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Estimation of VOC Emission in Petroleum Refinery ETP and Comparative Analysis with Measured VOC Emission Rate

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ABSTRACT

Wastewater streams generated in petroleum refinery contains a considerable amount of Volatile Organic Compounds (VOC) other than oil & grease, total suspended solids (TSS), total dissolved solids (TDS), inorganic compounds. The major VOCs present in refinery wastewater are 2,2,4-Trimethylpentane, Benzene, Biphenyl, Cresols, Cumene, Ethylbenzene, Hexane, Methyl tertiary-butyl ether, Naphthalene, Phenol, Styrene, Toluene, Xylene, 1,3-Butadiene. In this study unit-wise wastewater generation and associated concentration of individual VOCs have been calculated for a refinery of 12 MMTPA crude processing capacity. On the basis of wastewater flow rate and VOC present in wastewater streams, the VOC emission rate has been estimated through WATER9 (version 2.0.0) software. The oil bearing units of Effluent Treatment Plant (ETP) are considered as VOC emitting units for prediction of unit-wise, component-wise and overall VOC emission rates. The result showed that the percentage conversion from liquid phase to vapor phase are high for 1,3-Butadiene (100%), Hexane (99.7%), Benzene (87.8%), 2,2,4-Trimethylpentane (83%), Toluene (70%) and the vapor emission to atmosphere are high for Hexane (38.5%), Toluene (25.3%), 2,2,4-Trimethylpentane (18%). The emission rate of BTEX was 39.9% of total VOC vapor emission. The total predicted VOC emission rates have been also compared with VOC values measured in different refineries.

Keywords *- Effluent Treatment Plant, Petroleum Refinery, VOC, Wastewater, WATER9*

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I. INTRODUCTION

Volatile organic compounds (VOCs) are organic compounds that have a high vapor pressure at ordinary room temperature and a low boiling point. Due to this a large numbers of molecules evaporate from the liquid or solid form of the compound and enter the surrounding air. Presence of some of these components in vapor phase may pose significant health risk for humans and environment [1]. Petroleum refining is a complex process, which involves physical & chemical processes related to hydrocarbons. Some of the common processes are Crude desalting, Distillation (Atmospheric & Vacuum), Fluid catalytic cracking, Catalytic reforming, Alkylation, Thermal cracking/Visbreaking, Catalytic hydrocracking, Coking, Isomerization, MTBE manufacture), Catalytic hydrotreating, Sweetening/ Merox process, Sulfur removal/Claus process, Lubricating oil manufacture, Bitumen blowing/ Asphalt production, Storage tanks (Crude & product), Closed blow down, Hydrogen generation. Waste water generated in the petroleum refinery during the refining of crude oil and other auxiliary activities has a significant quantities of hydrocarbon which in turn becomes a major source of VOC emission [2]. Different VOCs generated in a typical petroleum refinery is given in Table-1. VOC emission from ETP is approximately 8-9% of total refinery VOC emission [3] [4].

Table-1: Different VOCs generated in a Petroleum Refinery

Process	Type of wastewater & Contaminants	VOC species [2]
Crude desalting	Desalting wastewater (salts, metals, solids, hydrogen sulfide, ammonia, phenol, oil)	Acetaldehyde Acrolein Analine Benzene 1,3-Butadiene Chloroform Cumene
Distillation (Atmospheric & Vacuum)	Sour water (hydrogen sulfide, ammonia, suspended solids, chlorides,	

