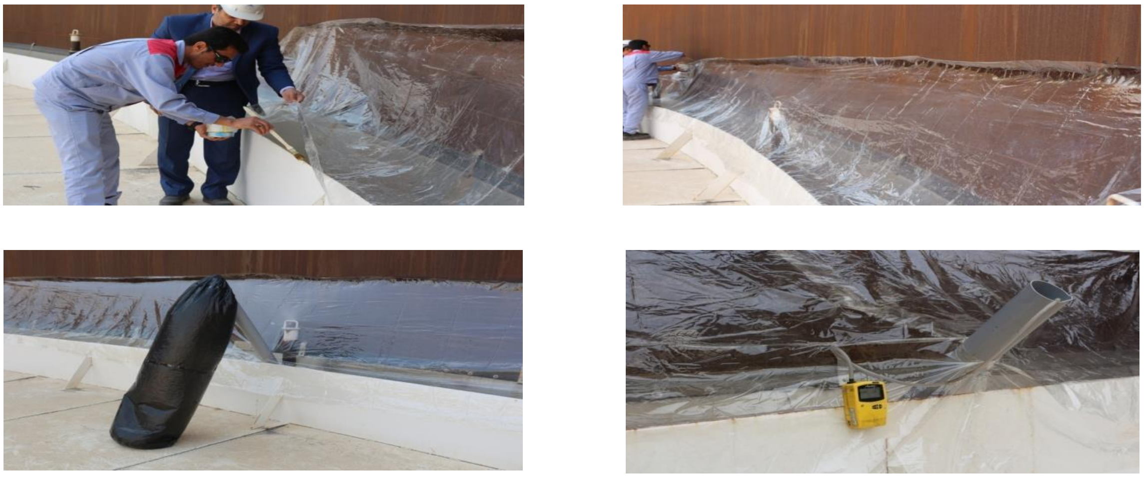

Fig. 3. The measurement method for the rim seal section of the floating roof tanks

It should be mentioned that the required information for TANKs 4.0.9d, including internal surface condition, was obtained based on technical inspection reports in the latest major and emergency repairs. Due to corrosion and subsidence of the foundation, the tanks undergo major repairs every 10 to 15 years, yet because of special conditions such as perforation of the tank floor due to soil salinity and external corrosion, rupture, and lack of proper sealing service, and roof drain repair, the emergency repairs of the tank take place at shorter time intervals. In this study, the 10 tanks selected for field measurements were under emergency repairs and their inspection reports were available. Also, the scaling of the tank's interior surface got inspected when the tank was in service and the roof of the tank was located at a low altitude. It should be noted that rust chiefly occurs at high altitude of the tank interior wall and in the areas of the body that have the most contact with open air. Therefore, the worst-case scenario was given to the software program.

RESULTS AND DISCUSSION

Having compared the filed measurements from 10 sample storage tanks, including 2 light naphtha, 2 heavy naphtha, 2 Euro-4 gasoline, 2 jet naphtha, 1 condensate (I), and 1 condensate (II) storage tanks in both hot and cold seasons with TANKs 4.0.9d's prediction, this paper concludes that in average field measurement results have been 10% higher than those, predicted by the software. Therefore, this value is added to all outputs of TANKs 4.0.9d. Table 4 compares field measurement results with the predictions of TANKs 4.0.9d. According to this table, more emission from the tanks' roof was related to deck fitting, which includes vents, deck supports, vacuum breakers, etc., followed by emissions from rim seal section.

