Process-based volatile organic compound emission inventory establishment method for the petroleum refining industry

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ABSTRACT

The petroleum refining industry is an important contributor to industrial volatile organic compounds (VOCs) emission. As a foundational work for VOCs control, previous VOCs inventories usually treated the petroleum refining industry as an integrated part resulting the unknown of VOCs emission characteristic among different units. Refined management has becoming an inevitability with the increasing strictness of environment standards. This study aims to develop a holistic method for VOCs emission inventory of the petroleum refining industry toward specificity, accuracy and economization, in which a source categorization was proposed from unit angle, and a systematic estimation method was developed from the material flow point of view. This method provides a more specific and accurate quantification method, especially for fugitive emission sources which is a pivotal but difficult problem in VOCs inventory establishment. Through application to a typical medium-scale refinery located in northern China, a unit-specific VOCs emission inventory with 48 emission sources and respective local VOCs emission factors (EFs) was established. Estimation results and economic cost of the developed method were compared with those of other methods. In this study, the integrated EF was 0.77 kg-VOCs/t-crude oil refined, which was in the same order with most previous studies. Inventory results implied that increasing hydrotreating unit, reducing chemical device and solvent-used unit (e.g., polypropylene production, furfural refining unit), upgrading catalytic reforming unit were beneficial to control VOCs emissions in this study. Using floating-roof tanks rather than fixed-roof tanks is an effective way to reduce VOCs emissions from storage tanks, which decrease 72%–86% of diesel storage emissions. Economic cost analysis showed that the advantage of this method lied in lower labor cost, and no subsequent monitoring cost. Suggestions proposed from this study provide feasible measures for local policy makers to control VOCs emission and determine abatement strategies of the petroleum chemical industry. Meanwhile, this study greatly helps enterprises promote the fine management of VOCs-containing materials from the overall processes to identify VOCs control emphasis.

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1. Introduction

Air pollution characterized by high concentration of ground-level ozone (O_3) and fine particulate matter (PM) has caused increasing concerns in China due to its significant adverse impact on human health (Dai et al., 2017; Rohde and Muller, 2015). Volatile organic compounds (VOCs) are key precursors for the formation of ozone and PM through complicated photochemical and physical reactions (Shao et al., 2009a, 2009b; Yuan et al., 2013). Ozone reduction is largely accomplished by the control of VOCs (Tang et al., 2012). Chinese government has been focusing on VOCs pollution problem. The 13th five-year plan for ecological and environmental protection made the reduction target that the total national VOCs should decreased by more than 10% during the 13th five year. *Standard for fugitive emission of volatile organic compounds* (MEEC, 2019b) and *comprehensive VOCs treatment scheme for key industries* (MEEC, 2019a) were successively published to promote VOCs prevention work, recently. The petroleum refining industry is an important contributor to VOCs emissions, accounting for approximately 3% of the total anthropogenic VOCs emissions (Wei et al., 2016). In 2015, the petrochemical industry become one of the

first batch of pilot industries to implement *VOCs Pollution Pilot Charge Method* published in China. Thus, a specific VOCs emission inventory of the petroleum refining industry is necessary and foundational for VOCs emissions reduction and equitable control policies.

In the past several years, VOCs emission inventories have been proposed from global (Piccot et al., 1992), national (Wu et al., 2016; Zhang et al., 2018) and regional scale (Huang et al., 2011; Louie et al., 2013; Lu et al., 2018; Yan and Lin, 2016; Zheng et al., 2016). In national or regional emission inventories, the petroleum refining industry is generally treated as an integrated VOCs emission source. As a result, VOCs emission characteristics among different units are still unclear. Though many VOCs inventories have being conducted from specific industrial angel, recently, inventories for the petroleum refining industry are very limited so far possibly due to its complicated processing flow schemes, diversiform emission sources and insufficient production data. Existed VOCs inventories about the petroleum refining industry mainly focused on species characteristics. For example (Wei et al., 2014), reported a speciation profiles of a petroleum refinery in Beijing based on three ambient samples and five inner devices samples (Mo et al., 2015). collected more specific process samples from a petrochemical plant in the Yangtze River Delta to analyze the key Volatile organic compound (VOC) species of various process units. However, current VOCs abatement policies are mainly based on VOCs emission amount (e.g., the reduction target made by the 13th five year plan). Therefore, it is very essential to establish a detailed VOCs emission inventory of the petroleum refining industry to support VOCs prevention and control work.

Source classification is the first step for inventory establishment, which is directly related to the calculation result. Many efforts have been made for the source classification. Zheng et al. (2017) quantified three emission sources of the petroleum refining industry (i.e., tank loss, leakage loss and refining wastewater volatile) in industrial VOCs inventory, which ignored product loading, stationary combustion and process vents sources. Huang et al. (2011) also presented three VOCs emission sources in regional inventory, namely oil refining, oil storage, tank breathing and emptying. However, oil storage losses generally refer to tank breathing and emptying losses in refinery. *Checking guideline for VOCs pollution sources in the petrochemical industry* (*checking guideline*) (MEEC, 2015b) published by Ministry of Environmental Protection in 2015 divided emission sources into five parts: equipment leaks, storage tanks, product loading, wastewater collection, and others. In brief, source classification of the aforementioned studies was relatively macroscopic. The petroleum refining industry employs a wide variety of processes with different arrangements. Emissions from the same sources vary with the process arrangement. The basic component of all refineries is production unit. Therefore, categorizing emission sources from unit level are more reasonable for the establishment of industrial inventories and factors.