	mercaptans, phenol, oil)	1,1-Dichloroethylene Diethanolamine Ethylbenzene Formaldehyde n-Hexane Methanol Methyl isobutyl ketone Methyl tert-butyl ether Styrene/ Vinyl Benzene 1,1,2,2-Tetrachloroethane Tetrachloroethylene Toluene 1,1,2-Trichloroethane Trichloroethylene Triethylamine 2,2,4-Trimethylpentane Vinyl chloride o-Xylene m-Xylene p-Xylene Xylenes (total) Semi Volatile/ Non-volatile organic compounds: PAHs (Polycyclic Aromatic Hydrocarbons) m-Cresol o-Cresol p-Cresol Cresols (total) Bis(2-ethyl hexyl) Phthalate di-n-Butyl phthalate Diethyl-phthalate Phenol Dioxin: 4D 2378j Dibenzofurans Polychlorinated biphenyls (total)
Fluid catalytic cracking	Sour water (hydrogen sulfide, ammonia, suspended solids, oil, phenols, cyanides)	
Catalytic reforming	Sour water (hydrogen sulfide, ammonia, suspended solids, mercaptans, oil)	
Alkylation	Spent potassium hydroxide stream (hydrofluoric acid)	
Thermal cracking/ Visbreaking	Sour water (hydrogen sulfide, ammonia, suspended solids, dissolved solids, phenol)	
Catalytic hydrocracking	Sour water (hydrogen sulfide, ammonia, suspended solids)	
Coking	Sour water (hydrogen sulfide, ammonia, and suspended solids)	
Isomerization	Sour water (hydrogen sulfide and ammonia) and caustic wash water (calcium chloride or other chloride salts)	
Ethers manufacture (MTBE)	Pretreatment wash water (nitrogen contaminants)	
Catalytic hydrotreating	Sour water (hydrogen sulfide, ammonia, suspended solids, and phenol)	
Chemical treating: sweetening/ Merox process	Wash water (spent caustic)	
Sulfur removal/Claus process	Sour water (hydrogen sulfide and ammonia)	
Lubricating oil manufacture	Steam stripping wastewater and solvent recovery wastewater (oil, solvents)	
Bitumen blowing/ Asphalt production	Oily process effluent	
Storage tanks (Crude & product)	Tank drain & wash effluent (oil, solids)	
Closed blow down	Oily blow down (oil)	
Hydrogen generation	Effluent from stripper column	

In this study, VOC emission rate was estimated for refinery having crude refining capacity of 12 MMTPA and having the following process units: Crude Distillation Unit/ Vacuum Distillation Unit (12 MMTPA), Catalytic reforming Unit (1.2 MMTPA), Hydrocracker Unit (1.97 MMTPA), Naphtha Hydrotreater & Diesel Hydrotreater Unit (3877500 MTPA), Catalytic cracking Unit (2 MMTPA), Hydrogen Generation Unit (85310 MTPA), Asphalt Plant/ Bitumen Blowing Unit (0.48 MMTPA), Product blending (9519200 MTPA Naphtha &

Diesel), Sulfur Recovery Unit (62050 MTPA -Elemental sulfur), Isomerization Unit (686930 MTPA), MEK dewaxing Unit/ Solvent Unit (0.2 MMTPA), Aromatic Extraction Unit (0.27 MMTPA), Lube oil/ specialty processing Unit (0.26 MMTPA), Tank drawdown/ Washings (12 MMTPA crude storage). The wastewater flow rate was calculated using the average flow factor for the above process units as 350 m3/hr. This includes all the process unit generated flows and washings/ drains from storage tanks. The calculated wastewater flow rate also matches with the values given in literature (0.1-5 m3 of wastewater generated per ton of crude processed) [4]. Benzene concentration was also calculated for overall combined wastewater routed to ETP considering process based on unit-wise average Benzene concentration in liquid phase [5]. Unit wise Wastewater generation and Benzene concentration in 12 MMTPA Petroleum Refinery is given in Table-2.

Table-2: Unit wise Wastewater generation and Benzene concentration in 12 MMTPA Petroleum Refinery

Units/ Processes in Refinery	Capacity (MT/yr)	Average Flow Factor [2] [5]	Wastewater flow rate (m3/hr)	Average Benzene concentration in Wastewater stream (ppmw) [2] [5]
Crude Distillation Unit/ Vacuum Distillation Unit	12000000	4.5 gal/bbl	171.04	12
Catalytic reforming Unit	1200000	1.5 gal/bbl	5.70	106
Hydrocracker Unit	1970000	2.6 gal/bbl	16.22	14
Naphtha Hydrotreater & Diesel Hydrotreater Unit	3877500	2.6 gal/bbl	31.93	6.3
Catalytic cracking Unit	2000000	2.4 gal/bbl	15.20	13
Hydrogen Generation Unit	85310	80 gal/MMft3	1.23	62
Asphalt Plant/ Bitumen Blowing Unit	480000	8.6 gal/bbl	13.07	40
Product blending	9519200	2.9 gal/bbl	87.44	24
Sulfur Recovery Unit	62050 (Elemental sulfur)	9.7 gal/ ton of sulphur	0.26	0.8
Isomerization Unit	686930	1.5 gal/bbl	3.26	33
MEK dewaxing Unit/ Solvent Unit	200000	0.011 gal/bbl	0.01	0.1
Aromatic Extraction Unit	270000	2.5 gal/bbl	2.14	40
Lube oil/specialty processing Unit	260000	2.5 gal/bbl	2.06	40
Tank drawdown/ Washings	12000000	0.02 gal/bbl	0.76	188
			Total Wastewater Generated: **350 m3/hr**	Average Benzene concentration in Combined wastewater: **16.70 ppmw**

