Study on the Pollutant Emissions Characteristics of Typical Petrochemical Enterprises in Hainan Province

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Abstract: Understanding the emissions characteristics of typical pollutant emissions sections in the petrochemical industry is the premise and basis for formulating targeted emissions reduction strategies. Through investigation and measurement, the emissions inventory in 2016 of eight typical petroleum refining enterprises and all petrol stations in Hainan Province were reasonably estimated. The results showed that volatile organic compound (VOC) emissions from typical petroleum refineries was 4972.2 tons in 2016, with the most three process links being organized discharge, volatile loss of organic liquid loading and unloading and leakage of static and static points of equipment. VOC emissions from these three links were 2268.3 tons, 648.3 tons and 631.6 tons respectively, accounting for 45.6%, 13.0% and 12.7% of the total VOC emissions, respectively. The three sections need to be paid more attention. In 2016, 1757.6 tons of VOCs were discharged from 482 service stations in Hainan Province, and the economic loss can reach to 14.9 million RMB. Service stations of Hainan Province are suggested to install more efficient oil and gas recovery facilities.

1. Introduction

The regional and compound-type atmospheric environment issues featuring with PM$_{2.5}$ and ozone become increasingly predominant [1-2] under the current grim atmospheric environment conditions in China. Such specific pollutants will endanger public health and affect social harmony stability. Acting as the crucial precursor to ozone and secondary organic particulate matter, VOCs represent a vital role in the process of atmospheric chemical reaction and thus have received widespread attention.

Petrochemical industry is a significant source [3-4] of VOCs and its emissions reduction is the highlight of national control on VOCs. In recent years, country level departments have successively launched a range of related industrial policies and environmental requirements. In December 2014, Ministry of Environmental Protection issued the Plan for the Comprehensive Treatment of Volatile Organic Compounds in the Petrochemical Industry (HF No. 199 [2014]) [5] and made explicit requirements for the VOCs pollution control in petrochemical industry. In June of 2015, Measures for the Pilot Project of Collecting Volatile Organic Compounds Pollution Discharge Fees (CS No. 71 [2015]) jointly issued by Ministry of Environmental Protection, Ministry of Environmental Protection and Ministry of Finance standardized the collection, application and management of VOCs pollution.
discharge fees in petrochemical industry. The Ministry of Environmental Protection released The 13th Five-Year Plan for the Protection of Ecological Environment (HDQ No. 121 [2017]) in October 2017, demanded an overall intension of pollution control on VOCs, stressed the emissions reduction in key business and regions, and suppressed the momentum of ozone. The series of measures indicate that pollution reduction in petrochemical industry would properly function in continuous improvement of air quality, and the full mastery of pollution status and degree of emissions sources in petrochemical industry is the premise and foundation of the development of targeted pollution prevention and control measures.

Hainan Province is located in the southernmost point of China and featured with the largest and sole provincial economical special zone. The general output of its petroleum refining, smelting and nuclear fuel processing accounted for 27.61% and 25.13% of the total industrial output value in Hainan Province respectively according to Hainan Statistical Yearbook in 2016[9] and Hainan Statistical Yearbook in 2017[10] published by Hainan Provincial Bureau of Statistics. However, there were rare reports on pollutant emissions in key pollution discharging procedures of Hainan petrochemical industry in previous studies.

Pollutant emissions source is considered as the cause of all contamination accidents. The study on emissions source plays a vital role in regional air quality management and prevention and control of contamination accident. For the purpose of filling the vacancy in the study on pollutant emissions of petrochemical industry of Hainan Province, the research created the emissions inventory of atmospheric pollutants in this industry specific to typical petrochemical enterprise and all petrol stations in Hainan Province, to provide scientific basis and theoretical foundation for studying regional and compound-type atmospheric environment issues. This study is of great significance for the implementation of pollution discharge permit reform pilot, of practical application value to the subsequent elaborating regulation of atmospheric environment and the establishment of targeted pollution prevention and control measures in Hainan Province, and of guiding significance for the improvement of environmental and economic benefits among petrochemical enterprises.

2. Materials and methods

2.1 Survey region and objects
This study chose the year of 2016 as the base year, and the objects of study covered eight typical petrochemical enterprises and all petrol stations in Hainan Province. With regard to the parameters for the study, nine kinds of substances, including VOCs, SO₂, NOₓ, CO, CO₂, NH₃, Total Suspended Particulates (TSP), Black Carbon (BC), and Organic Carbon (OC) were for the former enterprises, and VOCs were mainly for the later petrol stations. Eight typical petrochemical enterprises in this study are mainly distributed in Dongfang City, Yangpu Economic Development Zone and Chengmai County.

