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Research and Application of VOCs Treatment in Petroleum Refinery Industry Based on LDAR

Liang-Chao CHEN[1,a], Jian-Feng YANG[1,b,*] and Xin-Yuan LU[2,c]

[1]College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, China

[2]China Special Equipment Inspection and Research Institute, China

[a]15001257838@163.com, [b]2004500017@mail.buct.edu.cn, [c]luxinyuan@csei.org.cn

*Corresponding author: Jian-Feng YANG

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Abstract. To combat air pollution and safety hazards caused by volatile organic compounds (VOCs) of dynamic and static sealing point of equipment in petroleum refinery industry. This paper, firstly, builds the five-part procedures based on leak detection and repair (LDAR) for VOCs treatment and assessment, which is applied to the atmospheric-vacuum distillation unit with 11746 sealing points for the first time. The detection result shows that there are 43 leak points among the sealing points. Then the emission quantity is calculated and statistically analyzed according to different detection value and seal types. In addition, by analyzing the leakage causes and taking corresponding repair measures, all the leak points are effectively repaired according to the re-inspection result. Finally, with the evaluating of emission quantity before and after repair for the unit, the effects of detection and control for leakage are obvious, which effectively reduce the air pollution.

Introduction

With the rapid development of the petroleum refinery industry, the leakage of VOCs in various equipment components and joints keeps increasing. Studies have shown that VOCs is an important product of photochemical reactions and one of the major contributors to the greenhouse effect, which not only causes atmospheric environment pollution, but also causes harm to human health [1, 2]. Leakage of equipment components and pipelines belongs to the leakage of dynamic and static sealing points of equipment, which is the second largest source of fugitive emission of VOCs after the storage and transportation process [3]. According to the estimation of the United States environmental protection agency (EPA), the VOCs emission generated by leakage of dynamic and static sealing points of equipment accounts for about 0.01% of the crude oil processing volume of the refinery and more than 20% of the total fugitive emission of VOCs [4]. As the main factor of VOCs leakage in petroleum refinery plant, the leakage of dynamic and static sealing points of equipment is not only the requirement of environmental protection and occupational health, but also an important means for enterprises to achieve energy saving, and finally improve their economic benefits [5, 6].

Leak Detection and Repair (LDAR), as a kind of technology for the detection and repair of the leakage of devices in industrial production activities, can help enterprises find and repair the leakage of equipment sealing components as early as possible, and help reduce the emission of VOCs, which has been adopted in more and more countries [7]. The implementation of LDAR started earlier abroad, which has accumulated 30~40 years of experience [8]. In the 1990s, the United States stipulated that the petrochemical industry must implement LDAR technology. After 10 years of development, good emission reduction results had been achieved. At present, many regions and countries, including Canada, the European Union and so on, refer to the method 21 of the United States as a template and basis for LDAR implementation. In the long-term application and development process, LDAR work abroad has formed a relatively complete implementation system, and has entered the track of legalization, standardization and specialization [9,10]. According to the assessment of LDAR implemented by the EPA [11], the leakage of VOCs from equipment in petroleum refinery enterprises can be reduced by 63%. LDAR implementation can improve environmental air quality, reduce the probability of production safety accidents, and finally improve the safety production environment and increase economic benefits of enterprises [12].

Aiming at the problems of late development and poor implementation effect of LDAR in China, and by combining with mature standards and methods at home and abroad, a reasonable and optimized implementation process based on LDAR technology was constructed for VOCs pollution source leaking from dynamic and static sealing points of equipment. Through the practical application of the atmospheric-vacuum distillation unit, the detection results were compared and analyzed from multiple perspectives; with the effective assessment of emissions, emission reduction effect was achieved obviously.