Table 4. Comparison of annual emissions of VOCs from rim seal and deck fitting of the tanks (EPA, TANKs 4.09d, 1999)

#	Emission from rim seal (lbs)	Field measurement from rim seal (lbs)	deviation %	Emission from deck fitting (lbs)	Field measurement from deck fitting (lbs)	deviation %
97	26589.3	29848.3	10.9	86906.5	95771.5	9.2
98	21419.2	23754.0	9.8	85728.5	95244.3	10.0
95	3816.2	4221.5	9.6	15273.9	17002.1	10.1
96	3817.0	4252.9	10.2	15274.0	17015.4	10.2
Tk69	9696.0	10859.5	10.7	31691.2	35081.0	9.6
61	29477.9	32484.6	9.2	38339.2	42706.5	10.2
75	5750.3	6355.9	9.5	7478.9	8289.3	9.7
83	2286.9	2536.9	9.8	7474.9	8269.7	9.6
1106	13287.5	14683.7	9.5	12942.0	14406.8	10.1
TK49	9696.0	10820.2	10.3	31691.2	35190.0	9.9
			ARD = 9.95			ARD = 9.86

Table 5. The amount of cumulative emission from external floating roof tanks (tons per year)

#	Tank no.	content	VOCs emission rate	Benzene emission rate	Toluene emission rate	Ethyl benzene emission rate	Xylene emission rate
1	67	Light naphtha	56.73	0.08	0.11	0.02	0.04
2	77	Light naphtha	56.71	0.08	0.11	0.11	0.04
3	87	Light naphtha	56.63	0.07	0.11	0.02	0.03
4	88	Light naphtha	56.68	0.08	0.11	0.02	0.04
5	97	Light naphtha	56.71	0.0	0.11	0.02	0.04
6	98	Light naphtha	53.56	0.07	0.11	0.02	0.04
7	105	Light naphtha	53.53	0.07	0.07	0.02	0.07
8	106	Light naphtha	53.53	0.07	0.10	0.02	0.03
9	71	Gasoline	25.08	0.04	0.14	0.01	0.05
10	72	Gasoline	25.03	0.05	0.14	0.01	0.05
11	73	Gasoline	33.90	0.07	0.19	0.02	0.06
12	74	Gasoline	33.93	0.07	0.19	0.02	0.06
13	61	Gasoline	34.09	0.07	0.02	0.02	0.07
14	62	Gasoline	34.16	0.07	0.02	0.02	0.08
15	63	Gasoline	33.51	0.06	0.18	0.02	0.07
16	53	Gasoline	33.84	0.06	0.18	0.02	0.06
17	85	Heavy naphtha	9.57	0.05	0.09	0.01	0.04
18	86	Heavy naphtha	9.57	0.05	0.08	0.01	0.03
19	95	Heavy naphtha	9.58	0.05	0.08	0.01	0.03
20	96	Heavy naphtha	4.65	0.01	0.02	0.0	0.03
21	93	Jet naphtha	4.65	0.01	0.02	0.0	0.02
22	94	Jet naphtha	4.18	0.01	0.02	0.0	0.02
23	75	Jet naphtha	6.67	0.02	0.02	0.01	0.03
24	76	Jet naphtha	6.67	0.02	0.03	0.01	0.03
25	83	Jet naphtha	4.93	0.02	0.02	0.0	0.02
26	84	Jet naphtha	4.93	0.02	0.02	0.0	0.02
27	1105	Condensate #1	13.48	0.02	0.01	0.01	0.02
28	1106	Condensate #1	13.48	0.02	0.01	0.01	0.02
29	1107	Condensate #1	13.48	0.02	0.01	0.01	0.02
30	TK69	Euro4 gasoline	20.74	0.05	0.18	0.02	0.06
31	TK57	Euro4 gasoline	20.74	0.05	0.18	0.02	0.06
32	TK49	Condensate #2	20.74	0.02	0.05	0.0	0.01
Total		7 types of products	865.7	1.45	3.05	0.05	1.28