The petrol stations in Hainan Province, with a total number of 482, are distributed in 18 counties and cities apart from Sansha City. The geographical location of 482 petrol stations in Hainan Province is shown in Figure 1.
To accurately understand the characteristic of each pollutant emissions link in petrochemical enterprises, the study on investigation scope of VOCs sources from petrochemical enterprises in Hainan Province included eight types of emissions source items, and the investigation scope of VOCs sources from petrol stations contained three types. The investigation scope of SO$_2$, NO$_x$, TSP, BC and CO source was confined in organized emissions during technology process, NH$_3$ source in wastewater treatment and organic waste gas collection device; CO and CO$_2$ in combustion emissions and technology process emissions. Table 1 shows the classification system of typical emissions list of air pollutants in Hainan petrochemical industry.

| Sector               | Pollutant | Emissions link                                                                 |
|----------------------|-----------|--------------------------------------------------------------------------------|
| Petrochemical enterprises | VOCs     | Equipment dynamic and static sealing point leakage                           |
|                      |           | Volatile losses of organic liquid storage and reconciliation                |
|                      |           | Organic liquid storage and volatile losses                                  |
|                      |           | Effusion in the process of wastewater gathering and transferring, storage and treatment |
|                      |           | Organized emissions during technology process                               |
|                      |           | Cooling tower and circulation water cooling system release                 |
|                      |           | Flare discharge                                                             |
|                      |           | Combustion flue gas emissions                                               |

Figure. 1 Map of geographical location of petrol stations in Hainan Province

2.2 Typical pollutant emissions links of petrochemical enterprises and petrol stations

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|                      |           | Flare discharge                                                             |
|                      |           | Combustion flue gas emissions                                               |
SO$_2$, NO$_X$, TSP, BC, OC
SO$_2$, NO$_X$, TSP, BC and OC
NH$_3$

Organized emissions during technology process
Wastewater treatment and organic waste gas collected device emissions

CO, CO$_2$

Combustion emissions and technology process emissions

Petrol station
VOCs

Oil tank breathing loss
Emissions from volatilization of refueling process
Loss in the process of oil discharge

2.3 Estimation method of typical emissions links of VOCs from petrochemical enterprises and data sources

2.3.1 Equipment dynamic and static sealing point leakage

Equipment sealing point leakage is identified as a small-scale emissions source throughout the whole manufacturing area in petrochemical enterprises and refers to the process of process medium at the joint of equipment modules entering into atmosphere. In this study, relative equation was adopted for estimating the volume of VOCs from equipment dynamic and static sealing point leakage. The relative equation provided the default zero emissions rate, limited rate of emissions and dependent equation. Where the net detection result was less than 1, default zero-value emissions rate should be deemed as the rate of emissions for the sealing point; and if net detection result was more than 50000 μmol/mol, then the limited rate of emissions should be considered as the rate of emissions for the sealing point. When the net detection value was between 1 and 50000, dependent equation should be adopted to calculate the rate of emissions of that sealing point.

$$e_{TOC} = \sum_{i=1}^{n} \begin{cases} e_{0,i} & (0 \leq SV < 1) \\ e_{p,i} & (SV \geq 50000) \\ e_{f,i} & (1 \leq SV < 50000) \end{cases}$$

Where: $e_{TOC}$ refers to emissions rate of TOC at the sealing point (kg/h); SV is the net detection value after correction (μmol/mol); $e_{0,i}$ is the default zero emissions rate at the sealing point i (kg/h); $e_{p,i}$ refers to the limited emissions rate at the sealing point i (kg/h) and $e_{f,i}$ is the accounting emissions rate of dependent equation at the sealing point i.

In the study, direct assessment on VOCs emissions was conducted according to the Leak Detection and Repair (LDAR) reports collected from five enterprises. With regard to the rest three enterprises which did not provide with LDAR reports, it should first investigate the pieces of valves, pumps, flanges, opening pipe fittings and other fastenings through system statistics and those of refining device, compressor room, refining unit and a dozens of other devices in field research of each enterprise, and then consult the emissions characteristics [13] concerning each point of junction released by EPA in 1995 (Table 2), thus the VOCs emissions from dynamic and static sealing point can be calculated by the above-mentioned formula.
2.3.2 Organic liquid storage and volatile losses

The VOCs loss of organic liquid storage tank is part and parcel of fugitive emissions source in petrochemical industry. Subject to different storage materials in storage tank, pollutants generated mainly include benzene series, organic chloride, organic ketone, amine, alcohol, ether, ester, acid, hydrocarbon compound, etc. Main types of storage tank in petrochemical enterprises in Hainan Province are fixed-roof tank and floating roof tank. Equation was adopted for estimation of organic liquid storage and volatile losses (refer to the Work Guideline of VOCs Source in Petrochemical Industry issued by the Ministry of Ecological Environment and the Emissions Factor of Pollutant (AP-42) by EPA)\(^{12}\). The basic idea is as follows:

\[
E_{\text{Storage tank}} = \sum_{i=1}^{n} \left( E_{\text{fixed-roof }, i} + E_{\text{floating-roof }, i} \right)
\]

(2)

Where: \(E_{\text{Storage tank}}\) refers to the annual VOCs emissions (t/a); \(E_{\text{fixed-roof }, i}\) refers to annual VOCs emissions of fixed-roof i (t/a); \(E_{\text{floating-roof }, i}\) refers to annual VOCs emissions of floating roof tank i (t/a).