Research on Leakage Detection and Evaluation Based On Ldar

The scope of leak detection for dynamic and static sealing points of equipment is related to VOCs flowing through or in contact with equipment or pipelines, mainly including pumps, compressors, agitators, valves, pressure relief equipment, sampling connection system, open valves or open pipelines, flanges, connectors and other. According to the LDAR technology and the demand of emission accounting, the working process of leakage detection of dynamic and static sealing points of equipment is set up as five parts: data collection, identification and analysis, field detection, leakage repair and statistical accounting, as shown in Figure 1.

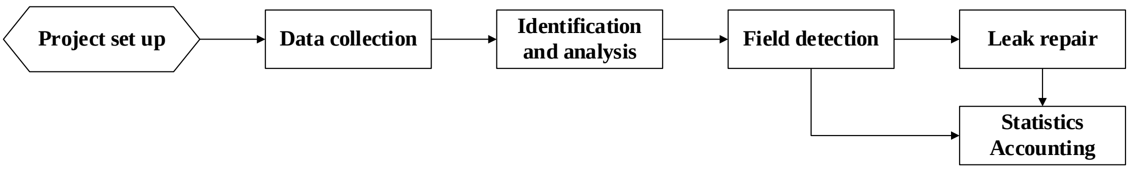

Fig. 1 Work flow of leak Detection and Evaluation for dynamic and static sealing points of equipment

Data collection is the process to collect basic documents and relevant evaluation reports of various processes and equipment of the unit. The process of identification and analysis process includes device and equipment suitability analysis, material identification, sealing point classification, site identification, information collection, account establishment, etc. Then equipment, gas and auxiliary materials should be prepared for field detection. After correction of the response factors, the bottom value of the environment should be tested and then the leakage amount of each sealing point should be detected. When the leakage condition is reached, the leakage process should be confirmed and the leak point should be affixed with the leak plate in time. The process are listed in Figure 2.

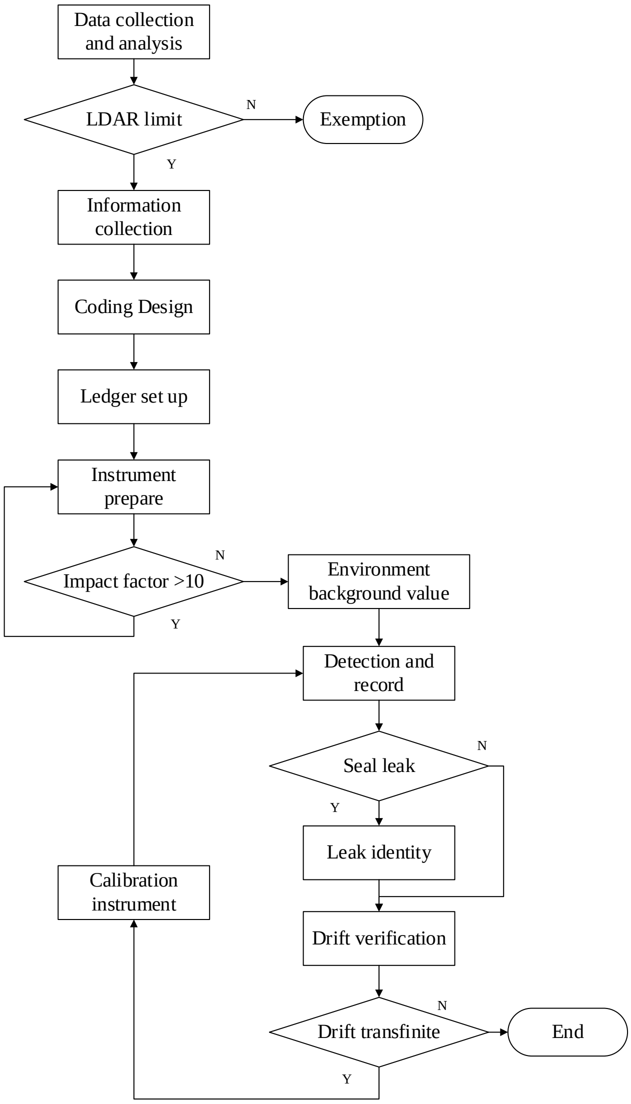

Fig. 2 Flow chart of data collection, identification and analysis and field detection