The accuracy of VOCs emissions is an ongoing problem for inventory establishment. Reliable and operable estimation method is the key point for the results' accuracy. Traditional EF and measurement methods are unsuitable for the petroleum refining industry. Traditional EFs were commonly derived from European or American refineries due to the relatively weak EF work in China (Wei et al., 2008, 2011; Zheng et al., 2017). To some extent, the result of EF method deviates from China's actual situation due to the gap between developed countries and China in processing flow scheme, production technology, and pollutant control level. Additionally, inventory results obtained by EF method that multiply activity level by respective pollutant emission factor are difficult to verify its reality, while results estimated from material flow angle can be guaranteed on the whole. China's government also released

local EFs for the petroleum industry in related documents, such as Chinese national emission limit standard of *Loss of Bulk Petroleum Liquid Products* (SINOPEC, 1989). However, it is neither systematized nor complete and outdated. Measurement method is an effective way to account pollutant emission amount for organized sources and can obtain chemical compositions, whereas it is not applicable to fugitive sources which are the major VOCs emission pattern in refinery. Measured concentrations of specific unit inner refinery are likely influenced by production condition and transmission among surrounding units. Wei et al. (2016) obtained an integrated VOCs emission rate (kg/h) of a northern refinery in China using inverse-dispersion method (IDM) based on measured ambient VOCs concentrations. However, specific units cannot be identified. Material flow method, which remove the influence of operation condition and transmission but cannot obtain species information, can get fugitive emissions based on annual input-output data. Thus, in this study, a systematic estimation method integrating material flow and measurement method and theoretical model was developed to improve the results' accuracy and reduce the economic cost of inventory establishment for the petroleum refining industry.

Notably, the document of *checking guideline* also presents a systematic emission measurement or estimation methods for five emission sources of petrochemical industry. *Checking guideline* is also an important reference for the petroleum industry to pay VOCs discharge fees. However, in *checking guideline*, most correlation equations and average EFs are still quoted from American relative documents, which are unsuitable for China's local emission situation. Moreover, economic cost and workload are large. For example, equipment leak estimation probably takes approximately 2 months for 10 workers to detect nearly hundreds of thousands of seals for a medium-scale refinery.

In this regard, this study developed a new method to establish a unit-specific VOCs emission inventory for the petroleum refining industry characterized by high resolution and less man-hour. The method involved unit-level source classification and material flow-based systematic estimation method. The estimation method system eliminates the drawback of independent method through integrating material flow and measurement and theoretical model. A unit-specific VOCs emission inventory was established for a typical medium-scaled refinery using this method. Simultaneously, the key control targets and series of reliable local VOCs emission factors were achieved. Results comparison and economic cost analysis was performed. This study provided initial foray to future EFs database development of national petroleum refining industry. Suggestions based on inventory results greatly help enterprise promote VOCs-containing materials management from the overall processes, and support local policy-makers to determinate VOCs abatement strategies for petroleum industry or petrochemical-based regions.

2. Method and data

2.1. Case introduction and system boundary

A typical medium-scale petroleum refinery with a refining capacity of 7.5 million tons crude oil per year, located in northern China, was selected as a case to establish the VOCs emission inventory. The refinery mainly produced gasoline, diesel, liquefied gas, petroleum coke, propylene and paving asphalt. In 2018, this refinery possessed 16 core refining units which can be divided into fuel oil production system and lube oil production system. The whole refinery process include pre-treating sector (crude oil desalting and dewatering), separation sector (atmospheric and vacuum distillation units), conversion sector (catalytic cracking

unit, delayed coking units, reforming, polymerization, MTBE), petroleum treating sector (diesel hydrotreating, s-zorb, deasphalting, lube oil hydrotreating, furfural refining, butanone-toluene dewaxing, acid gas removal, LPG separation), feedstock and product handling sector (storage and blending, loading and unloading). Auxiliary systems were also taken int consideration. Catalytic cracking unit was installed desulfurization and dust removal facility. A full-scale wastewater treatment system was equipped, in which important VOCs emission units (i.e., oil/water separators, flotation units, equalization tanks and biological treatment units) were all covered and vented to a waste gas treatment device. VOCs emissions from loading operations were disposed by catalytic incinerators after recovery. Storage tanks were divided into three basic types: vertical fixed roof, external floating roof, internal floating roof. All of them has no control devices. Fig. 1 shows the processing follow scheme.

The system boundary was the physical boundary of refinery. Historically, all refining process can transform feedstocks inputs to product outputs independently, and therefore no two refiners are exactly the same. This paper established a system boundary from receipt of crude for storage at the refinery to storage preparatory to shipping the refined products from the refinery that include 16 core refining units and 6 utility systems that support these core processes, which coved most of the petroleum handling and refining operations.

2.2. Source identification

This section first developed a VOCs source classification in terms of unit angle. Source-tracing method, which involved tracing the material flow of all units, identifying potential emission point, establishing VOCs emission forms, and analyzing emission cause, was used to classify emission sources. Finally, a high-resolution emission inventory including 7 categories and 48 sub-sources was developed based on the production processes and emission features. Table 1 lists details of the classification.

(1) Emissions from refining units, including equipment leakage and process vents. Equipment leakage refers to emissions from all types of seals (e.g., pump, compressor) and valves (e.g., pipeline, open ended, vessel relief) and flanges and drains. Emissions from Process vents primarily occur during coke cooling and cutting operations in delayed coking unit.

(2) Emissions from storage tanks, including breathing losses and working losses. Emissions from storage tanks are attributed to changes in temperature, pressure, and liquid levels. It mainly occurs during petroleum liquid storing and tank filling or dispensing operations. Storage tanks may emit significant level of VOCs depending on the design and construction of the tank and characteristics of stored petroleum liquids.

(3) Emissions from stationary combustion sources. The combustion sources include two kinds based on combustion purposes: process heaters and boilers primarily using refinery gas and natural gas as fuel to indirectly preheat feedstock or process fluids, incinerators and reforming furnaces to dispose tail gases.

(4) Emissions from product loading. Although most refinery feedstocks and products are transported by pipelines, some are transported by trucks, rail cars, and marine vessels. Thus, when liquids are loaded into the tanks, organic vapors in "empty" cargo tanks will be displaced to the atmosphere which resulted loading losses.