According to the LDAR report from six enterprises, Final Report of Comprehensive Regulation on VOCs from Petrochemical Industry in Chengmai County in 2016, and Study Report on the Investigation and Comprehensive Remediation of VOCs in Hainan Petrochemical Industry, the study conducted the loss assessment of VOCs in organic liquid storage tank. As for the rest two enterprises, the above-mentioned algorithm was applied to estimate the VOCs emissions from organic liquid storage and volatile losses according to the types, solvent and numbers of tanks.

2.3.3 Volatile losses in handling organic liquids

The VOCs emissions in the loading process of gasoline, diesel, naphtha, benzene and other organic liquid from petrochemical enterprises relates to material properties, environment temperature, turnover of materials, loading system, loading mode, transfer mode, tank truck conditions and the availability of vapor collecting system. emission coefficient method and the formula in Emissions Factor of Pollutant (AP-42) by EPA\(^{13}\) are adopted to estimate the volatile losses in handling organic liquids. The given emission coefficient is adopted for the estimation of emission coefficient from loading loss.

\[
E_{\text{handling}} = \frac{L \times V}{1000} \times (1 - \eta)
\]

(3)

Note: kg/h /emissions source in the table refers to TOC emissions per hour of each emissions source (kg).
a. The data was selected from 1995b report by EPA. For closed sampling site, if sampling bottle joins the sampling site, then the emissions factor of fastenings should be adopted, and if there’s no connection between them, the emissions factor of opening pipeline should apply.
b. SV refers to the net detection value from device detection (μmol/mol).
Where: LL refers to the emission coefficient from loading loss (kg/m³); η refers to the gross controlling efficiency (%). When handling system is not equipped with vapor equilibrium processing system, η is valued 0. When on the condition of vacuum loading (vacuum degree is kept under -0.37 kPa) or tank truck is connected to oil-gas recovery system with flanged joint and rigid tube bolt, then η is valued 100%. Concerning the emission coefficient from loading loss, it should cover two circumstances, including road loading and ship loading.

Among the detected eight enterprises, two enterprises conducted estimation on volatile losses in handling organic liquids. One of them, whose business scope mainly included shipping and truck loading outward transport for product export, entrusted eight ports for shipping and loading of product export and VOCs resulting from shipping and loading were missed in scope of statistics by enterprise. Furthermore, considering the fact that there was no gasoline product rollout since the commencement of work, VOCs from automobile transport was deemed 0 t/a. As for the other enterprise, the data referred to the Investigation and Checking on VOCs in Hainan Province and Research Report of Integrated Regulation. The study investigated the loading mode, load materials and loading capacity of the rest four enterprises, adopted the above-mentioned formula to estimate the VOCs emissions from volatile losses in handling organic liquids according to the emissions factor of localization railway and road loading loss listed in Table 3, and determined the VOCs emissions from volatile losses in handling organic liquids of eight petrochemical enterprises in Hainan Province.

### Table 3 Railway and road load loss emission factors

| Loading materials | Bottom/undersurface loading (kg/m³) | Splashing loading(kg/m³) |
|-------------------|------------------------------------|--------------------------|
|                   | New or cleaned tank truck          | Normal operating (ordinary) tank truck | New or cleaned tank truck | Normal operating (ordinary) tank truck |
| Gasoline          | 0.812                              | 1.624                    | 2.355                      | 1.624                      |
| Kerosene          | 0.518                              | 1.036                    | 1.503                      | 1.036                      |
| Diesel            | 0.076                              | 0.152                    | 0.220                      | 0.152                      |
| Light naphtha     | 1.137                              | 2.275                    | 3.298                      | 2.275                      |
| Heavy naphtha     | 0.426                              | 0.851                    | 1.234                      | 0.851                      |
| Crude oil         | 0.276                              | 0.552                    | 0.800                      | 0.552                      |
| Light waste oil   | 0.559                              | 1.118                    | 1.621                      | 1.118                      |
| Heavy waste oil   | 0.362                              | 0.724                    | 1.049                      | 0.724                      |

Note: The loading temperature is valued 25°C based on the maximum check of Reid vapor pressure in design or standard.

2.3.4 Effusion in the process of wastewater gathering and transferring, storage and treatment

The VOCs emissions from wastewater collection and processing system enjoy a large proportion and are mainly affected by the property and temperature of wastewater, weather conditions, wastewater processing method, etc. The estimation of effusion in the process of wastewater gathering and transferring, storage and treatment adopts emission coefficient method. The formula is as follows:

\[
E_{\text{Wastewater}} = 10^{-3} \times S \times Q \times H
\]  

(4)

Where: S refers to emission coefficient; Q refers to processing volume of wastewater (m³/h); H refers to annual running time of processing device (h/a).