Among the individual VOC components that are present in a typical refinery wastewater, the following components mostly constitute total VOC concentration: 2,2,4-Trimethylpentane, Benzene, Biphenyl, Cresols, Cumene, Ethylbenzene, Hexane,Methyl tertiary-butyl ether, Naphthalene, Phenol, Styrene, Toluene, Xylene, 1,3-Butadiene [2] [5]. The individual VOCs are also calculated based on Benzene mass concentration ratio [2]. VOC species concentration in liquid waste water calculated based on 350 m3/hr of combined wastewater flow rate has been given in Table-3.

Table-3: Concentration of individual VOCs in Refinery Wastewater

Sl. No.	VOC species	Mass Concentration Ratio of Compounds to the Concentration of Benzene [2]	Average Concentration (ppmw)
1	Benzene	1	16.70
2	Biphenyl	0.034	0.57
3	1,3-Butadiene	0.0006	0.01
4	Cresols	0.25	4.18
5	Cumene (Iso Propyle Benzene)	0.37	6.18
6	Ethylbenzene	0.88	14.70
7	Hexane(-n)	3.5	58.45
8	Methyl tertiary-butyl ether	0.58	9.69
9	Naphthalene	0.29	4.84
10	Phenol	0.18	3.01
11	Styrene (Ethenylbenzene)	0.58	9.69
12	Toluene	3.3	55.11
13	2,2,4-Trimethylpentane	1.97	32.90
14	Xylene	3.6	60.12

VOC can depart in vapor phase by phenomenon viz. volatilization, biological decomposition, adsorption, migration, runoff, photochemical decomposition, hydrolysis, oxidation/ reduction, hydroxyl radical reactions. For, wastewater VOC emission, volatilization (physical phenomenon) and biological decomposition (chemical phenomenon) are mostly important [6]. Volatilization occurs when VOCs dissolved in liquid wastewater released to surrounding atmosphere. The mass transfer of VOC components is function of concentration in liquid phase relative to equilibrium concentration. As the concentration of VOC in atmosphere generally far less than the equilibrium concentration, the transfer of VOC component happens from liquid wastewater to atmosphere. The rate of volatilization can be calculated by the following equations [7]:

$$r_{voc} = -K_L a_{voc} (C - C_s) \quad \text{-- Eq. (1)}$$

$$K_L a_{voc} = K_L a_{o_2} \left(\frac{D_{voc}}{D_{o_2}} \right)^n \quad \text{-- Eq. (2)}$$

Where,

r_{voc} = rate of VOC mass transfer, µg/m^3.h
$K_L a_{voc}$ = overall VOC mass transfer co-efficient, l/h
C = concentration of VOC in liquid, µg/m^3
C_s = saturation concentration of VOC in liquid, µg/m^3
$K_L a_{o_2}$ = system oxygen mass transfer co-efficient, l/h
D_{voc} = diffusion coefficient of VOC in water, cm^2/s
D_{o_2} = diffusion coefficient of oxygen in water, cm^2/s
n = 0.1 to 0.8 [8]

The values of the parameters can be found in literatures. However, the values and calculation process are sometimes different in different literatures and depends on type of unit, type of process, temperatures and if the surface area is laminar or turbulent. Also the overall mass transfer coefficient is a composite of the overall mass transfer coefficient for turbulent surface area and the overall mass transfer coefficient for laminar flow surface area based on the weighted average as follows [2] :

$$K_{OL} = \frac{K_{OL,t} A_t + K_{OL,q} A_q}{A} \quad \text{-- Eq. (3)}$$

Where, K_{OL} = overall VOC mass transfer co-efficient, l/h
$K_{OL,t}$ = overall VOC mass transfer co-efficient, l/h
A_t =Turbulent surface area (m^2)