(5) Emissions from waste water collection, treatment and storage system. Fugitive VOCs and dissolved gases that reside in the surface of water are likely evaporated to the atmosphere
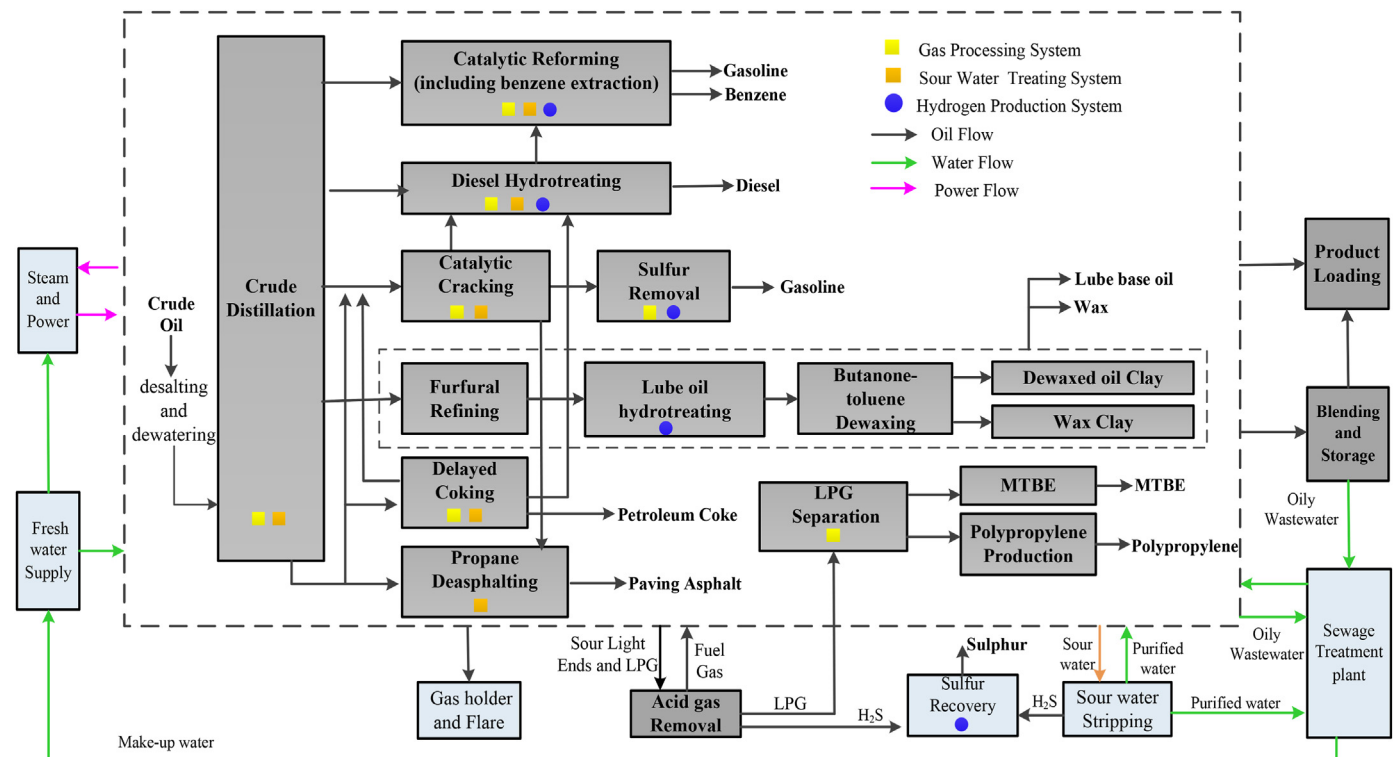

Fig. 1. Processing flow scheme and system boundary of typical medium-scale refinery in China (color should be used in this fig) (Note: the dotted line means the boundary of the refining unit system and the auxiliary system). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
VOCs emission source classification and respective estimation method.

Emission category	Emission source	Estimation method	Emission category	Emission source	Estimation method
Refining unit	Crude Distillation	oil mass balance	Storage tank	Diesel	theoretical model [a]
	Catalytic Cracking	oil mass balance		Dirty oil	theoretical model
	Catalytic Reforming	oil mass balance		Crude oil	theoretical model
	Diesel Hydrotreating	oil mass balance		Lube distillate	theoretical model
	Delayed Coking	oil mass balance		Slurry oil	theoretical model
	Deasphalting	oil mass balance		Residual oil	theoretical model
	S-zrob	oil mass balance		Furfural refined oil	theoretical model
	Acid Gas Removal	oil mass balance		Waxy oil	theoretical model
	LPG Separation	oil mass balance		Gasoline	theoretical model
	MTBE	oil mass balance		Catalytic gasoline	theoretical model
	Polypropylene Production	oil mass balance		Naphtha	theoretical model
	Furfural Refining	oil mass balance		Diesel distillate	theoretical model
	Benzene Extraction	oil mass balance		White oil	theoretical model
	Lube Hydrocracking	oil mass balance		MTBE	theoretical model
	Butanone-toluene Dewaxing	oil mass balance		Methanol	theoretical model
	Dewaxed Oil Clay	oil mass balance		Benzene	theoretical model
Stationary combustion	Catalytic Cracking desulfurization tower	measurement	Product loading	Gasoline	measurement
	Sulfur recovery incinerator	measurement		Diesel	measurement
	Polypropylene production	measurement		Naphtha	measurement
	Power boiler	carbon balance		Benzene	measurement
	Diesel Hydrotreating heater	carbon balance	Waste water treatment	With control devices	measurement
	Catalytic Reforming heater	carbon balance	Flare system	\	measurement
	Atmospheric distillation heater	carbon balance	Cooling tower	\	emission factors
	Delayed coking heater	carbon balance			
	S-zorb heater	carbon balance			

[a] a tank-specific model presented in *Design guideline for energy conservation of petroleum depots (SH/T 3002-2000) (design guideline)*.

from separators and ponds, such as aeration ponds and air flotation, which involve extensive contact of waste water and air.