Through field research in six enterprises, the wastewater quantity and annual running time were obtained in this study; by referring to the VOCs emission factors (see Table 4) in petrochemical wastewater treatment facilities of AP-42[13] by EPA and the VOCs Emission factors of Industry Procedures and Operating Units (Including Equipment Module), Control Efficiency and Other Metrological Provisions under Air Pollution Control Fee Declaration of Stationary Pollution Source in
the Public or Private Premises [14] from Taiwan, the study drew upon the above-mentioned formulas and calculated the VOCs emissions in the process of wastewater gathering and transferring, storage and treatment. As for the rest two enterprises, the related data can be obtained by referring to the LDAR report.

| Table 4 VOCs emission factors in petrochemical wastewater treatment facilities |
|---------------------------------|----------------------------------|
| Scope of application | Emissions coefficient (kg/m³) |
| Wastewater treatment plant-wastewater processing facilities | 0.005 |
| Wastewater collection system and oil water separation | 0.024<sup>a</sup> |
| Note: | a. Applicable for those without capping or waste gas collection and treatment system. b. Applicable for those with waste gas collection and treatment system. |

2.3.5 Organized emissions during technology process

Organized emissions during technology process refers to the process engineering or device of petrochemical enterprises using 15m or above exhaust funnel or vent nozzle to exhaust pollutants (VOCs) during production, apart from combustion flue gas and flare, and is a fixed point source. Practical measurement is adopted for organized emissions during technology process, which may reduce assumptions on data applicability, fuel characteristics and effectiveness of control measures of emissions. The formula of offline detection emission amount is as follows:

\[
E_i = \sum_{n=1}^{N} \left( Q_n \times \left[ 1 - \left( f_{H,O,n-1} \right) \right] \times \frac{T_n}{T_0} \times \frac{P_n}{P_0} \times (C_i)_n \times H \times 10^9 \right)
\]  

(5)

Where: \( E_i \) refers to the emissions of pollutant i (t/a); \( N \) refers to the times of the annual measurement; \( n \) refers to the serial number of measurement; \( Q_n \) refers to the quantity of flow (wet basis) of process exhaust for the nth time (m³/h); \( \left( f_{H,O} \right)_n \) refers to the water content of process exhaust for the nth time (m³/m³); \( T_n \) refers to the temperature of quantity of flow for the nth time (K); \( T_0 \) refers to the mean pressure under standard state, 101.325 kPa; \( P_n \) refers to the mean pressure of flow (K); \( (C_i)_n \) refers to the concentration (dry basis and standard state) of pollutant i in process exhaust for the nth time (mg/m³); \( H \) refers to the interval between two measurements (h).

The study utilized gas chromatograph to conduct the field test on organized emissions during technology process from two typical petrochemical enterprises in Hainan Province, and calculated based on Formula 5. Due to the similarity of production process type between one of the six enterprises and the field detected enterprise, the measured data were used when estimating the value of the enterprise. With regard to the rest five enterprises, emission coefficient method was adopted for evaluating the VOCs emissions according to the product type and product output investigated.

2.3.6 Cooling tower, circulating water cooling system release

Due to the halfway reuse water treatment, the addition of water quality stabilizer and process material leakage, the pollutants are brought to circulating cooling water, and routed to the atmosphere through flashing, stripping and blowing of circulating water cooling tower. The pollutant source of circulating water cooling system is generated during the process. The cooling tower, circulating water cooling system release adopts the emission coefficient method as follows:

\[
E_{\text{Cooling tower}} = \sum_{i=1}^{n} \left( \text{Flow}_{\text{Cooling water}} \times EF \times t_i \right)
\]  

(6)

Where: EF refers to emission coefficient.
EF in this study refers to the given value in AP-42[13] by EPA, as shown in Table 5. The study investigated the circulating water flow rate and operation time of cooling tower of eight enterprises in the field, and drew upon Formula 6 to obtain VOCs emissions of that link.

Table 5 Default VOCs emission factors for cooling tower 5-stage method

| Types of cooling tower                      | Emission factors (kg/m³) |
|---------------------------------------------|--------------------------|
| Ventilation, reverse flow                   | 7.19×10⁻⁷                |
| Ventilation, transverse flow                | 7.19×10⁻⁷                |
| Unspecified ventilation or flow pattern    | 7.19×10⁻⁷                |
| Natural ventilation                         | 7.19×10⁻⁷                |

2.3.7 Flare discharge

Flare system is mainly applied to process exhaust, excess fuel gas and flammable organic compounds in purging exhaust gas in regular or abnormal production (including startups and shutdowns, inspection maintenance, device fault, overpressure, etc.) of petrochemical industry that process unit cannot recycle. Heat value coefficient method is adopted for the estimation of flare discharge.