$K_{OL,q}$ = overall VOC mass transfer co-efficient, l/h

A_q = Laminar flow surface area (m^2)

A = Total surface area (m^2)

Biological decomposition phenomenon happens when the organic compounds are broken down by microbial metabolism. The rate of biological decomposition depends on the type of compound and microbial activity. The rate of population or growth rate is function of concentration of biomass and specific growth rate coefficient [6].

The VOC in vapor phase can be measured by (1) Direct measurement- Gas Chromatography/ Mass Spectrometry (GC/MS) analysis, Flame Ionisation Detectors (FIDs), Photo Ionisation Detectors (PIDs,) Differential Absorption Light Detection and Ranging (DIAL) method [9], Solar Occultation Flux (SOF) method [3] etc. (2) Mass or material balance- Inlet and outlet concentration balance of individual VOC components in liquid and vapor phase gives an average VOC estimation. This material balance estimation method is complicated [10]. (3) Predictive Software based on the emission factors- WATER9, TOXCHEM, BASTE etc.

II. MATERIALS & METHODS

WATER9 Software

For estimation of VOC component in vapor phase, the USEPA developed WATER9 (version 2.0.0) software been have used in this study. This software is widely used and can take care of VOC emission phenomenon [10]. WATER9 can evaluate a full facility that contains multiple wastewater inlet streams, multiple collection systems, and complex treatment configurations. The Major steps in calculating VOC emission rate through WATER9 software are: (1) Identification and selection of VOC compounds from the master list of over 2000 compounds along with their compound-specific data (2) Specifying the operating parameters of the wastewater treatment facility together with project specific data (3) Generation of output data i.e. the compound-specific short-term and long-term predicted air emission rate from the facility. It is used to estimate air emissions from site specific water treatment plants (consisting of sumps, tanks, oil separators etc.). The software provides output results for unit-wise VOC emission, component-wise, total VOC emission rates [11].

Input to WATER9: VOC concentrations in wastewater, wastewater flow rate & VOC emitting unit data

The VOC components and concentration selected in WATER9 as per the given in Table 3. The combined inlet flow rate of ETP is taken as 350 m3/hr (as calculated). A typical ETP of petroleum refinery generally have three treatment sections: (1) Oil treatment section (for removal of oil& grease, TSS), (2) Biological section (for removal of BOD, COD, ammoniacal nitrogen, sulphides) and (3) Polishing section (for removal of residual TSS, COD, odour). For calculations of VOC emission, oil bearing units of ETP viz. API oil separator, Equalisation tank feed sump, Equalisation tank, TPI oil separator, Flash mixing tank, Flocculation tank, DAF oil separator, Slop oil sump, Oily sludge sump, Slop oil tank have been considered to calculate VOC emission rate. This is based on the fact that oil & grease which are also hydrocarbon no longer remain in wastewater after oil treatment section and vaporization of VOC components are almost complete before biological treatment section. Process flow diagram (PFD) for the oil bearing units in ETP is given in Figure-1.

