Odor Treatment in Refinery

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1 Control standards on odor pollutants. The emission source of odor in refinery.

✓ Odor:
means any smell that stimulates our olfactory organ, arouses general dislike or displeasure and damages our health.

✓ Odor substances:
means sulfide, ammonia, chlorine, nitrogen oxides, ozone, hydrocarbons, alcohols, aldehydes, ketones, esters, phenols, amines, organic acid, organic halide, etc.
1 Control standards on odor pollutants. The emission source of odor in refinery.

✓ Emission source of odor in refinery:
means exhaust stacks of flue gas; devices of sewage gathering, transferring and processing; material (sewage) tank; intermediate tank of oil; loading and unloading operations to materials; leakage of equipment and pipe valve; tail gas from various processes, etc.
1 Control standards on odor pollutants. The emission source of odor in refinery.

✓ Some emission standards on odor in China:

"GB14554-93 Emission standards for odor pollutants",
"GB16297-1996 Integrated emission standard of air pollutants",
"GB8195-2011 Health protection zone for petroleum processing industry",
"Discharge standards for petroleum refining industry (2014.04.10)",
"the provincial standard of Beijing, DB11/447-2007 Emission standards of air pollutants for refining and petrochemicals manufacturing industry", etc.
1 Control standards on odor pollutants. The emission source of odor in refinery.

✓ Standard GB14554-93: Height of stack is 15m, emission rate of H$_2$S is $\leq 0.33$ kg/h, and methyl mercaptan is $\leq 0.04$ kg/h.

✓ Standard GB16297-1996: The concentration of non-methane hydrocarbons (NMHC) is $\leq 120$ mg/m$^3$.

✓ The provincial standard of Tianjin city, DB12/524-2014: The concentration of NMHC is $\leq 80$ mg/m$^3$.

✓ Now, Chinese people have very high demands for environmental quality, so Sinopec will set the control goal that fugitive emission of waste gas including hydrogen sulfide, organic sulfide and NMHC should meet the demand of Zero Emissions.
Exhaust gas which come from oil separation tank and flotation tank in sewage treatment plant has a foul smell. The concentration of NMHC is 2000-30000 mg/m³, there is also some odor substances such as H₂S, NH₃ and organic sulfide. The concentration of odor can be more than 20000 OU/m³.

In China, nearly 20 refineries have adopted the technology of “Desulfurization and Concentration Homogenization of Total Hydrocarbon-Catalytic Oxidation” to treat this exhaust gas. After purification, the concentration of NMHC is < 100 mg/m³, the concentration of odor is < 100 OU/m³.
2 VOC exhaust gas from refinery sewage treatment plant is treated by catalytic combustion
Odor from bio-treatment devices such as aeration tank contains sludge droplets, hydrogen sulfide, organic sulfide and benzene series, etc. The concentration of odor is 2000-5000 OU/m³.

(1) Treatment method of “washing-adsorption”
Waste gas from aeration tank is treated by “washing-adsorption”. After purification, the sulfide, odor and NMHC meet the gas concentration index of emission standard GB14554-93 and GB16297-1996.
3  Odor Treatment for aeration tank of sewage treatment plant

continued(1)

Of this, the concentration of odor drop from 2000-3000 OU/m³ to 600 OU/m³. The deodorization efficiency is 70%-80%.

(2) Treatment method of incineration

Waste gas from aeration tank could also be incinerated by transferring to heating furnace. The deodorization efficiency is >99%.
3 Odor Treatment for aeration tank of sewage treatment plant
4 Emissions control of oil vapor which come from storage tanks with volatile oil liquid

(1) Crude oil, gasoline, naphtha and other oil products with high volatility should be stored in floating roof tank.

outward floating roof tank (double deck)  inner floating roof tank
4 Emissions control of oil vapor which come from storage tanks with volatile oil liquid

Vapour pressure, kPa

76.6

27.6

22.7

5.2

2.8

15 75 100 151

Tank volume ,m³

Pressure tank or control facility

Standard of Beijing

Floating roof tank or fixed roof tank+control facility

USA, China

Chinese Taiwan
4 Emissions control of oil vapor which come from storage tanks with volatile oil liquid

(2) Encouraging to perform gas emission reduction in both tank farm and loading operation, the measures include gas balance, degassing tank of feed, connecting pipe network for the gas which come from the top of tank.
The technology is applied to treat the waste gas containing high concentration of sulfide and VOC.