Table 5 shows the amount of VOCs and BTEX emission rates from external floating roof storage tanks and their fittings, obtained using TANKs 4.0.9d after exerting 10% correction factor. It can be seen in Table 5 that the maximum amount of VOCs, emitted from the external floating roof storage tanks, pertained to light naphtha and the minimum amounts of VOCs, to jet naphtha storage tanks. This is in direct relation with the RVP of these two products, the values of which have been presented in Table 1, previously. According to Table 1, light naphtha had the highest and jet naphtha had the lowest RVP among the oil products of the shipping port. Furthermore, Table 5 shows that the maximum amount of benzene from the external floating roof storage tanks was related to light naphtha storage tanks, labeled 67, 77, and 88. Maximum amount of toluene from the external floating roof storage tanks belonged to gasoline tanks 73, 74, 61, 62, 63, and Euro-4 gasoline tanks of TK57 and TK 69. Maximum ethylbenzene and xylene, emitted from the external floating roof storage tanks, were related to light naphtha 77, and gasoline 105, 61, 62, and 63 storage tanks, respectively. Indeed, as shown in the last row of Table 5, the contribution of BTEX in total VOCs emission was relatively insignificant at less than 1%.

Fig. 4 shows the amount of annual emission of VOCs from the external floating roof storage tanks in different months of a year. Analysis of the cumulative emission rate in Fig. 4 reveals that the maximum and minimum emission from the external floating roof storage tanks occurred in Jul and Oct, respectively.

Table 6 shows VOCs emission rates from internal floating roof storage tanks and their fittings. As can be seen in this table, these tanks were constructed simultaneously to store methyl tert-butyl ether (MTBE). Working under similar operating, mechanical, and capacity conditions, they displayed approximately similar VOCs emission. The tanks only stored MTBE and its vapor was taken as VOC, with no BTEX components existing in their content. MTBE is an additive for gasoline to enhance its octane number. It is produced from methanol and isobutylene. The internal floating roof storage tanks have a floating roof, covered by a fixed roof, which protects the tank content from wind and rain; thus the storage tanks have a low vapors emission.

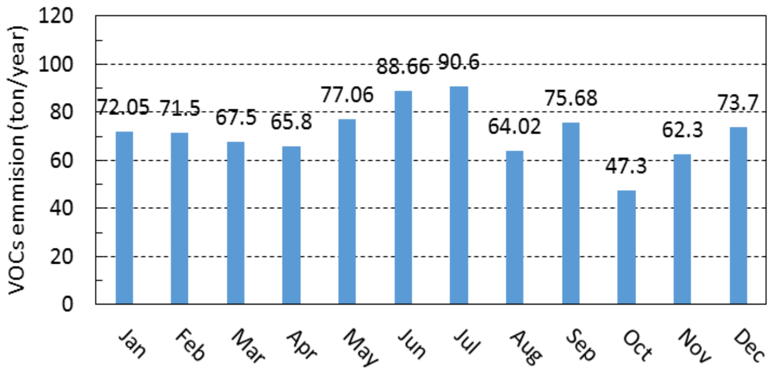

Fig. 4. Monthly cumulative emission of VOCs from the external floating roof tanks

Table 6. The amount of cumulative emissions from internal floating roof tanks (EPA, TANKs 4.0.9d, 1999)

#	Content	VOCs emission rate (tons per year)
82	MTBE	4.03
91	MTBE	3.99
101	MTBE	4.03
92	MTBE	3.99
Total		16.04

Fig. 5 illustrates the emission rates of VOCs from internal floating roof storage tanks in different months of the year. Analysis of trend of cumulative emission rates in Fig. 5 reveals that maximum and minimum emission rates occurred in Aug and Jan, respectively, with the former being about twice the size of the former. As can be seen in Figs. 4 and 5, maximum emission rates from both types of floating roof storage tanks occurred in hot season (Jul and Aug) due to higher wind speed and higher ambient temperature in these months. The meteorological data have been presented in Table 2 previously.

Fig. 6 compares the VOCs' emission rate from internal and external floating roof storage tanks in hot and cold seasons. The paper considered six months, from May to Oct, as the hot season, and remaining six, from Nov to Apr, as the cold season. As can be seen, the emission rate from the external floating roof storage tanks in the hot season was higher than the cold season, being about 57% of the total emission from the storage tanks. Also, for the internal floating roof storage tanks, the emission rate in hot season was about 65% of the total emission during a year. Indeed, it can be observed clearly that the emission rates from the external floating roof storage tanks were extremely higher than those of the internal floating roof storage tanks in both hot and cold seasons.