(1) Heat value coefficient method

\[
E_{\text{flare}_i} = \sum_{n=1}^{N} Q_{\text{std},n} \times LHV_n \times EF_i \times 10^{-3}
\]

Where:
- \(E_{\text{flare}_i}\) refers to the emissions of pollutant \(i\) in flare exhaust (t/a or t/ emissions event);
- \(N\) refers to the measure times per annum or per emissions event (times/a or times/emissions event);
- \(n\) refers to the serial number of measurement;
- \(Q_{\text{std},n}\) refers to the gas (dry basis, standard state) volume accessed to flare for the \(n^{th}\) time (m³);
- \(LHV_n\) refers to the low heat value of gas (dry basis, standard state) volume accessing to flare for the \(n^{th}\) time (m³);
- \(EF_i\) refers to the emission coefficient of pollutant \(i\) (kg/MJ).

(2) Emissions from abnormal operation or breakdown

\[
E_{\text{flarebreakdown}_i} = E_{\text{normalflare}_i} \times \left(1 - \frac{1}{1 - \text{Feff}}\right) \times t
\]

Where:
- \(E_{\text{flarebreakdown}_i}\) refers to the emissions of pollutant \(i\) under breakdown or dead status of flare (kg/ emissions event);
- \(E_{\text{normalflare}_i}\) refers to the emissions flow rate of pollutant \(i\) during normal operation of flare (kg/h);
- \(\text{Feff}\) refers to the default combustion efficiency of flare (%), with default value of 98%;
- \(t\) refers to the duration of breakdown (h/emissions event).

In this study, the emissions factor of flare under regular production refers to EPA (1995)[13]; the emissions factor of total hydrocarbons was 6.02kg/MJ. The average flow rate of flare from eight enterprises was obtained from survey. Assuming that the low heat value of flare exhaust from all eight enterprises was 38.5MJ/m³, the maximum continuous emission duration 3h, the accident frequency 3 times/year, the combustion efficiency 98%, the maximum continuous emission duration of breakdown or shutdowns 1h and the failure frequency twice/year, then the VOCs emissions from flare can be calculated adopting Formulas 7 and 8.

2.3.8 Combustion flue gas emissions

Combustion flue gas pollution source refers to the process device heating furnace, power station boiler, internal combustion engine and gas turbine of self-provided power plant in petrochemical industry. The emission coefficient method is adopted for estimating the combustion flue gas emissions:

\[
E_{\text{combustionfluegas}_i} = 10^{-3} \times EF_i \times Q_{\text{fuel}} \times H
\]

Where:
- \(E_{\text{combustionfluegas}_i}\) refers to the VOCs emissions of exhaust funnel of the \(i^{th}\) facility (t/a);
- \(Q_{\text{fuel}}\) refers to consumption of fuel. The coal is expressed in the unit of t/h, natural gas with m³/h and liquefied petroleum gas (liquid state) with m³/h; \(EF_i\) refers to the emission coefficient (kgVOCs/specific fuel consumption);
- \(H\) refers to the annual running time of device (h).
The emission factor of combustion flue gas in the study was based on literature research[15]. The specific values are shown in Table 6 (The VOCs emission coefficients were based on the test data of TOC). Through field research of eight enterprises, the types of fuel and fuel consumption were obtained and the VOCs emissions in this link can be obtained accordingly.

| Component         | Emissions factor |
|-------------------|------------------|
| Natural gas       | $1.762 \times 10^{-4}$ |
| Liquefied butane  | 0.132            |
| Liquefied propane | 0.120            |

### 2.4 Emissions estimation of typical pollutants from petrochemical industry

Other pollutants mentioned in Section 2.1 mainly include SO$_2$, NO$_x$ and other seven kinds of gas. SO$_2$, NO$_x$, TSP and OC are organized emissions, and their estimation methods are identical to that of organized VOCs emissions, as shown in Formula 5. NH$_3$ mainly is mainly discharged from wastewater treatment and waste gas collection device, and the estimation refers to the monitoring report provided by the enterprise.