(6) Emissions from flare system. Emissions from flare system are mainly produced by the combustion of excess refinery fuel gas, purged products, and waste gases during startups, shutdowns, and malfunctions. Few emissions come from pilot burner which is used to maintain the appropriate heating value for good combustion.

(7) Emissions from cooling towers. In cooling towers, water is cooled to near ambient temperature for reuse. VOCs contained in water will emit to the atmosphere due to stripping in the cooling tower and drift loss.

2.3. Estimation method

2.3.1. Emissions from refining units

VOCs originate from oil material in refinery. Thus, unit-level oil flow situation was analyzed to estimate VOCs emissions from refining units. Fig. 2 showed the detailed oil flow model. For each unit, the input feedstock oils are equal to the output oil products, sour light ends to gas holder used to maintain stable operation condition, oils and sulfide and ammonia nitrogen contained in wastewater, oils in solid waste and VOCs emitted to atmosphere.
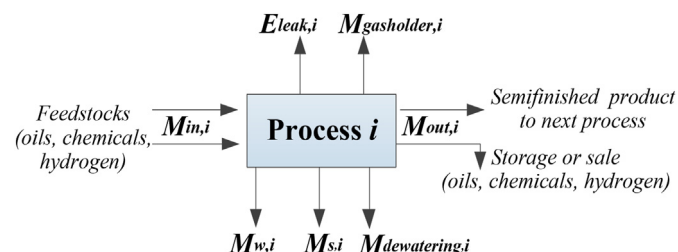

Fig. 2. Oil flow model for each production unit.

Input materials included oils, chemicals, hydrogen and newly added solvents. Hydrogen was taken into consider due to its participation in chemical reactions as raw material or product, eventually enter to wastewater with the form of sulfide and ammonia nitrogen in hydrotreating units. Output products refer to semi-finished products to next unit, final products to storage tanks, dirty oil mainly produced from gas-liquid separator. Water removed from crude oil by electrical desalting and dewatering operation before crude oil distillation should be added to the oil outputs, which is usually neglected in current accounting works. The oils and sulfide and ammonia nitrogen in wastewater were calculated by the amounts of wastewater and their mass concentration, respectively. The removed water was derived from multiplying the quantity of crude oil input, water content in crude oil, and dewatering efficiency. VOCs emissions from refining units can be formulated using equations (1) and (2).

To ensure accuracy of the result, the summation of each units' losses was also verified by the losses of the entire refinery where refinery was regard as a whole. Compared with measurement, correlation equations and average EFs, oil material balance can eliminate uncertainty brought by instantaneous concentrations and abroad EFs using local annual input-output data. This method can trace material or element metabolism situation from the entire life cycle to recognize major loss units and significantly reduce the economic cost. The detailed economic cost analysis was performed in part 3.6.

$$E_{unit} = \sum_{i=1}^{n} (E_{leak,i}) \tag{1}$$

$$E_{leak,i} = M_{in,i} - M_{out,i} - M_{w,i} - M_{s,i} - M_{gas\,holder,i} - M_{dewatering,i} \tag{2}$$

Where, E_{unit} is the total VOCs emissions from refining unit (unit: t/a); $E_{leak,i}$ is the amount of VOCs to atmosphere in unit i (unit: t/a); n is the number of unit in refinery; $M_{in,i}$ and $M_{out,i}$ are the mass amounts of input feedstock and output product in unit i (unit: t/a),

respectively; $M_{w,i}$ and $M_{s,i}$ are the mass amounts of oil, sulfide and ammonia nitrogen to wastewater and solid waste in unit i (unit: t/a), respectively; $M_{gas\ holder,i}$ is the mass amount of refinery gas to gas holder in unit i (unit: t/a); $M_{dewatering,i}$ is the quantity of water removed by electrical desalting and dewatering operations in unit i (unit: t/a).

2.3.2. Emissions from storage tanks

Emissions from storage tanks were calculated by subtracting the treated VOCs from the theoretical vapored VOCs. Theoretical vapored VOCs were estimated by tank-specific modeling presented in *Design guideline for energy conservation of petroleum depots* (*design guideline*) (NBPC, 2000). The detailed estimation procedures of tank-specific modeling in *design guideline* were presented in supplementary material S1. The treated VOCs were formulated by multiplying the quantity of VOCs collected by the control device and the removal efficiency.

Currently, estimation methods used to calculate theoretical vapored VOCs include EF, material balance and tank-specific modeling. EF is generally considered the minimum acceptable method in the petroleum industry because of its macroscopic and unspecific. Material balance method is a valid method to quantify VOCs emissions. However, the liquid production input and output data of each tank required by material balance method are not precise enough. Tank-specific modeling method, which combines the theory model based on ideal gas equations and empirical parameters, is an effective method in terms of anticipated accuracy.

In China, *checking guideline* base on AP-42 (EPA, 2012) and *design guideline* developed by Sinopec group of China are extensively accepted models to estimate VOCs emissions from storage tanks (Li et al., 2013; Lu et al., 2006). However, some studies have found that accounting results of *checking guideline* are apparently lower than the actual measured emission amounts (Liu et al., 2017), possibly due to the differences in design and construction of the tanks and the meteorological parameters among different countries. To ensure the accuracy and localization, *design guideline* based on China's refinery situation was selected in this study. Even so, *checking guideline* provides more comprehensive parameters than *design guideline*. For example, 43 types of deck-fitting loss factors are provided in *checking guideline* and only 19 types in *design guideline*. The values of deck-fitting loss factors are also different between the two methods. The estimation equations of inner-floating tanks and vertical fixed-roof tanks also have slight variation. In this study, models in *checking guideline* were also used to calculate emissions to make a comparison.