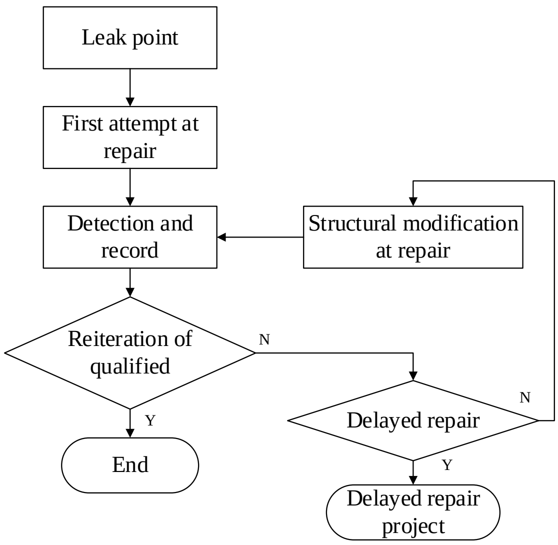

Fig. 3 Leakage maintenance flow chart

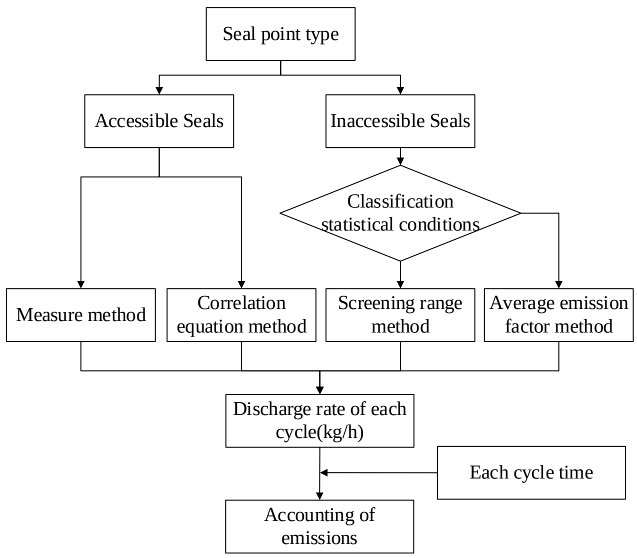

Fig. 4 Emission statistics accounting flow chart

Once the leakage points detected by field detection, they should be repaired and re-detection in time. The leakage points that meet the requirements for delayed repair are managed according to the internal maintenance management methods and procedures of the enterprise. The process of leakage maintenance are shown in Figure 3.

The statistics accounting method is chose as shown in Figure 4 according to the situation of LDAR. The accuracy of calculation for emission rate results from high to low are as follows: measured method, correlation equation method, screening range method, average emission factor method. Combining with emission time the emission quantity could be calculated.

Application of Leakage Detection and Evaluation on Atmospheric-Vacuum Distillation Unit

Field detection is divided into two parts: emission baseline test and stage detection. Most of China's LDAR projects in refining and chemical enterprises are implemented for the first time. Therefore, a comprehensive test is conducted on all applicable components of LDAR projects to establish the emission baseline. After that, the phase detection is carried out according to the corresponding testing regulations and the process of LDAR.

Leakage Detection

A 5 million t/a atmospheric-vacuum distillation unit was investigated and detected to the VOCs source for the first time. First of all, the relevant technical data are collected, including process P&ID diagram, production scale, material balance table, raw and auxiliary materials, product name, physical and chemical properties, material composition table (name, composition, phase state, density, temperature) in each pipeline, (pressure, etc.), identify material components (VOC/HAP, gaseous/vapor, light, heavy, exempted substances). Then it begins to enter the device area to take pictures of the sealing points and mark the sealing points to code and document all the sealing points that are included in the LDAR range. Through data acquisition, identification and evaluation process, 1593 photos and 11746 seal points are set in the unit. The number and proportion of different sealing point types and different medium states are shown in Figure 5.