The major emissions of CO$_2$ and CO are from combustion and technology process, and coefficient method is adopted for estimation. The CO$_2$ combustion emissions are calculated based on the heat values of different fuels and corresponding emissions factors. The emissions factors of CO$_2$ of various fuels are shown in Table 7 and the formula is as follows:

$$\sum CE_i = \sum \left[ FQ_i \times (HV_i \times 1000) \times \frac{EF_i}{1000} \right]$$  \hspace{1cm} (10)

Where: $CE_i$ refers to CO$_2$ emissions produced by i fuel combustion (t); $FQ_i$ refers to the amount of i fuel (t); $HV_i$ refers to the lower heat value of fuel i (MJ/kg or MJ/Nm$^3$); $EF_i$ refers to the emissions factor of fuel i (kgCO$_2$/MJ).

| Type of fuels         | Low heat values MJ/kg | Emission factors kg/MJ |
|----------------------|-----------------------|------------------------|
| Standard coal        | 29.271                | 0.0840                 |
| Crude oil            | 41.816                | 0.0711                 |
| Fuel oil             | 41.816                | 0.0755                 |
| Gasoline             | 43.070                | 0.0675                 |
| Kerosene             | 43.070                | 0.0694                 |
| Diesel               | 42.652                | 0.0726                 |
| Liquefied gas        | 50.179                | 0.0616                 |
| Refinery dry gas     | 46.055                | 0.0482                 |
| Oil field gas        | 38.931 MJ/m$^3$       | 0.0543                 |
| Coalmine gas         | 14.636-16.726 MJ/m$^3$| 0.0373                 |
| Coke oven gas        | 18.003 MJ/m$^3$       | 0.0373                 |
| Petroleum coke       | 28.032                | 0.0957                 |
| Supply from state grid| ---                  | 0.86 kg/kWh            |
| Supply of heat of enterprise’s self-provided power plant | --- | 150 kg/GJ |

Note: 1. The low heat value data refer to the comprehensive GB/T 2589-2008 General Principles for Calculation of the Comprehensive Energy Consumption, and the emission factors of various fuels refer to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories[16] adopted by National Development and Reform Commission. 2. The state grid power supply and enterprise-owned power station heating emission factors are from the data released by the National Development and Reform Commission and the statistics and calculation from the enterprise-owned power stations in petrochemical industry.

The CO$_2$ process emissions refer to the process of natural gas-based vapor transforming into
hydrogen devices. The simplified CO₂ emission factor: 4.736 tons of CO₂/10000 Nm³ hydrogen products.

The calculation of CO combustion emissions is based on the emissions factors of CO. Table 8 shows the emissions factor of CO of various fuels and the formula is as follows:

\[
\sum CE_i = \sum \left[ FQ_i \times \frac{EF_i}{1000} \right]
\] (11)

Where: CEᵢ refers to the CO emissions produced by the combustion of fuel i (t); FQᵢ refers to the amount of fuel i (t); EFᵢ refers to the emissions factor of fuel i (kgCO₂/MJ).

Table 8 CO emission factors corresponding to various fuels

| Type of fuels                        | Emission factors (kg/t) |
|-------------------------------------|-------------------------|
| Diesel oil                          | 0.6                     |
| Fuel oil                            | 0.6                     |
| Liquefied petroleum gas             | 0.36                    |
| Natural gas                         | 1.3×10⁻³ kg/m³          |
| Coal gas                            | 1.3×10⁻³ kg/m³          |

Note: From U.S. EPA (2002). Compilation of Air Pollutant Emission factors (AP-42), 5th ed[CD]. Washington, D.C[13]

2.5 Estimation on VOCs inventories in petrol stations

VOCs emissions is greatly sourced from oil products evaporation in urban petrol stations, and highly reactive VOCs contained in oil product steam will cause a range of environmental issues and are deemed as a potential risk. The VOCs emissions from petrol stations are classed into oil tank breathing loss, volatilization in refueling process and loss in discharging process. The emission coefficient method is adopted for estimation and the formula is as follows:

\[
E(i, j, k, l) = EF(j, k, l) \times AC(i, j, k) \times (1 - \eta)
\] (12)

Where: i refers to the geographical range or Internet; j refers to the emissions process; k refers to time; l refers to the type of emissions; EF refers to emission factors; AC refers to activity level; η refers to the recovery efficiency of oil gas (%).

In this study, the emission factor data of each VOCs emission step in the petrol stations was obtained mainly through literature research [17]. Table 9 shows the emission factors of different models and fuel types, and the oil and gas recovery efficiency in this study was 85%.

Table 9 Emission factors for different vehicle types and fuel types

|                      | Gasoline       | Diesel oil     |
|----------------------|----------------|----------------|
|                      | Oil tank       | Volatilization | Oil tank      | Volatilization | Loss in discharging |
|                      | breathing loss | in refueling   | breathing loss| in refueling   | process            |
| Automobile           | 0.16           | 2.49           | 2.3           | —             | —                  |
| Motorbike            | 0.16           | 2.49           | 2.3           | —             | 0.048              |
| Trailer              | —              | —              | —             | 0.048         | 0.027              |
| Tractor              | —              | —              | —             | 0.048         | 0.027              |