2.3.3. Emissions from stationary combustion sources

According to the different burning fuel, carbon element flow situation was analyzed to estimate emissions from refinery fuel gas-burned sources and direct measurement method for tail gas-burned sources. Carbon contained in refinery fuel gas turns into VOCs, PM, CO_2, and CO after combustion. In this study, the molecular weight of VOCs and TSP are supposed to be 12 (Zhang et al., 2000). VOCs from refinery fuel gas-burned sources were calculated by equations (3) and (4).

$$E_{combustion} = \sum_{i=0}^{n} AD_{f,i} \times NC_{f,i} \times \gamma_{VOC} \qquad (3)$$

$$\gamma_{VOC} = \frac{12}{12}C_{VOC} \bigg/ \left(\frac{12}{12}C_{VOC} + \frac{12}{12}C_{PM} + \frac{3}{11}C_{CO2} + \frac{3}{7}C_{CO} \right) \qquad (4)$$

Where, $E_{combustion}$ is VOCs emission from refinery fuel gas-burned sources (unit: t), $AD_{f,i}$ is the activity data of fuel f in emission source i (unit: t), $NC_{f,i}$ is the average carbon content of fuel f in emission source i (unit: %m), γ_{VOC} is the ratio of the carbon contained in VOCs with that contained in total emissions. $C_{VOC}, C_{PM}, C_{CO2}, C_{CO}$ represent measured emission concentrations of VOCs, PM, CO_2 and CO (unit: mg/m^3), respectively.

Equation (3)- (4) were not applicable to tail gas-burned sources. Firstly, the carbon contained in tail gas is difficult to measure due to temperature limitation and production safety in sampling. Secondly, some emissions from tail gas were disposed by pollutants control devices resulting the carbon in tail gas isn't equal to that in CO_2, CO, PM and VOCs emitted to the atmosphere. Thus, measurement method was used to calculate VOCs from tail gas-burned sources.

2.3.4. Other sources

In most refineries in China, product loading and wastewater treatment system are equipped with VOCs control devices under the requirement of national or industrial standards. Thus, measurement method was adopted to evaluate VOCs emissions from wastewater treatment. Emissions from product loading were calculated by the measurement method recommend by *checking guideline*. Material method was used to estimate VOCs emissions from flare system. EF method was used to estimate VOCs emissions from cooling towers. The detailed estimation methods of product loading, wastewater treatment system, flare system, and cooling towers sources were presented in supplementary material S2.

2.4. Data collection

The input-output materials data of each unit were derived from meter measurements equipped in pipelines. Solid waste amounts were obtained from refinery statistical system. The concentrations of oil purity, sulfide and ammonia nitrogen in wastewater were obtained from refinery routine monitoring reports (measured once a week in refinery). The details required by oil mass balance were shown in Fig. S1. The information about 123 storage tanks were acquired from refinery statistical system (see Tables S2—S4). The refinery fuel consumption and its carbon mass content were obtained from refinery meter measurement and routine monitoring reports, respectively (see Table S5). The data needed for product loading system, wastewater treatment system, flare system, and cooling towers were collected through refinery statistical system and routine monitoring reports (see Tables S6—S9).

To fill the data gap, measurement campaign was carried out for stationary combustion sources to obtain VOCs, PM, CO_2, and CO emission concentrations. Table 2 list the sampling information. The concentrations of CO and CO_2 were measured by portable gas detector (ET93-CO, JEK500BK-CO2). PM samples were collected by a smoke automatic test instrument (Laoying-3012H) and analyzed using weight method. VOCs samples were collected through 3L PVF bags and analyzed with U.S.EPA methods TO-15. The VOCs samples were concentrated using a pre-concentrator(Entech 7100, USA) and transferred into the gas chromatography-mass spectrometry (GC-MS) system (GC, HP-7890B; MS, HP-5977B). The VOCs were introduced to a DB-624 column with an MS to analyze C_4-C_{12} hydrocarbons and a PLOT column to analyze C_2-C_4 hydrocarbons.

3. Results and discussion

3.1. Total VOCs emissions

The emission inventory and corresponding factors are provided in Table S1. The dominated contributors were storage tanks and refining units, accounting for 66.60% and 26.97% of the total, respectively. Cooling tower, product loading, stationary

Table 2
Sampling information of stationary combustion sources.

Number	Emission source	Samples	Monitoring pollutant	Emission type
1	Catalytic Cracking desulfurization tower	4	VOCs	point source
2	Sulfur recovery incinerator	4	VOCs	point source
3	Polypropylene production	4	VOCs	
4	Power boiler	8	VOCs, CO, CO_2, PM	point source
5	Diesel Hydrotreating heater	8	VOCs, CO, CO_2, PM	point source
6	Catalytic Reforming heater	8	VOCs, CO, CO_2, PM	point source
7	Atmospheric distillation heater	8	VOCs, CO, CO_2, PM	point source
8	S-zorb heater	8	VOCs, CO, CO_2, PM	point source
9	Delayed coking heater	8	VOCs, CO, CO_2, PM	point source

combustion, wastewater treatment, and flare system sources contributed 6.43% of the total together. Refining units and storage tanks were the priority control objects for refineries to reduce VOCs emission. Table 3 summarizes the integrated VOCs EFs of the petroleum refining industry reported by current studies. The results showed a significant difference, which ranged from 0.07 to 2.65. The EFs of United Stats Environmental Protection Agency (EPA) (1.82) and European Environment Agency (EEA) (0.07−0.61) (Marlene Plejdrup and Richardson, 2019) were an average petroleum refining industry factor of America and Europe. This study obtained 0.77 kg/t, which was lower than (Wei et al., 2016) (1.44) but larger than *checking guideline* (0.52). The differences were the results of different estimation methods (Wei et al., 2016). achieved EF using ISC3 model. However, ISC3 model is difficult to branch out into specific unit. Checking guideline method likely underestimated emissions compared with other references and this study. The detailed differences between guideline and this study is analyzed in the later section. To sum up, this study was in the same order with most previous studies, which confirmed the reliability and operability of the estimation method proposed in this study.