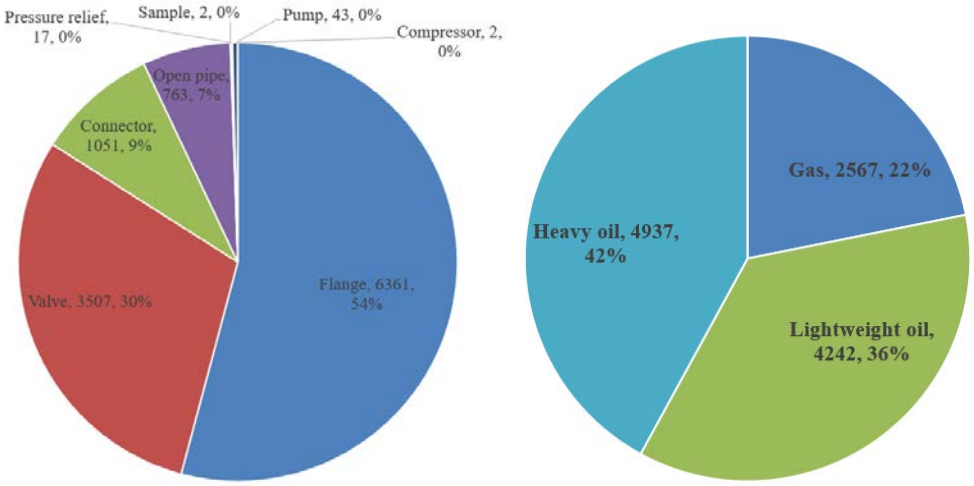

Fig. 5 Statistical results of sealing point types and medium states

The field current work practice is curried out using the flame ionization detector (FID) combined with photo ionization detector (PID). Calibration gas and detect gas are used hydrogen and methane gas. The defined leakage value is 500 μmol/mol, 11746 seal points are detected and 44 leak points are found. The leakage occurs mainly in valve, open pipe, connection and flange, in which the leakage point of flange is the most, and the leakage rate of open pipe is the highest. The number of leakage points and leakage rate of different types of sealing points are shown in Table 1. The total leakage rate of sealing points is 0.37%, and the highest leakage rate comes from open pipelines (1.57%).

Table 1 Statistics of leakage number and leakage rate of different sealing point types

Sealing point type	Sealing points number	Leakage points number	Leakage rate
Flange	6361	4	0.06
Valve	3507	17	0.48
Connector	1051	10	0.95
Open pipe	763	12	1.57
Sample	2	0	0
Pressure relief	17	0	0
Pump	43	0	0
Compressor	2	0	0
Total	11746	43	0.37

By comparing the number and percentage of components at different concentrations (Table 2), it is found that the maximum leakage point of detection concentration is 56.82% in the range of 500-2000 μmol/mol, followed by the leak point with detection concentration greater than or equal to 10000 μmol/mol (20.45%), and the number of leak point of the opening pipeline is the most in this range.

Table 2 Number and proportion of leakage points in different range of detection concentration

Detection concentration [μmol/mol]	Leakage points number					Percentage
	Valve	Flange	Open pipe	Connector	Total	
500~2000	9	3	8	5	25	56.82
2000~5000	2	0	0	2	4	9.09
5000~10000	4	0	1	1	6	13.64
≥10000	2	1	4	2	9	20.45

The state of leakage point medium is analyzed by medium state. It can be seen from Figure 6 most of the leakage points are light oil and gas, so light oil and gas are more likely to leak then heavy oil.