3. Results and Discussion

3.1 Emission characteristics of pollutants from typical petrochemical enterprises in Hainan Province

3.1.1 Characteristic of VOCs emission links from typical petrochemical enterprises in Hainan Province

The emission characteristics of typical petrochemical enterprises in Hainan Province were obtained (see Fig.
2) according to the typical VOCs emission links from petrochemical industry introduced in Section 2.3. From Fig. 2, it is known that VOCs ranked the top in eight typical organized emission links of petrochemical enterprises in Hainan Province in 2016, reached 2268.3 tons which accounted for 45.6% of total VOCs emissions, so urgent treatment was needed for emission reduction and control. Through investigation, it is found that organized emissions were mainly produced from in-plant industrial boiler, heating furnace and incinerator which were continuous emission elevated sources and the types and emission amount of pollutants were bound up with different technological types, production status and device conditions. At present, the waste gas control and treatment technology against organized emissions are relatively mature, and the corresponding detection and evaluation methodology are improved incrementally. Therefore, the petrochemical industry should strictly control the emissions in strict accordance with laws and regulations, and further control organized VOCs emissions by optimizing manufacturing technique, improving equipment performance and other methods.

The second largest VOCs emission link was volatile losses in handling organic liquids with an emission load of 648.3 tons, accounting for 13.0%. The handling mode of petrochemical industry in Hainan Province mainly included shiphandling and auto loading. Despite that the VOCs volatilization amount in shiphandling was not covered in the study due to limited information, the emissions from shiphandling should not be neglected[20] according to the previous research. The department concerned in Hainan Province should supervise and urge enterprises to timely update and install oil vapor recovery device with higher recovery efficiency and reduce the loss of oil gas in handling process to boost economic benefit for enterprises. The third largest VOCs emission link was equipment dynamic and static sealing point leakage with emission load of 631.6 tons, accounting for 12.7% which was commensurate with volatile losses in handling organic liquids. With regard to the VOCs emission control of static and static seal point leakage in devices, regular inspection and maintenance of all flanges, valves, pump and other easy-to-leak elements in petrochemical industry were conducted according to the Operating Instructions on Leak Detection and Renovation in petrochemical industry issued by the Ministry of Ecological Environment, timely replace damaged parts, reduce the leakage rate and establish perfect dynamic and static sealing point record for the convenience of management.

In general, all the four links, including volatile losses in handling organic liquids, equipment dynamic and static sealing point leakage, volatile losses of organic liquid storage and reconciliation and effusion in the process of wastewater gathering and transferring, storage and treatment, belonged to pollution caused by the volatilization and leakage of VOCs, accounting for 40.5% of total VOCs emissions in eight links. And the above-mentioned process may be prevented and controlled by installing high-efficient recovery devices, which is an effective method of improving the use ratio of oil gas and creating enterprise economic profits, as well as major direction of VOCs prevention and control.
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Fig 2 (a) Typical emissions sources of VOCs emissions from typical Petrochemical Enterprises in Hainan Province; (b) Contribution rate of typical VOCs emissions sources from typical Petrochemical Enterprises in Hainan Province

3.1.2 SO2, NOx, TSP, BC, OC and NH3 emissions in petrochemical industry
With regard to the emissions of SO2, NOx, TSP, BC, OC and NH3 from two petrochemical enterprises in Hainan Province, the detection should consult the assay method of related standards[22] issued by the Ministry of Environmental Protection. Specifically, exhaust gas tester was used for particulate matter, visible spectrophotometer for nitric oxide, black carbon gauge for BC, carbon analyzer for OC. As for other enterprises, the basis of emissions should be based on the opinion letter of environmental protection acceptance of completed project in 2016 and the monitoring report provided by local detecting test station/testing company. NH3 was mainly sourced from wastewater treatment and waste gas collection device. It revealed according to survey that there were merely three enterprises of eight in Hainan Province equipped with wastewater treatment and waste gas collection devices, and other enterprises chose to entrust a third-party enterprise to handle this problem. The estimation of NH3 from these three enterprises referred to the monitoring report provided by corresponding enterprises.

The emissions of SO2, NOx, TSP, BC, OC and NH3 from eight petrochemical enterprises in Hainan Province were finally obtained through survey and estimation, as shown in Table 10, with emission load
of 3864.98 tons and 1774.25 tons respectively, accounting for 4.0% and 9.6% of total industrial emissions of SO2 and NOx respectively. The results turned out that SO2 and NOx had large emissions in the petrochemical industry in Hainan Province, and desulfurization and denitrification devices with higher installation efficiency should be installed to reduce SO2 and NOx emissions. Where NOx and VOCs, the vital precursor to ozone, were discharged at the same time in petrochemical enterprises, they would greatly promote the generation of ozone and lead to atmospheric pollution. Therefore, the control of these two materials should be fastened in petrochemical industry.

