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Proposal of a Method for Evaluating Odour Emissions from Refinery Storage Tanks

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Oil refineries are one of the greatest type of industrial plant which can lead to emission of VOC and sulphur compounds. Such emissions often originate a problem of odour pollution in the human settlements located around the refinery. In many cases, odour nuisances lead the local authorities to intervene, sometimes by closing the whole plant. Odour emissions in refineries typically arise from the operating process: the aim of this work is to propose a method for the evaluation of the Odour Emission Rates from the different sources of a refinery. More in detail, the proposed method aims to quantify the Odour Emission Rate from the fugitive emissions relevant to storage tanks, whose evaluation is very complex due to the difficulty of determining both a representative odour concentration and an emitted air flow representative of this kind of sources. This method first quantifies the mass emission from the tanks, by means of the software US EPA TANKS 4.09, and after the so called "Hydrocarbon Odour Emission Capacity", associated with different hydrocarbons mixtures. By coupling this information, it is finally possible to give an estimate of the Odour Emission Rate deriving from a storage tank and use it in an atmospheric dispersion model.

1. Introduction

A refinery plant essentially consists of a complex set of process steps intended to increase the value of mineral oil and natural gas in order to obtain various hydrocarbon mixtures and chemical intermediates with high economic value. The oil and gas industrial sector, in Europe alone, meets more than 65% of energy requirements (European Commission, 2015), spanning a wide variety of sectors including transport, household energy, energy for services and others besides. Refineries enable Europe to hold a leading position at global level with regard to industry and guaranteed prices for consumers (European Commission, 2015).

The principal atmospheric emissions of these plants are CO_2, SOx, NOx, VOCs and particulate matter. Nonetheless, odour emissions are also considered as environmentally damaging, and these are mainly associated with sulphur compounds and nitrogen compounds as well as certain aromatic and aliphatic hydrocarbons (Luginaah et al., 2002).

Problems linked to odour pollution have emerged in recent years, and have led to complaints from the population. As a matter of facts, in Europe and North America, a significant percentage of the total protests regarding regional discomfort are due to olfactory annoyance (Leonardos, 1996). As far as Italy is concerned, a national statistic (Istat, 2015) has revealed that, in 2014, 34.4% of families reported problems of atmospheric pollution and 18.4% complained of disturbances linked to unpleasant odour. The risk associated with these potential protest actions could, in the worst-case scenario, result in interruption of the industrial activities from which the emission originates, with consequent huge production and economic losses (Van Harreveld, 2001).

In order to assess the odour concentration of a gas mixture, it is necessary to refer to the method standardised by EN 13725:2003, the European standard on determination of a mixture's odour concentration by dynamic olfactometry. This form of sensory analysis uses a dilution instrument (olfactometer) to present a specific odour to a panel of appropriately selected and trained persons. The measurement obtained in this way is based on the sensation perceived by the examiners and is habitually expressed in units of odour per cubic meter of neutral air (ou_E/m^3).

This number is normally associated with an information relating to the flow rate of gas emitted, in order to define the Odour Emission Rate (OER), expressed in ou_E/s.

In a refinery plant, various types of odour emissions are present. These may be subdivided into three main categories:

- Point source emissions
- Diffuse area source emissions
- Fugitive emissions from tanks

For each emission source category, different strategies are required for quantification of the emission flow rate.

1.1 Point source emissions

Taking into consideration vented point source emissions, quantification of the emission flow rate is relatively simple (Capelli et al., 2013) and may be obtained using the equation:

$$OER = C_{od} \cdot Q_{air,20°C}$$ (1)

where C_{od} is the odour concentration, measured in ou_E/m^3, and $Q_{air,20°C}$ is the air flow rate emitted, expressed in m^3/s. For calculation of the OER, the EN 13725:2003 standard requires consideration of the value normalised at 20°C.

In refineries, this type of source includes the chimneys used to vent fumes originating from furnaces or FCCs, characterised by high temperatures and high emission rates and heights.

Vapour recovery units, often referred to using the acronym VRUs, are another point source category present in refineries. These systems are designed to reduce the VOCs emitted during loading and unloading of tanks, road tankers and rail tankers. Devices of this type adopt various technological solutions (absorption, condensation, etc.). However, they tend to have in common a discontinuous flow of the emission linked to the product's movements, low temperatures (~ ambient temperature) and low flow rates (1000 ÷ 10000 Nm3/h).

1.2 Diffuse Area Source Emissions

Refinery plants also often contain waste water treatment systems for process water, cooling water, sewage water, water from yard cleaning and rainwater which, depending on its origin, is subject to a variety of contaminants such as hydrocarbons, inorganics, metals and salts. Prior to release into natural waterways or discharge into sewers, the polluted water undergoes specific treatments in order to bring its contaminant values within the legal limits.