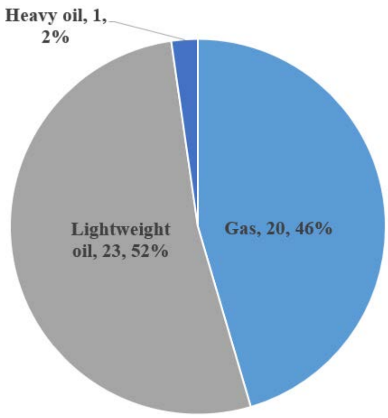

Fig. 6 Number and proportion of leakage points in different medium states

Leakage Cause Analysis

According to the type of leakage point, the main reason for the leakage of valve and open pipeline are improper switch or rust of valve, which leads to the failure of valve close, and the aging of equipment. The aging of gasket, raw material belt, packing, etc., the rusty of thread, the insufficient pretightening force during installation, and the easy volatilize and permeate of the gas medium may cause the leakage of flanges and connectors, which eventually causes the serious leakage. It also reflects the unfulfillment of the management of sealing point in workshop, whose management still stays at the level of correction maintenance instead of routine maintenance.

As mentioned in the earlier, firstly, the medium at which the leakage occurs is gas and light oil. Secondly, according to the operating condition of seal points, the leakage point is easy to occur in the parts with higher temperature (> 100 °C), such as the outlet line of the furnace and the outlet line of the bottom of tower. In addition, there are more leakage points in the higher-pressure position where the medium is pressurized by the machine pump. It can be seen that the high temperature medium is more easily to volatilize and the high-pressure medium is more easily to leak from the sealing points, which are important reasons for the serious leakage of VOCs in these locations.

Leakage Repair

Leakage repair requires the first attempt at repair within 5 days after the discovery of the leakage point. If the leak has not been eliminated after the first attempt, it should be repaired again or moved into the delay maintenance list. The deadline for final maintenance should be 15 days from the date of discovery of the leakage, or in accordance with the installation maintenance plan.

After the detection of the unit, the main on-stream repairing measures of the leakage points include increasing the pretightening force and pipe cap, plugging the head, adding clamping device, plugging with pressure, replacing gasket or raw material tape, etc. The leakage points, which cannot be dealt with immediately, should be hung with red warning card. After repairing, all 11746 sealing points were re-detected, and the leakage points were payed close attention to detect. The results showed that the number of leakage points was zero, and all leakage points of detected seal were successfully repaired.

Accounting of Emissions

According to the default zero emission rate, the limited emission rate and the relevant equations in the American EPA and China Petrochemical Industry working Guide [11, 13], the emission rate of the measured net detection value of the seal point is calculated. The different net detection values is calculated by using Formula (1) and different equipment parts emission rate are referred to the Table 3. For closed sampling points, when the sampling bottle is connected to the sampling port, the value of the "connector" is used; when the sampling bottle is not connected to the sampling port, the value of "open valve or open line" is used.

Table 3 Equipment component emission rate calculation table for petroleum refinery industry

Component type (All medium State)	Default zero emission rate [kg/h]	Limiting emission rate [kg/h]	Correlation equation emission rate [kg/h]
Pump	2.4E-05	0.16	$5.03E\text{-}05 \times SV^{0.610}$
Compressor	4.0E-06	0.11	$1.36E\text{-}05 \times SV^{0.589}$
Stirrer	4.0E-06	0.11	$1.36E\text{-}05 \times SV^{0.589}$
Valve	7.8E-06	0.14	$2.29E\text{-}06 \times SV^{0.746}$
Pressure relief	4.0E-06	0.11	$1.36E\text{-}05 \times SV^{0.589}$
Connector	7.5E-06	0.030	$1.53E\text{-}06 \times SV^{0.735}$
Flange	3.1E-07	0.084	$4.61E\text{-}06 \times SV^{0.703}$
Open pipe	2.0E-06	0.079	$2.20E\text{-}06 \times SV^{0.704}$
Others	4.0E-06	0.11	$1.36E\text{-}05 \times SV^{0.589}$

$$e_{TOC}\begin{cases} e_0 & (0 \le \mathrm{SV} < 1) \\ e_p & (SV \ge 50000) \\ e_f & (1 \le SV < 50000) \end{cases}. \quad (1)$$

Where e_{TOC} is TOC emissions rate of seal (kg/h), SV is adjusted net detection value (μmol/mol), e_0 is default zero emission rate of a seal point (kg/h), e_p is limiting emission rate of a seal point, and e_f is correlation equation emission rate of a seal point.