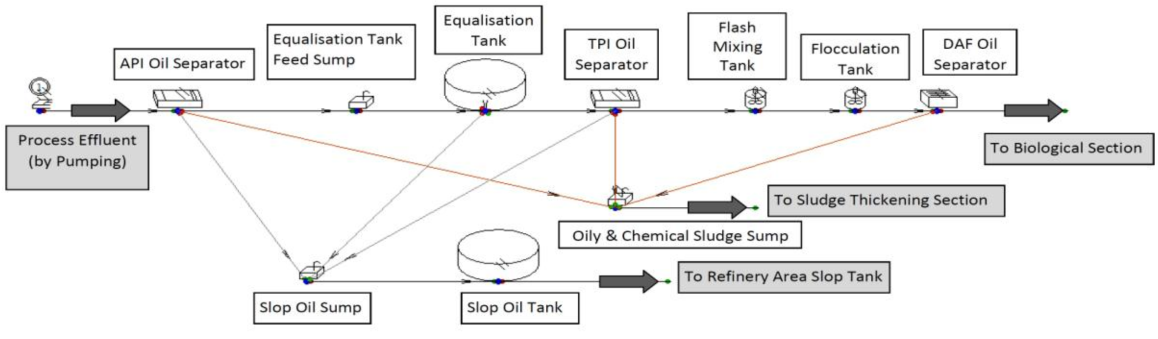

Figure-1: Process Flow Diagram of Refinery ETP

For emission rate estimations through WATER9 software, the following have been assumed: (a) all the VOCs generated in process units will be routed to ETP and no volatilization loss is considered in between (b) Ambient temperature is 35-40 deg. C (c) Oil separators are not covered (d) The process wastewater includes desalter de-sludging effluent.

API separator is the major bulk oil removal system which removes oil & grease having particle size >150 µm and TSS by gravity separation. Equalisation tank is holding tank and equalises flow & quality for downstream treatment. TPI separator removes oil& grease having particle size > 60µm and TSS by gravity separation. In DAF separator, the emulsified & free oil are removed with the help of coagulant/ flocculant and micro-bubbles produced by dissolved air. The slop oil recovered from API separator, Equalisation tank, TPI separator are collected in Slop oil sump/ Slop oil Tank. Then it is pumped to Refinery slop oil tank. The oily & chemical sludge from API separator, TPI separator and DAF separator are collected in Oily & chemical sludge sump. It is then thickened or bio-remediated. The inlet & outlet parameters (Flow rates, pH, Oil & grease, TSS, temperature) and equipment details are given in Table-4 & 5. The surface area, volume, oil & sludge calculations are based on standard industrial engineering practices and literatures [12] [13].

Table-4: Inlet and Outlet Parameters (Unit 1 to Unit 7)

	API Oil separator (Unit 1)		Equalisation Tank Feed Sump (Unit 2)	Equalisation Tank (Unit 3)		TPI Oil Separator (Unit 4)		Flash Mixing Tank (Unit 5) / Flocculation Tank (Unit 6)		DAF Oil Separator (Unit 7)	
Parameter	Inlet	Outlet	Inlet/ Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Flow rate (m3/hr)	350	314.02	314.02	314.02	304.60	304.60	298.86	298.86	298.86	298.86	296.42
Temperature (Deg. C)	40		40	35		35		35		35	
pH	6.5		6.5	6.5		6.5		7		7	
Oil & Grease (ppm)	10200	2200	2200	2200	1000	1000	280	280	280	280	14
Free oil (ppm)	10000	2000	2000	2000	800	800	80	80	80	80	4
Emulsified oil (ppm)	200	200	200	200	200	200	200	200	200	200	10
TSS (ppm)	200	60	60	60	60	60	18	18	118	118	24

Table-5: Inlet and Outlet Parameters (Unit 8 to Unit 10)

	Slop Oil Sump (Unit 8)	Oily Sludge Sump (Unit 9)	Slop Oil Tank (Unit 10)	
Parameter	Inlet/Outlet	Inlet/Outlet	Inlet	Outlet
Flow rate (m3/hr) From API	35	0.98		
Flow rate (m3/hr) From Equalisation Tank	9.42	0		
Flow rate (m3/hr) From TPI	5.48	0.26		
Flow rate (m3/hr) From DAF	0	2.44		
Total Flow rate (m3/hr)	49.9	3.68	49.9	21.23
% of Oil	5-10	5	5-10	20
% of TSS	0	5	0	0

III. RESULTS AND DISCUSSION

VOC transformation from liquid phase to vapor phase

The output from WATER9 software provided details of VOC emission rate both component wise, equipment wise and also overall total VOC emission in vapor phase. Individual component-wise conversion from liquid phase to their respective vapor phase is in given in Table-6. From the table it can be seen that more than 99% of 1,3-Butadiene, Hexane(-n) in liquid wastewater converted to vapor phase. Less than 1% of Biphenyl, Cresols and Phenol in liquid wastewater converted to vapor phase. Benzene, Toluene and 2,2,4-Trimethylpentane have been also converted to vapor phase significantly. The fraction conversion (f_e) of these VOC components is dependent on type of units, temperature, surface area & residence time. A comparison of inlet concentration and vapor phase transformation is shown in Figure-2.