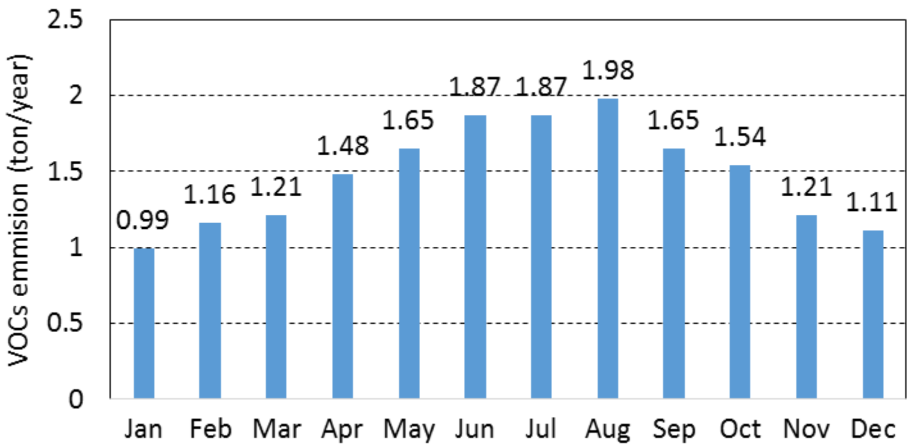

Fig. 5. Monthly cumulative VOCs emission from internal floating roof tanks

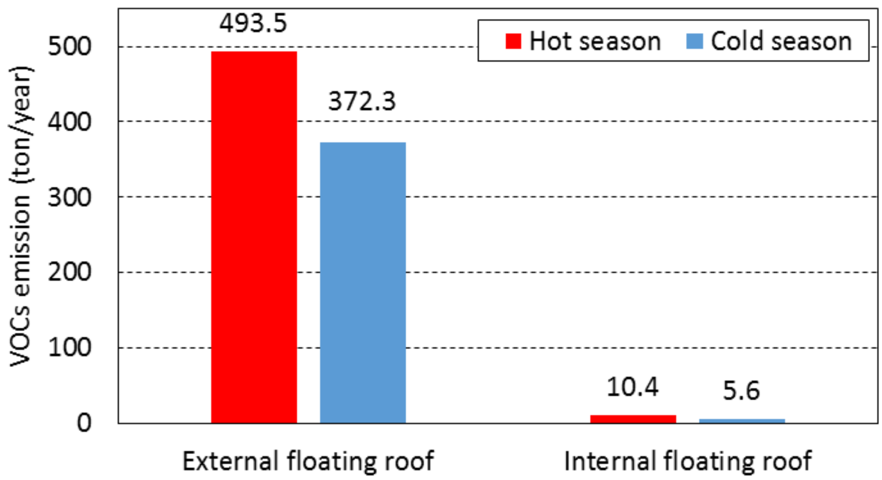

Fig. 6. Emission of VOCs from the tanks during hot and cold seasons

Table 7 shows the cumulative emission rates from the pump stations of the shipping port. According to Table 7, maximum BTEX emission rates from the pump stations of the port included xylene, toluene, ethyl benzene, and benzene pollutants, respectively. Indeed, pump station of CF unit and pump stations 3 and 4 had the maximum VOCs emission rates in a year, which is higher than 10 tons/year.

Table 8 shows the cumulative emission rates of different BTEX components from wastewater pool. As can be seen in this table, maximum amounts of emission rate from the wastewater pool were related to xylene, ethyl benzene, and benzene, in decreasing order. Toluene was not observed in wastewater pool. Indeed, it can be said that the emission rate of VOCs from wastewater pool was less than 10% of the emission rate from pump stations, thus necessitating more attention to the pump station emissions. As can be seen in Table 5-8, total emission rate of VOCs from Mahshahr Port was 933.25 tons/year, 92.8% of which was related to external floating roof storage tanks, 1.7% to the internal floating roof storage tanks, 5.1% to the pump stations, and 0.4% to the wastewater pool.