After calculation for the first inspection, the total emission quantity of all detected seal points is 2120.4kg/a. The calculated results of each component are shown in Figure 7, in which the emission of valve is the largest, which is directly related to the number of valves and the number of leakage points among the sealing points. According to the medium state of sealing point, the emission of gas medium accounts for 72% of the total emission, light oil and heavy oil occupy 17% and 11%, respectively. It can be seen that the gas medium sealing part is the main part of VOCs emission for the atmospheric-vacuum distillation unit.

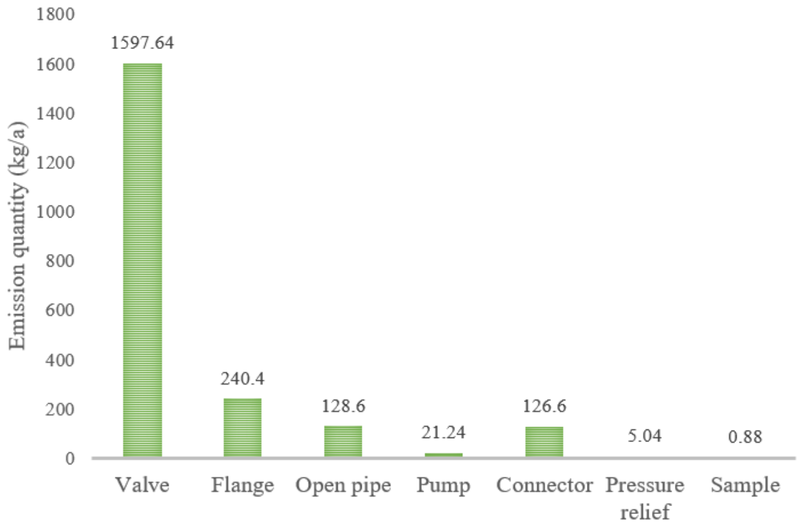

Fig. 7 The emission quantity of each component

According to the re-detection results, the emission of the seal point after repair is calculated. The estimated emission reduction is 1545.77 kg/a and the reduction ratio is 72.90%. The repair effect is obvious and the leakage loss of VOCs is greatly reduced.

Conclusion

1) Through the research of LDAR technology and emission estimation method, the workflow of leak detection of dynamic and static sealing point of equipment in petroleum refinery industry is established and the operation steps of each flow are listed.

2) The sealing point of the 5 million t/a atmospheric-vacuum distillation unit is detected and repaired based on LDAR. In the unit, 11746 sealing points of equipment are detected and 43 leakage points are found out. The on-stream maintenance and repair for leak point are taken by increasing the pretightening force, adding pipe cap, plug, punching tool, sealing device with pressure, replacing gasket or raw material belt and so on, which make all leakage repaired.

3) The statistical analysis shows that valves, connectors and flanges are easier to leak than other sealing forms. Sealing points where the medium state are gas and light oil are more likely to leak. Operational condition of sealing points at high temperature and high pressure are vulnerable to leak.

4) By comparing and calculating the emission quantity before and after the repair, the VOCs emission reduction effect for dynamic and static sealing point of equipment is obvious after LDAR implementation. It can be seen that the LDAR technology can bring direct or indirect economic and environmental benefits to enterprises, which reduces VOCs emissions, directly reduces oil losses, and then improves environmental quality.

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