3.2. Refining unit source

Fig. 3 shows VOCs emission contribution and emission factor of each unit. The largest four contributors were Catalytic cracking unit, Catalytic reforming unit, Diesel hydrotreating unit and Acid gas removal unit, which accounted for 22%, 16%, 14%, and 13% of total emissions, respectively. The emission amounts related to various factor, such as production scale, process scheme, equipment configuration, operation conditions, materials properties and general maintenance practices. The four contributors were core refining units, which were composed of large amounts of components and connections (e.g., pumps, compressor, valves) that develop leaks. Additionally, the above-mentioned units mostly used light liquid materials as feedstocks. Aimed at these units, increasing leak detection and repair (LDAR) frequency, replacing old equipment and adopting high quality connections help great in reduce VOCs losses. Catalytic reforming and acid gas removal unit were the key targets to control VOCs in this study due to their large emissions and high emission factors. Though small contributions of Polypropylene production, Furfural refining unit and LPG separation unit, they were important control focus because of the higher emission factors which result in emissions discharge rapidly when

production scale increase.

Currently, EFs related to refining unit were very limited. Table 4 list some results of other methods (Zheng et al., 2017). obtained refining units EF (0.8) through local test. However, it's difficult to analyze their result due to lack of detailed method information. The EF of *checking guideline* (0.079) was estimated combing correlation equations method that relate mass emission rate (unit: kg/h) to detected net screening value (unit: ppm) and average EF method for millions of seals. The low EF of *checking guideline* was possibly due to the instantaneous detected net screening values, which only represented emission level in the monitoring period and not the average emission level for a period. The value changed largely with the operation condition and general maintenance practices. Nevertheless, the oil mass balance method in this study can eliminate aforementioned disadvantages through annual material input and output balance data. The other reason could be attributed to the equation parameters, which were cited from American petroleum industry. The difference of equipment configuration, production process, and control level between American and China resulted in underestimate emissions. Measurement methods in *checking guideline* are also very technically challenging and costly due to the numerous diversiform emission points (Placet et al., 2000).

3.3. Storage tank source

Fig. 4 shows VOCs emission results of organic liquid storage tanks. Diesel and crude oil tanks played dominate roles with the share of 39.6% and 32.8% of the total. Gasoline tanks ranked third with a share of 13.1%, followed by naphtha tanks (5.6%). 60%−90% of their emissions come from working losses. Table 5 provides VOCs emissions per turnover amount for different tank types and mediums to seek potential reduction measures. VOCs emissions from storage tanks are closely related to the tank type, storage medium and turnover amount. Crude oil and gasoline were commonly stored by floating-roof tanks because of their strong volatility, while diesel is generally stored by fixed-roof in current China. Based on the accounting results, the EF of fixed-roof tank was 3−7 times as high as that of inner and external floating-roof tanks, which implies that 72%−86% of VOCs emissions from diesel tanks would be decreased if diesel was stored by floating-roof tank. Adjusting stored temperature and turnover amounts, enhancing sealing type, adopting oil products on-line blending technology

Table 3
Comparison of the integrated VOCs emission factor among different methods.

Emission source	Unit	Emissions factor				
		This study	*checking guideline*	EPA	EEA	Other reference
Refinery	kg/t-crude oil	0.77	0.52	1.82	0.07−0.61[a]	1.44, 1.08−2.65

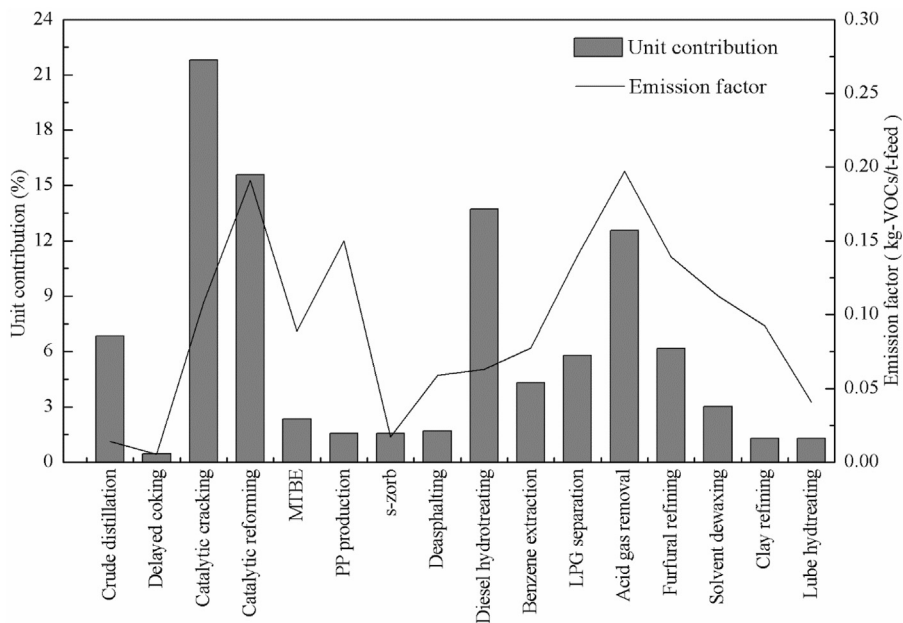[a] EMEP/EEA air pollutant emission inventory guidebook 2019.

Fig. 3. VOCs emissions contribution and emission factor of each unit.

Table 4
VOCs emission amounts and EFs of each refining process with different methods.

Emission source	Emission factor (kg-VOCs/t-crude oil)		
	This study	*Checking guideline*	Other reference
Refining unit area	0.207	0.079	0.8

that oils were blended in pipeline rather than in tanks, were effective measures to control emissions from storage tanks. Additionally, organic chemicals (e.g., MTBE and benzene) and dirty oil had higher EFs than other oil materials, which were important focus in the future. In heavy pollution weather, the blending operation can shut down to alleviate the environmental burden.