There are various diffuse types of liquid tank exposed to the atmosphere (separators, flocculators, sludge thickeners, etc.) which may be defined as diffuse area source emissions, i.e. without an identifiable outward flow. Characterization of these emission sources is less simple than in the case of vented point sources.

So-called hood sampling methods are used which make it possible to isolate a defined section of the emission surface area and measure the odour concentration at the hood outlet (Jiang and Kaye, 1996) (Hudson and Ayoko, 2008) (Capelli et al., 2009).

In order to estimate the OER value, in the case of an air source without an outward flow, it is first necessary to determine the specific odour emission rate (SOER), a quantity indicating the odour units emitted per unit of time and surface area. This parameter, expressed in odour units per square metre and per second ($ou_E/s/m^2$), is calculated by multiplying the odour concentration value by the flow rate of neutral air introduced into the dynamic hood used for sampling and then dividing by the base area of the hood itself (Capelli et al., 2013):

$$SOER = \frac{C_{od,hood} \cdot Q_{air,hood}}{A_{hood}}$$ (2)

Once the parameters A_{hood} and $Q_{air,hood}$ are known, it is then possible to calculate the SOER of the area sources sampled.

Equation 3 indicates how to relate the SOER to the odour emission rate of the source (Capelli et al., 2013).

$$OER = SOER \cdot A_{source}$$ (3)

where SOER is the specific odour emission rate expressed in $ou_E/s/m^2$ and A_{source} is the emitting surface area expressed in m^2.

The innovative aspect presented in this study, which is significant in relation to the usual inspections regarding odour in refineries, is the characterisation of emission flow rates deriving from storage in and movement into tanks of the various hydrocarbon cuts. 40% of a refinery's total VOC emissions originate, indeed, from fugitive losses from such storage (European Commission, 2015) and these must not, therefore, be overlooked in assessment of the refinery's total odour emissions. Specifically, this study focuses on the assessment of emissions originating from fixed roof and floating roof tanks.

1.3 Fugitive Emissions from Tanks

Over half the surface area of a refinery plant is occupied by storage tanks. These systems serve to store various types of product: primarily mineral oil, the raw material to be treated, but also the various types of semi-finished product resulting from operations performed for separation and chemical modification of hydrocarbon chains. Tanks are also used to store finished products which, in turn, are blended (mixed) for subsequent dispatch for sale.

In this study, two types of tanks are analysed in depth: fixed roof tanks and floating roof tanks.

1.3.1 Fixed Roof Tanks

Fixed roof tanks are utilised in refineries for storage of heavier products such as diesel, bitumen and fuel oils. The upper part of their construction (the roof) is immobile in relation to the lower part (the shell) (US EPA, 2006, 1999).

Their contents are normally characterised by low volatility and a true vapour pressure (TVP) of less than 14 kPa (European Commission, 2015). This structure may include a variety of instrumentation on the roof (valves, air vents, openings, gauges, etc.), selected based on the operational requirements.

The vapour emissions typical of these tanks which are capable of generating an olfactory nuisance are (US EPA, 1999):

- Filling losses; in order for the tank to be filled, saturated vapour present inside the tank, above the stored liquid phase, is released into the atmosphere.
- Respiration losses; the tank is fitted with air release valves in order to compensate for the pressure and temperature differences generated from day to night.

1.3.2 Floating Roof Tanks

Floating roof tanks must be constructed in such a way that the upper part (the roof) lays on the liquid surface and therefore moves jointly with the liquid, i.e. vertically in relation to the lower part (the shell) (US EPA, 2006, 1999).

Typically, the liquid contained in this type of tank is a light hydrocarbon with a vapour pressure above 14 kPa but below 86 kPa under normal storage conditions (European Commission, 2015). The roof floats on the stored liquid (e.g. mineral oil or gasoline) in such a way as to prevent the formation of vapour and thus air-fuel mixtures which could fall within the explosive limits of the mixture itself.

In the case of floating roof tanks, the roof may, once again, be fitted with instrumentation based on the operational requirements.

These tanks have different vapour losses to those of fixed roof tanks, correlated to (US EPA, 1999):

- Losses from the rim seals and roof equipment; these are mainly influenced by the stock vapour pressure.
- Wall losses; during emptying of the tank, a liquid film is left 'clinging' to the walls, and its evaporation causes emissions into the atmosphere.

A floating roof tank can provide a 95% reduction in total losses compared to a fixed roof tank and therefore a consequent saving in terms of product stocks (European Commission, 2015).

Currently, the United States Environmental Protection Agency (EPA), whose objective is to protect human health and the environment, recommends use of the TANKS 4.09d software to assess the VOC mass emissions from the different tank types, but this does not appear sufficient for the purpose of assessing odour emissions (US EPA, 2006, 1999).