Table 7. The amount of cumulative emission from pump houses (tons per year)

#	VOCs emission rate	Benzene emission rate	Toluene emission rate	Ethylbenzene emission rate	Xylene emission rate
2	3.62	0.0	0.02	0.01	0.02
3	12.43	0.01	0.04	0.01	0.07
4	11.2	0.01	0.03	0.01	0.03
5	3.9	0.0	0.02	0.01	0.0
CF (Common Facilities)	13.08	0.01	0.07	0.01	0.07
MTBE 5	0.03	--	--	--	--
MTBE 7	3.62	--	--	--	--
Total	47.88	0.03	0.18	0.05	0.19

Table 8. Cumulative emission from the oil removal pool (tons per year) (EPA, Water9, 2001)

Wastewater pool	VOCs emission rate	Benzene emission rate	Toluene emission rate	Ethyl benzene emission rate	Xylene emission rate
	3.63	0.01	0	0.02	0.06
Total	3.63	0.01	0	0.02	0.06

The paper chose to propose control strategies in order to reduce VOCs emission from storage tanks by considering two categories of storage tanks in the shipping port, including internal and external floating roof tanks with one storage tank in each category (one with the maximum emission). Different control strategies were examined by applying some variations in the tank's appearance, after which time the software program was run with new conditions and the emission rate from the tank was re-calculated. For example, estimation of annual emission from Tank 67 (an external floating roof one) is presented here under different conditions after applying design and mechanical variations.

Under the current condition, the roof of the Tank 67 is of Panton type, schematically illustrated in Fig. 7. If its design is changed to "double deck" roof which, as shown in Fig. 8, the prediction of Tanks 4.0.9d shows that about 0.68 tons/year (equal to 1.31%) of the exit vapors is reduced. According to Fig. 7, Panton type floating roof is in accordance with API 650 standard. This roof is among the most economical floating roofs in the market. Panton type floating roofs reduce the vaporization loss of the stored products, thus protecting the environment from toxic gas emissions to the atmosphere. In the Panton type roofs, the central parts of the roof have just a one-layer roof and only in the area around the roof (attached to the rim), are double-layer roofs with hollow space between the layers implemented. The steel singular layer of the center deck might crack under the up and down movement stresses. This fault must be inspected and fixed immediately to avoid any oil product loss from the center deck.

Double-deck floating roofs have two-layer roofs, which are more resistant to cracking in steel and roof welding, and have lower emission of oil products to the atmosphere. However, double-deck roofs are more expensive.

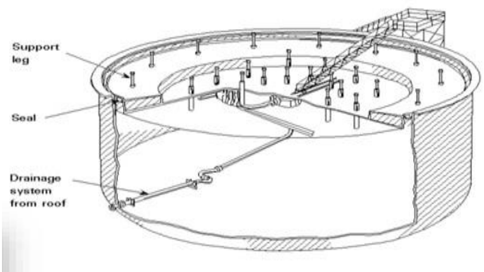

Fig. 7. Ponton deck floating roof tank

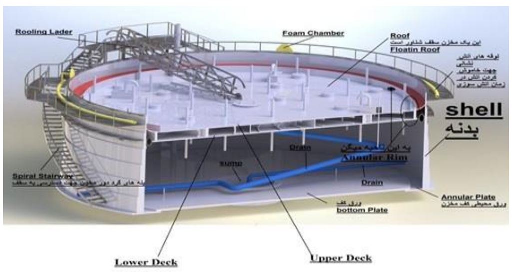

Fig. 8. Double-deck floating roof tank

Another suggestion for control strategies is to replace secondary sealing of the external floating roof storage tanks. Under current conditions, the secondary sealings of the storage tanks in the shipping port are of weather-shield type. If these sealings change to “rim-mounted” type, the emission rate from the external floating roof storage tank could be reduced up to 8.75 tons/year (i.e., 16.96% of the total emission).