Table-6: Percentage of Inlet VOC concentrations converted to vapor phase

VOC species	Inlet VOC concentration (ppmw)	Converted to Vapor Phase (ppmw)	Converted to Vapor Phase (%)
Benzene	16.70	14.66	87.78
Biphenyl	0.57	0.00	0.26
1,3-Butadiene	0.01	0.01	100.00
Cresols	4.18	0.00	0.03
Cumene (Isopropylebenzene)	6.18	1.65	26.73
Ethylbenzene	14.70	6.33	43.06
Hexane(-n)	58.45	58.26	99.68
Methyl tertiary-butyl ether	9.69	0.43	4.49
Naphthalene	4.84	0.11	2.26
Phenol	3.01	0.02	0.55
Styrene (Ethenylbenzene)	9.69	3.31	34.16
Toluene	55.11	38.60	70.04
2,2,4-Trimethylpentane	32.90	27.30	82.99
Xylene	60.12	1.20	1.99

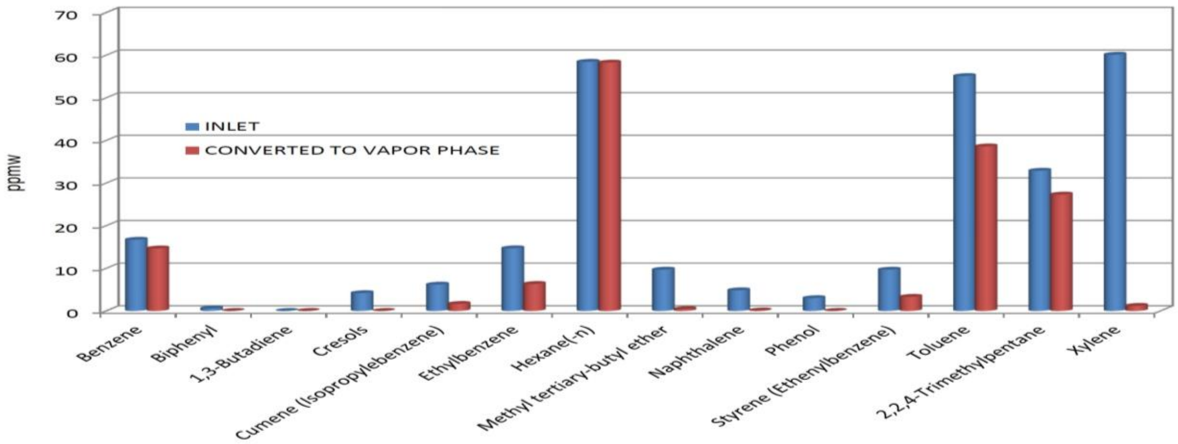

Figure-2: Inlet VOC concentrations Vs. VOC concentrations converted to vapor phase

Component wise and Total VOC emission

Component wise and total VOC emission rate is given in Table-7. Total emission from all ETP units is 465.58 tons/yr (53.14 kg/hr). Highest emission rate of individual VOC component is of Hexane(-n) (179 Ton/yr) followed by Toluene (118 Ton/yr) and 2,2,4-Trimethylpentane (83.7 Ton/yr). Total BTEX emission is 185.97 tons/yr which is 39.94% of total VOC emission rate. Percentage of VOC species in total vapor phase emission is compared in Figure-3.

Table-7: Individual VOC concentrations Vs. total VOC emission

VOC Species	Emissions (kg/hr)	Emissions (Ton/yr)	% of VOC in total emission
Benzene	5.15	44.90	9.64
Biphenyl	0.00	0.00	0.00
1,3-Butadiene	0.00	0.03	0.01
Cresols	0.00	0.00	0.00

Cumene (Isopropylebenzene)	0.58	5.06	1.09
Ethylbenzene	2.21	19.40	4.17
Hexane(-n)	20.38	179.00	38.45
Methyl tertiary-butyl ether	0.15	1.33	0.29
Naphthalene	0.04	0.34	0.07
Phenol	0.01	0.05	0.01
Styrene (Ethenylbenzene)	1.16	10.10	2.17
Toluene	13.50	118.00	25.34
2,2,4-Trimethylpentane	9.54	83.70	17.98
Xylene	0.42	3.67	0.79
Total	53.14	465.58	100.00