The aim of this study is therefore to propose a method for defining the odorous emissions from these tanks. Using the VOC mass flow rates emitted by the tanks, which may be modelled using the TANKS software and the experimental parameter known as OEC (odour emission capacity, expressed in ou_E/quantity unit) (Frechen, 2009) (VDI, 2017) to olfactometrically characterize the VOC flow rates emitted by each specific product present in the tank, it is possible to assess the odour flow rate emitted in a given time period.

2. Materials And Methods

2.1 Olfactometric Characterisation of Sources

While the sampling methods for chimneys, VRUs and effluent treatment tanks are clearly defined, as far as development of the study of fixed and floating roof tanks is concerned, it is necessary to measure or assess diffuse losses and be capable of determining the odour concentration and relative associated flow rate.

Gaseous emissions originating from these sources are due to non-accidental losses of volatile organic substances from the installations' sealing components. In the case of fixed roof tanks, the majority of leaks are due to the presence of air release valves on the top of these structures, while floating roof tanks owe most of their losses to evaporation phenomena (Rao et al., 2005).

No unequivocal method exists for determining such odorous losses from sources of this type. Below is proposed a methodology for assessment of the odour emission rate (OER) representative of this class of source and necessary to atmospheric dispersion software for modelling of odour dispersion.

2.1.1 Method for Assessment of Odorous Emissions

Quantification of chemical compound leaks from storage tanks is not a simple matter (Chambers et al., 2008), since these are difficult to measure directly and the measurements are influenced by multiple factors, primarily of an environmental nature, such as temperature, solar radiation and wind speed (US EPA, 2006, 1999) (Jovanovic et al., 2010).

TANKS simulation software (US EPA, 1999) is capable of simulating fugitive losses from hydrocarbon storage tanks. In particular, once the model's input parameters have been defined, the program returns the mass of hydrocarbons released per unit of time (which may be a single month or an entire year). In short, using this software, it is possible to estimate the mass of organic compounds, or VOCs, released by a given tank in a unit of time (kg/y).

This data does not, in the first instance, provide any information on diffuse odour emissions since it relates exclusively to mass. Indeed, as is well known, no direct correlation exists between the mixture's chemical composition and its effective olfactory properties (Rice and Koziel, 2015). This phenomenon can be explained by the existence of chemical and physical interactions between the various compounds present in odorous mixtures, meaning that the actual effects may be greater or lesser than the sum of the contributions of the individual substances (Zhao et al., 2014).

To obtain the odour emission rate correlated to the fugitive mass, it is therefore necessary to know the quantity of odour that a certain quantity of hydrocarbon mixture can potentially release, which may be expressed in units of odour per unit of mass (ou$_E$/kg).

In order to establish the correlation between the quantity of hydrocarbon mixture and the respective quantity of odour, a trial may be conducted to determine specific hydrocarbon mixture's capacity to emit odour. The technique for determining a similar value, known in literature as OEC (odour emission capacity) (Frechen, 2012, 2009), was originally proposed by Köster and Frechen in 1998. Their intention was to assess the odorous potential, expressed in ou_E/m_{liquid}^3, of a known volume of waste water (30 litres) which owes its olfactory characteristics to the volatile organic and inorganic compounds dissolved in it.

The case in point, for illustrative purposes, presents analysis performed on three different hydrocarbon products (different "cuts"), each of which has its own odour. The total odour of the three cuts was considered in relation to the mass that evaporated during the trial. In this way, it was possible to assess the OEC value of each hydrocarbon mixture in ou$_E$/kg. Having obtained the hydrocarbon odour emission capacity, HCOEC, (in ou$_E$/kg) and knowing the total losses emitted by the tanks (in kg/y), it is possible to determine the OER using the equation:

$$OER = HCOEC \cdot L_{tot} \tag{4}$$

where OER is the odour emission rate, expressed in ou$_E$/s, HCOEC is the odour emission capacity per unit of weight, expressed in ou$_E$/kg, and L$_{tot}$ represents the total hydrocarbon mass losses from the tank, expressed in kg/s and obtained from the result of the TANKS simulation.

2.1.2 Calculation of the Hydrocarbon Odour Emission Capacity (HCOEC)

To measure the hydrocarbon odour emission capacity (HCOEC) of certain oil cuts (diesel, petroleum and gasoline), the following laboratory instrumentation was used:

- Glass bubbler, hermetically sealed with a Teflon gasket, with a volume of 1.5 litres;
- Air flow meter, with a measurement range of 50-550 l/h;
- Teflon tubes with a 6- and 8-mm diameter;
- Perforated Teflon O-ring;
- Synthetic air cylinders.

The air is fed to the bubbler, and its flow rate is checked and maintained constant using a flow meter. Downstream of the flow meter a bubbler is positioned, i.e. a hermetically sealed container, fitted with two sealed ports. Through the first port enters a Teflon tube, with a 6-mm diameter, which channels the air to a perforated diffuser collar positioned on the bottom of the bubbler. In the other port, there is a second tube, of the same dimensions as the first, from which it is possible to perform air bag sampling for olfactometric analysis.