Oil gas is absorbed by diesel of low temperature (5-10°C);

H₂S is absorbed by caustic liquor.
The concentration of H$_2$S in vent gas which come from tank farm of sour water is up to 50000 mg/m$^3$, NH$_3$ is up to 4000mg/m$^3$, NMHC is 600000 mg/m$^3$. Treated by technology of "Low Temperature Diesel Absorption", vapor recovery efficiency is more than 96%, absorption efficiency of H$_2$S and NH$_3$ is 60%-90%; then the tail gas is absorbed by NaOH solution. In the purified gas, the concentration of NMHC is <20000mg/m$^3$, the concentration of H$_2$S is <5mg/m$^3$. There are almost 20 units have run in China.

Application example: the treatment to vent gas from tank farm of sour water
Application example: the treatment to vent gas from tank farm of sour water
Application example: Tail gas deodorization and oil vapour recovery for oxidation sweetening unit

✓ The concentration of organic sulfide in gasoline sweetening unit is 500-700mg/m³, NMHC is 500000-900000mg/m³. The technology of “Low temperature diesel absorption” is applied to treat this gas with pressure of 0.2MPa and absorption temperature of 7-10 °C.

✓ After purifying, the concentration of oil vapour is 4800-5400mg/m³, the concentration of organic sulfide can reach undetected level. The vapour recovery efficiency is more than 98%, the removal efficiency of organic sulfide is 100%. Then absorption gas is transferred into incinerator of Claus unit, the concentration of NMHC is <20mg/m³.
Application example: Tail gas deodorization and oil vapour recovery for oxidation Sweetening
6 Technology on oil gas recovery during loading

- Technology on oil gas recovery during loading:
  1. absorption
  2. adsorption
  3. condensation
  4. membrane separation
The technology of “low-temperature diesel absorption” is applied in oil vapour treatment when loading gasoline and napatha. The absorption temperature is 5-10℃, the recovery efficiency of oil vapour is up to 95%, the concentration of oil vapour in purified gas is <10000mg/m³.
The technology of “activated carbon adsorption – vacuum desorption regeneration” is applied to treat oil vapour which come from gasoline loading. The recovery rate of oil vapour is up to 96%, the concentration of oil vapour in purified gas is <20000mg/m³.
The concentration of NMHC in gasoline vapour is 300000-500000 mg/m³. The technology of “condensation by three stage mechanical refrigeration-regenerative combustion to non-condensable gas” is applied to treat the vapour.

The oil recovery efficiency of condensable gas is 85%-90%, with the temperature of -70°C. The concentration of NMHC in non-condensable gas is 40000-60000 mg/m³.

Then transferring the non-condensable tail gas to regenerative combustion device to purify, the concentration of NMHC is <100mg/m³.
(3) condensation
（4）membrane separation

✓ Object to treat: some vapour of gasoline, BTX, solvent oil, MTBE, and naphtha, etc.
✓ After purifying: the concentration of NMHC is < 10000 mg/m³, the concentration of C₆H₆ is < 12mg/m³.
7 Odor pollution control during maintenance, examine and repair work of equipment

- Examining and repairing in a closed space;
- Conveying overhaul materials by category;
- Using end-of-pipe pollution control technology.

Refining unit

- Washing waste water
- Purging waste oil

Waste oil

Waste oil tank

Waste gas treatment device

Flare (gas holder recovery)

Cutting water

Condensate

Condensate oil
8 Pollution control on leakage of equipments and pipe valves: LDAR

- Pollution control on leakage of equipments and pipe valves: Performing leak detection and repair (LDAR) programe.
- In USA and Europe, the LDAR is required to be performed in refinery; In China, LDAR is on trail.
- Usually, portable detection instruments are used to detect leakage, there are also some refinery use infrared thermal image instrument as aids.
9 Treating the waste gas in a centralized way as much as possible. Purified gas discharge at high altitude

✓ In one refinery, there are a variety of waste gas emissions, and each gas have multiple sources. So treating the waste gas in a centralized way not only can reduce device investment and operating costs, benefit to resource and energy recovery, make operation and management professional, but also be conducive to achieve concentration emission, high altitude emission.

✓ At the same time, there is also disadvantage that investment of waste gas pipeline, transportation costs and system security requirements is higher, and the land to use should be concentrative.
Thank you!