Table 10 Summary of SO2, NOX, TSP, BC, OC and NH3 emissions

|          | SO2   | NOx   | TSP   | BC    | OC    | NH3  |
|----------|-------|-------|-------|-------|-------|------|
| Emissions (t/a) | 3864.98 | 1774.25 | 339.70 | 11.97 | 10.47 | 0.17 |

3.1.3 CO2, CO emissions from typical petrochemical enterprises

CO2 and CO were mainly sourced from the combustion of heating furnace or boiler fuel in the enterprises, and CO was produced when the fuel was not fully burned. The calculation on CO2 and CO emissions was conducted according to types and use level of fuels and hydrogen product output. In this study, the information of fuel used was obtained from six enterprises of eight, and estimation was conducted according to types of products and output by linear regression as for the rest two enterprises. Eventually, CO2 and CO emissions from the petrochemical enterprises in Hainan Province were $1.3110^6$ tons and 744.17 tons, accounting for 4.0% and 0.6% of total CO2 and CO emissions in Hainan industry accordingly. Low emissions of CO indicated that the combustion process in heating furnace or boiler fuel were fully burned from eight petrochemical enterprises and thus CO emissions were at a low level.

3.2 VOCs emissions and distributions from petrol stations in Hainan Province

The study applied emission factor method and conducted estimate analysis on five aspects, including tank loading and unloading of gasoline, vehicle oiling, oil tank breathing, tank truck loading and unloading of diesel oil and vehicle oiling in petrol stations of Hainan Province. The inventory data of motor vehicles was cited from Statistical Analysis on Motor Vehicles and Drivers from Hainan Province in October 2016 from Traffic Police Corps of Public Security Department in Hainan Province, and the motor vehicles concerned included automobile, motorbike, trailer and tractor. On the basis of survey, it is found that the annual oil consumption of single automobile was 2.10 t/a, and by analogy the annual oil consumption of single motorbike presumably was 20% of automobile, the annual oil consumption of single trailer was 4 times of automobile and the annual oil consumption of single tractor was almost as much as that of automobile. Table 11 shows the details of VOCs emissions from petrol stations in Hainan Province.

It can be seen from Table 11 that the VOCs emissions from petrol stations in Hainan Province was 1757.64 tons. The losing fuel oil was calculated at RMB 8000 per ton, and the direct economic losses can reach RMB 1.41 million, which was rather severe. From the perspective of vehicle type, the VOCs emissions from vehicle oiling accounted for 83.4%, which was caused by numerous automobiles and lengthy fueling time, followed by motorbike, which accounted for 16.5%, the number of motorbikes was commensurate with that of automobiles and motorbike was seen as the major trip mode for local residents in Hainan Province. With regard to the VOCs emissions, refueling and oil unloading turned out to be the major processes in VOCs emissions, accounting for 50.3% and 46.5% respectively. Therefore, control on these two processes was key to address oil-gas escape of petrol stations. Effect on human health and ozone formation of petrol stations cannot be neglected due to its location in crowded place and high chemical activity of VOCs substances contained in oil product vapor, therefore petrol stations in Hainan should timely update and install oil and gas recovery facilities with higher recovery efficiency.
Table 11 Summary of VOCs emissions from petrol stations in Hainan Province

| Class of vehicle | Motor vehicle population (unit) | Annual oil consumption of a single bicycle (ton) | Breathing loss of tank truck (ton) | Volatilization of refueling process (ton) | Loss in oil unloading process (ton) | VOCs emission from petrol station (ton) |
|------------------|---------------------------------|------------------------------------------------|----------------------------------|----------------------------------------|-----------------------------------|----------------------------------------|
| Automobile       | 942089                          | 2.10                                           | 47.38                            | 737.17                                 | 680.92                            | 1465.46                                |
| Motorbike        | 934328                          | 0.42                                           | 9.40                             | 146.22                                 | 135.06                            | 290.68                                 |
| Trailer          | 2462                            | 8.38                                           | -----                            | 0.15                                   | 0.084                             | 0.23                                   |
| Tractor          | 54200                           | 2.10                                           | -----                            | 0.82                                   | 0.046                             | 1.28                                   |
| Total            |                                 |                                                |                                  |                                        |                                   |                                        |

4. Conclusions
The VOCs emissions from eight petrochemical enterprises in Hainan Province in 2016 were 2268.3, 648.3 and 631.6 tons respectively, accounting for 45.6%, 13.0% and 12.7% of the total VOC emissions respectively. The above-mentioned three links need to be paid more attention in VOCs prevention and control in the petrochemical industry in Hainan Province.

A mass of SO2 and NOx were also emitted from the petrochemical enterprises in Hainan Province, with the emissions of 3864.98 tons and 1774.25 tons respectively, and the large emissions of NOx and NMVOCs would accelerate the ozone formation and severally threatened the air quality.

It shows that, by emission coefficient method, the VOCs emissions from 482 petrol stations in Hainan Province in 2016 were 1757.6 tons, which caused a direct economic loss of RMB 14.9 million or so. Therefore, the patrol stations of Hainan Province are suggested to install more efficient oil and gas recovery facilities.

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