As for the second strategy, it must be said that changing the secondary sealing from weather shield to rim mounted is very important due to its impacts on VOCs reduction. Figure 9 (a) and (b) show the secondary sealing of weather shield and rim mounted, respectively. As can be seen in Fig. 9 (a), weather shield secondary sealing is consisted of metal sheets that are installed on top of the rim area of the tank and are used to prevent direct sunlight and wind in the space between the tank’s shell and the floating roof.

The rim mounted secondary sealing, like the weather shield, is installed on top of the rim area of the tank. As illustrated in Fig. 9 (b), in rim mounted design, rubber insulation layer is also used under metal sheets. In addition, the metal sheets are of compression plate type and made of galvanized steel. The combination of rubber and compression plate, while giving the necessary strength to prevent direct sunlight and wind, acts as a vapor barrier, preventing the vapors’ emission from inside the tank to the atmosphere.

(a) (b)

Fig. 9. Different types of the secondary seals (a) weather shield and (b) rim mounted

All in all, by applying these two strategies for each external floating roof storage tank, a reduction of 18.27% in the emission rate was obtained. If this change had been applied to the other external floating roof storage tanks of the shipping port, total emission rates from the storage tanks would have declined by up to 158.16 tons/year. In the end, it is possible to evaluate the costs of oil product loss in the shipping port, and also the amount of saving due to the suggested control strategies for one-year period. If the costs of emitted light vapors are considered as gasoline in Iran (0.2 \$/lit), total volume of the equivalent gasoline can be calculated as follows:

933.25 tons of gasoline/year × 1356 lit/tons =1’265’487 lit of gasoline/year (4)

where 1356 l/tons is a conversion factor, used as an average density of the products.

1’265’487 lit of gasoline/year × 0.2 \$/lit = 253’097 \$/year (5)

Therefore, the total cost of organic vapor losses was estimated at 253’000 \$ annually.

The saving which would come after applying the suggested variations can be calculated as follows:

158.16 tons of gasoline/year × 1356 lit/tons = 214’465 lit of gasoline/year (6)

214’465 lit of gasoline/year × 0.2 \$/lit = 42’893 \$/year (7)

As a result, by applying the control strategies on the externa floating roof storage tanks, it will be possible save up to 43’000 \$/year.

CONCLUSION

The present study calculated total emission loss of VOCs from 40 sources in foreshore part of Abadan refinery shipping port in Mahshahr, which included 32 external and internal floating roof storage tanks, 7 pump stations, and one wastewater pool. TANKs 4.0.9d together with field measurement was used to calculate oil products’ vapor loss from the storage tanks, while WATER9 was employed for the wastewater pool. Also for estimation of leakage emission from pump stations and pipelines, this paper used the emission factors, proposed by EPA. Results showed that there was a total vapor loss of 933.25 tons/year from all emission sources, with 881.74 tons/year (94.5%) related to the storage tanks, 47.88 tons/year (5.1%) to the pump stations, and 3.66 tons/year (0.4%) to the wastewater pool. BTEX annual emission rates from all the emission sources of the shipping port included benzene (1.49 tons/year), toluene (3.23 tons/year), ethyl benzene (0.57 tons/year), and xylene (1.53 tons/year).

Maximum emission from the storage tanks’ roofs was firstly related to the deck fitting section, including the vents, deck supports, vacuum breaker, etc., and secondly to the rim seal section. Maximum and minimum emission rates from the external floating roof storage tanks happened in Jul and Oct, respectively, whereas maximum and minimum emission rates from the internal floating roof storage tanks belonged to Aug and Jan, respectively. The emission rates from the external floating roof storage tanks in the hot season were higher than those of the cold season, being about 57% of the total emission rate from this type of tank. For internal floating roof storage tanks, the emission rates in the hot season were about 65% of the total emission rate of this type of storage tank. Hence according to the results from this study, by changing the type of tank’s roof from Panton to double-deck, and also changing the secondary sealings type from weather-shield to rim-mounted, the emission rate from the external floating roof storage tanks could decline by up to 158 tons/year, which is equivalent to 42’893 $/year saving in the costs.

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The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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