Table 6 presents EFs results reported by current documents. Corresponding EFs were additional calculated using *checking guideline* method to make a comparison. The integrated EF of this study was near 1.3 times as high as *checking guideline*, and lower than China national limited standard (GB 11085-89). The distance between *design guideline* and *checking guideline* were mainly attributed to the difference of estimation formulas and parameters, especially formulas of fixed floating tank losses and parameters of inner-floating tank breathing losses. It is understandable that the result was lower than limited standard that represented maximum permissible loss for the petroleum industry in China. Against a previous literature (Zheng et al., 2017), the integrated EF (0.5) obtained through on-site test was 4.5 times as high as this study (Wei
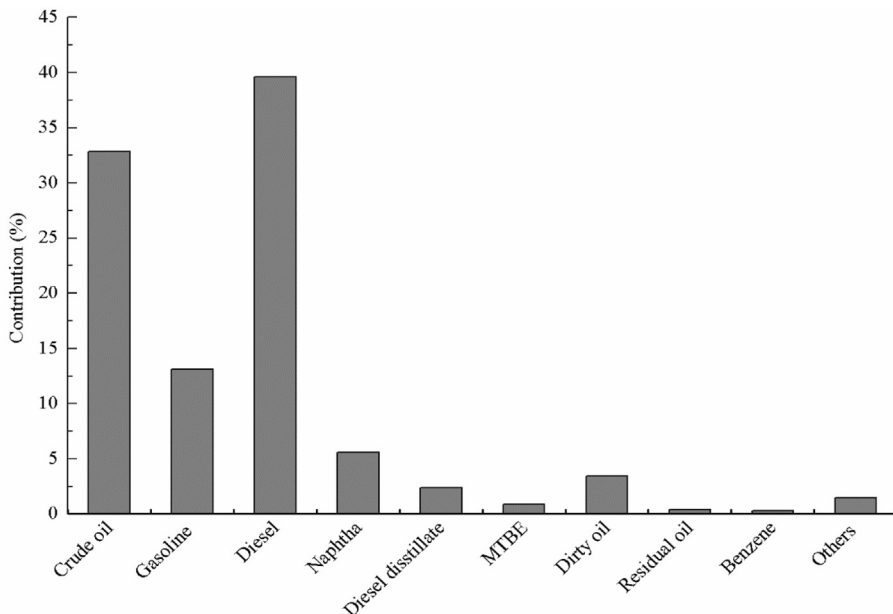

Fig. 4. VOCs emission contribution of specific storage tank to the total emissions.

Table 5
VOCs EFs of different type of storage tank.

Medium stored	Emission factors (kg-VOCs/t-turnover)		
	Vertical fixed-roof	Inner floating-roof	External floating-roof
Diesel	0.261	0.073	0.036
Dirty oil	4.871		1.369
Crude oil			0.079
Lube distillate	0.007		
Slurry oil	0.013		
Residual oil	0.008		
Furfural refined oil	0.002		
Waxy oil	0.004		
Gasoline		0.087	
Catalytic gasoline		0.364	
Naphtha		0.089	
Diesel distillate		0.057	
White oil		0.094	
MTBE		0.356	
Methanol		0.158	
Benzene		0.145	

Table 6
VOCs emission factors of storage tanks among different methods.

Product stored	Emission factors (kg-VOCs/t-turnover)				
	Design guideline	*Checking guideline*	GB 11085-89	EEA	Other reference
Diesel	0.243	0.263			0.161
Crude oil	0.079	0.054	0.123		0.171
Gasoline	0.087	0.041	0.156	0.1–0.4	0.064
Total	0.097	0.074			0.5

Total: storage tanks were estimated as a whole. EF was calculated by dividing VOCs emissions by total turnover amounts.

et al., 2008). estimated VOCs EFs of diesel, crude oil, and gasoline using empirical formula. However, the detailed formula, tank type and oil properties were not provided. Nevertheless, the results of (Wei et al., 2008) and this study were of the same order of magnitude. The gasoline EF of EEA seems slightly higher than other results from Chinese local refinery, which possibly was influenced by differences between country.

3.4. Combustion source emissions

The EFs of carbon balance method and measurement are list in Table 7. Specifics were in supporting material Table S5. EFs of numbers 5–9 showed that carbon balance method results were approximately 4 times higher than measurement. The differences, on the one hand, was attributed to the instantaneity of VOCs concentrations and exhausted gases flow rate used by measurement method. Limited samples cannot represent actual emission level very well. On the other hand, carbon in refinery fuel gas used by carbon balance method covers all possible VOCs emission ways.

Measurement results, to some extent, cannot include all VOC compositions. For example, only 67 VOC compositions are included in gas chromatography/mass spectrometry measurement method (MEEC, 2015a). That further increased the gap between the two results. Moreover, using VOCs emission ratio rather than direct VOCs emission concentration can decrease the influence of production condition change.

3.5. Other sources

Table 8 lists VOCs EFs of other sources. Specifics were provided in Tables S6–S9. In terms of product loading sources, VOCs not collected by oil-gas recovery system contributed 28.98% to the total. The remaining 71.02% come from oil-gas recovery system emissions. The difference between Wei et al. (2008) (0.034) and this study is likely due to the efficiency of recovery system. Not only removal efficient and emission concentration but also collection efficient should be taken attention for VOCs reduction.

The EF of waste water treatment of this study (0.0018) and

Table 7
VOCs emission factors of combustion sources among carbon balance and measurement.

Number	Emission source	Fuel	Emission factor		
			Unit	This study	Measurement
1	Catalytic Cracking desulfurization tower	coke	kg/t-coke		0.008
2	Sulfur recovery incinerator	tail gas	kg/t-sulfur		0.096
3	Polypropylene production (PP)	tail gas	kg/t-PP		0.001
4	Power boiler	natural gas, refinery fuel gas	kg/t-fuel		0.004
5	Diesel Hydrotreating heater	refinery fuel gas	kg/t-fuel	0.034	0.008
6	Catalytic Reforming heater	refinery fuel gas	kg/t-fuel	0.034	0.007
7	Atmospheric distillation heater	refinery fuel gas	kg/t-fuel	0.019	0.005
8	Delayed coking heater	refinery fuel gas	kg/t-fuel	0.019	0.010
9	S-zorb heater	refinery fuel gas	kg/t-fuel	0.024	0.007

Table 8
VOCs emission factors of product loading and waste water treatment with other studies.