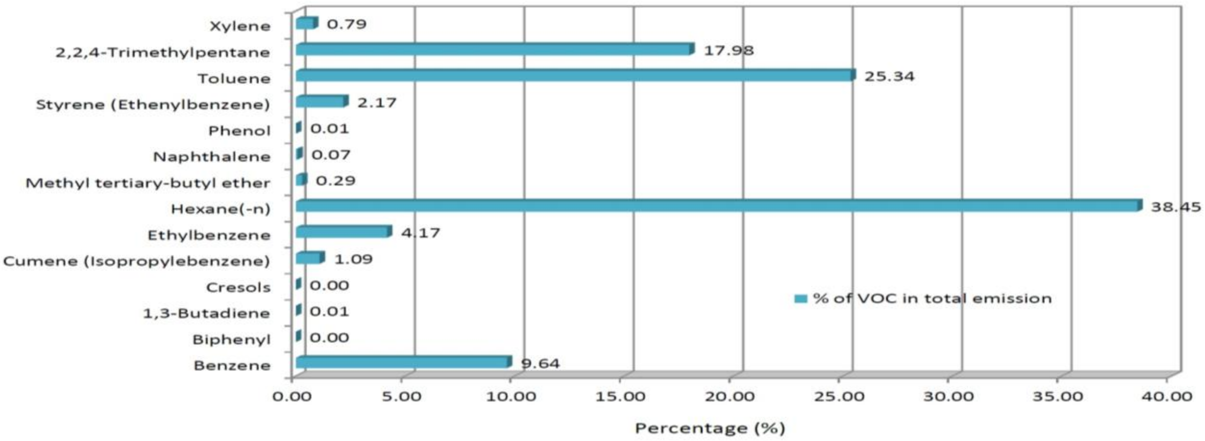

Figure-3: Percentage of individual VOC species in total emission

Comparison with measured values

For the purpose of validation, WATER9 predicted overall VOC emission rate was compared with the following measured VOC values in ETP area of two European refineries:

Refinery A has a design crude processing capacity of 6 MMTPA and actual production capacity was 5 MMTPA. VOC Emission was measured in Refinery A in 1988, 1989, 1992, 1995 & 1999 by DIAL (Spectrasyne) method [14]. The maximum and minimum values of VOC recorded in ETP area was 480 tons/yr and 80 tons/yr. For the purpose of comparison with WATER9 predicted VOC value, these measured VOC emissions value can be extrapolated for 12 MMTPA. The extrapolated maximum & minimum values calculated as 1152 tons/yr (Measured value – 1) and 192 tons/yr (Measured value – 2) respectively.

Refinery B has a crude processing capacity of 10 MMTPA. VOC Emission was measured in Refinery B in 1992, 1995 & 1999 by DIAL (Spectrasyne) method [14]. The maximum and minimum values of VOC recorded in ETP area was 1350 tons/yr and 480 tons/yr. For the purpose of comparison with WATER9 predicted VOC value, the measured VOC emissions values can be extrapolated for 12 MMTPA. The extrapolated maximum & minimum values calculated as 1620 tons/yr (Measured value – 3) and 576 tons/yr (Measured value – 4) respectively.

The predicted values and measured values are tabulated in Table-8. The predicted value (465.58 tons/yr) is lower than the measured values in 3 out of 4 cases. Measured value- 4 is 1.2 times the predicted value, Measured value- 1 is 2.5 times the predicted value and Measured value 3 is 3.5 times the predicted value. Measured value 2 is lower than the predicted value. These data also supports the trend where the VOC emission measured globally by DIAL method is higher than the predicted VOC emission in refinery ETP area in most cases [4]. VOC predicted by WATER9 software Vs. Measured VOC values shown in Figure-4.