During the trial, air flow rates of 250 and 500 l/h, were made to flow into the bubbler and several air samples were collected by sampling the air flowing out of the bubbler. The samples collected as described above underwent dynamic olfactometry analysis, in accordance with the EN 13725:2003 standard.

The samples of liquid, with a volume of 1 litre, present in the bubbler were weighed using laboratory scales with tolerance of 0.1 g in order to verify the evaporation over time of the oil cut analyzed depending on the flow rate conveyed to the bubbler.

Each bubbler test was continued to the point of reaching evaporation of at least 50% of the hydrocarbon cut initially loaded in order to analyze the most volatile emission.

In accordance with (VDI, 2017), the product loaded for bubbling being extremely odorous, it was decided to reduce the quantity of liquid tested, increase the air flow blown in and increase the analysis times in relation to those for bubbling of waste water.

All the trials were conducted at the ambient temperature and pressure of the laboratory and at environmental conditions very close to P= 1 atm and T = 20°C.

A diagram illustrating the flows of the experimental apparatus is shown in the following Figure 1:
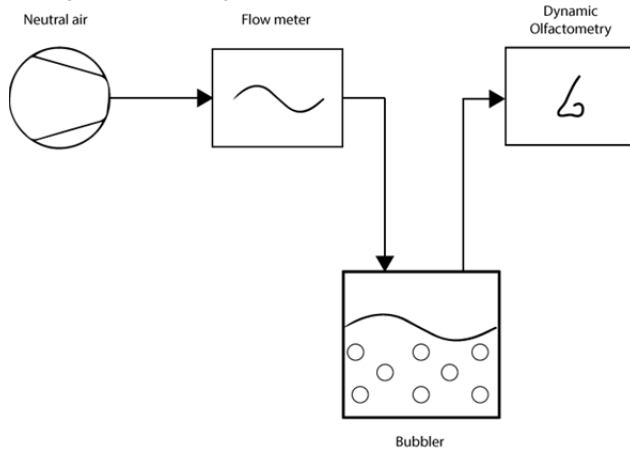

Figure 1. Diagram illustrating the flows of the experimental apparatus.

The quantity of odour emitted at time instant (dt), with a constant conveyed air flow, may be calculated as:

$$Od_{inst}[ou_E] = Q_{air}\left[\frac{m^3}{s}\right] \cdot C_{od}\left[\frac{ou_E}{m^3}\right] \cdot dt[s] \tag{5}$$

where Q_{air} is the air flow conveyed to the bubbler, C_{od} is the odour measured in the sample of outflowing air, and dt is the duration of the time instant during which the constant air flow is conveyed to the bubbler.

The total quantity of odour emitted through evaporation of a cut, in a time interval t_{tot}, may be calculated as:

$$Od_{total} = \int_0^{t_{tot}} Q_{air} \cdot C_{od}(t) \cdot dt \tag{6}$$

Due to the nature of the mixtures analysed and the evaporation caused by natural stripping of the air bubbled into the liquid, we may consider the quantity of odour emitted to be correlated to the loss of mass of the liquid sample. In this way, it is possible to calculate the odour emission capacity of the evaporated portion of the cut as:

$$HCOEC\left[\frac{ou_E}{kg}\right] = \frac{Od_{total}[ou_E]}{m_{evap}[kg]} \tag{7}$$

where HCOEC is the value of the odour emission capacity of the cut considered, expressed in ou_E/kg, Od_{total} is the quantity of odour emitted, expressed in ou_E and calculable using equation 7, and m_{evap} is the mass evaporated during the time (t_{tot}), expressed in kg, measurable as the weight difference of the bubbler between the beginning and end of bubbling.

3. Conclusions

Like many types of industrial plant, an oil refinery produces atmospheric emissions, which can lead to problems with the resident population in the neighbouring area. This study brings the picture of refinery odour sources into focus and describes the methods for quantification of emission flow rates.

The most innovative aspect of the study is the proposal of an approach for the assessment of OERs resulting from fugitive losses from hydrocarbon storage tanks. Indeed, this type of emission is normally overlooked in odour impact assessments due to the difficulties associated with their quantification.

The approach to solving this problem was twofold: on one hand, EPA TANKS 4.09d software was used to estimate the VOC emissions from tanks and, on the other, a methodology was proposed for a trial to be conducted in order to assess the HCOEC (hydrocarbon odour emission capacity) of a liquid, expressed in ou_E/kg, thus permitting assessment of the odour emissivity of the VOCs emitted by the tanks. In this way, it was possible to calculate an OER for each tank type and each oil cut contained within it.

Further trials and repeatability tests will be conducted in subsequent laboratory experiments.

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