Emission sources	Unit	Emission factor		
		This study	Industrial factor	Other reference
Product loading	kg/t-load	0.043		
gasoline	kg/t-load	0.042	1.3[a]	0.034
diesel	kg/t-load	0.004	0.1[a]	
Naphtha	kg/t-load	0.293		
Benzene	kg/t-load	0.088		
Waste water treatment	kg/m^3	0.0018	0.005[b]	0.12

[a] Loss of bulk petroleum liquid product (GB11085-89); b: *Checking guideline for VOCs pollution sources in the petrochemical industry.*

industrial factor (0.005) were in the same order of magnitude. The wastewater EFs influenced significantly by the control technology equipped with refinery. Industrial EF represented average emission level in petroleum refining industry. The lower EF of this study indicated the high VOCs control efficiency of this refinery. In this refinery, the important VOCs emission units in wastewater treatment system were all covered and the collected VOCs were all destroyed in a catalytic combustion tower.

3.6. Economic cost analysis

The economic cost of the measurement method and the comprehensive method developed by this study were compared roughly. Table S10 in supporting document presents the basic information needed for different methods' economic cost accounting. The final estimation results are seen in Table 9. The economic cost differences between the two methods were mainly originated from refining units and stationary combustion sources. Thus, only refining units and stationary combustion sources were involved.

The total economic cost of measurement method was 660300 RMB/year, which is nearly 12 times and 37 times as much as comprehensive method in the first and second year. The labor cost for the detection of nearly hundreds of thousands of seals accounted for the great economic cost in measurement method. Additionally, the monitoring cost for stationary sources should be conducted every year due to the change of VOCs emission concentration and gas flow velocity when refining scale changed. Whereas, the VOCs emission concentration ratio used by the comprehensive method would be steady when refining scale change. Thus, in the second year, the measurement method produces monitoring cost, while the comprehensive method does not. The above results indicated that the economic advantage of the comprehensive method lied in no upfront equipment investment, lower labor cost, and no subsequent monitoring cost. Compared with the measurement method, this study can save nearly 1.24 million RMB in the first two years.

Overall, the establishment method developed in this study has the advantage of high resolution and well economy. The comprehensive estimation method from material flow angle can trace VOCs emissions from original sources to control VOCs-containing materials from the entire process. Less economic cost is also beneficial to extend its application to industrial level. The method

may not completely reflect the real emissions due to inevitable measurement error. However, a detailed and explicit source classification and relative accurate estimation method can be used to develop an effective and reliable approach to establish VOCs emission inventory for the petroleum refining industry in China.

Notably, the specific inventory is positive as demonstrated by the usefulness of this method. It can provide well references for medium-scale refiners. The integrated EF may be unsuitable for large-sized refineries or refineries with other new units.

4. Conclusions

A new VOCs emission inventory establishment method, which involved unit-level source categorization and material flow-based estimation method, was developed for the petroleum refining industry. Using this method, a process-specific inventory of typical medium-scale refinery including 48 emission sources and series of local EFs was proposed. The integrated VOCs EF of a medium-scale refinery was 0.77 kg/t-crude oil in this study. Storage tanks and refining units were the dominated contributors, accounting for 67% and 27% of the total respectively. Diesel and crude oil tanks were the largest emission sources for storage sources, which shared 72% of total tank emissions. The major emission units were Catalytic cracking unit, Catalytic reforming unit, Diesel hydrotreating unit and Acid gas removal unit. In terms of production loading sources, except emissions from oil-gas recovery system, approximately 29% of VOCs were not collected by recovery system. Economy cost analysis results showed the advantage of the comprehensive method in equipment investment, labor cost and monitoring cost. The reliability was also verified by comparison with previous methods. Compared with traditional EF and measurement inventory establishment method, the method in this study could obtain fugitive VOCs emissions from original sources and eliminate the instantaneity influence of measurement.

In the past years, VOCs pollutants have not been sufficiently considered in China. The increase in air pollution problem has made VOCs control the major agenda in the 13th Five-Year plan. However, the foundational works of VOCs emission estimation and control and management study in China are relatively weak. The current study can serve as the first step to VOCs emission estimation. Additional refinery cases from different areas, processing flow schemes, unit types, and emission control technologies should be

Table 9
The economic cost results of the two methods.

Emission category	The first year's cost (RMB)		The second year's cost (RMB)	
	Measurement	This study	Measurement	This study
Labor cost in process refining emission accounting	624000	18000	624000	18000
Monitoring cost in stationary combustion	36300	36300	36300	0
Total	**660300**	**54300**	**660300**	**18000**

further studied to achieve industrial VOCs EFs. According to the calculation results, increasing leak detection and repair (LDAR) frequency of Catalytic cracking unit, Catalytic reforming unit, Diesel hydrotreating unit and Acid gas removal unit is important to reduce refining units VOCs emissions. Using floating-roof tanks rather than fixed-roof tanks is an effective measure to reduce VOCs emissions from storage tanks. Additionally, Improving VOCs emission standard and installing continuous emission monitoring system are future control directions for refineries and government to reduce VOCs emissions for improving air quality.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yeye Liu: Conceptualization, Investigation, Writing - original draft. **Feng Han:** Investigation, Writing - review & editing. **Wei Liu:** Funding acquisition. **Xiaowei Cui:** Formal analysis, Writing - review & editing. **Xiaoyu Luan:** Formal analysis, Writing - review & editing. **Zhaojie Cui:** Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2020.121609.

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