Table-8: VOC Emission predicted by WATER9 software and Measured VOC values

Sl. No.	Parameter	Total VOC Emission rate (Ton/yr)
1	Predicted value by WATER9 Software (For 12 MMTPA Refinery)	465.58
2	Measured value 1 (Extrapolated maximum VOC value measured in Refinery A)	1152.00
3	Measured value 2 (Extrapolated minimum VOC value measured in Refinery A)	192.00
4	Measured value 3 (Extrapolated maximum VOC value measured in Refinery B)	1620.00
5	Measured value 4 (Extrapolated minimum VOC value measured in Refinery B)	576.00

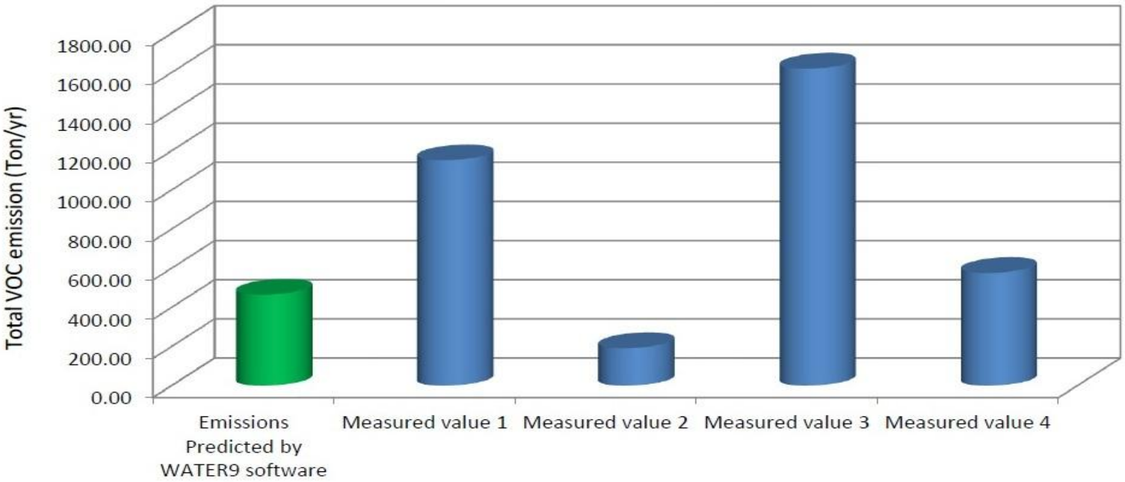

Figure-4: VOC predicted by WATER9 software Vs. Measured VOC values

The following factors might be some of the reasons for the difference observed between the measured and predicted VOC values: (1) Process configuration of refineries: it may be different though the capacities are same and hence the flow rate of wastewater & its quality are different (2) Difference in crude oil quality: in this case, the effluent quality and flow rate from desalter will vary and so the VOC concentration in wastewater (3) VOC emission rate measured in ambient air will generally be different from predicted VOC values of ETP units due to addition/ dilution of VOC components emitted from adjacent units/ storage tanks.

IV. CONCLUSION

As per statutory environment requirement, a VOC collection and treatment system is required to be installed for refinery ETP area and at least 90% of VOC should be treated/ removed [15]. In view of this, for designing a effective VOC collection and treatment system, it is necessary to properly estimate the VOC emission rate that can be generated in ETP. In this study the VOC components selected are the most commonly present in petroleum refinery having process units as described earlier. Average concentration of VOC in combined wastewater at inlet of ETP was calculated and the same was taken as input to the WATER9 software. Oil bearing units in ETP were considered as VOC emitting units and data of these units were also input to WATER9. As the flow rate and quality of wastewater varies day to day depending on the intermittent but frequent processes like washings, de-sludging, tankage cleaning etc., it is required to design a suitable VOC system on the basis of most probable wastewater flow rate and associated VOC emission rate. The total VOC emission rate estimated in this study with a suitable design margin (generally 10%) can be taken for designing VOC handling and treatment system for refinery ETP. The design value (42.7 Ton/yr per MMTPA of crude processed) is almost matching with values (40 Ton/yr per MMTPA of crude processed) given in literatures [4].

The VOC emitting oil bearing units of ETP should be covered and vents shall be connected to a VOC treatment unit for effective treatment and removal of VOCs. Estimating or measuring of only BTEX compounds would not give total VOC emission as data of this study shows BTEX component emission is less than 40% of total VOC emission.

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