Report

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An overview of HCN emissions from FCCU’s and their potential impacts on human health

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An overview of HCN emissions from FCCU's and their potential impacts on human health

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ABSTRACT

This report provides an overview of the monitoring methods and abatement techniques available for hydrogen cyanide (HCN) emissions in fluid catalytic cracking units (FCCU's). Recommendations are made for emission factors (EF's) that can be used to estimate HCN emissions from European FCCU's (for two different operating modes, namely full and partial coke burn) for E-PRTR reporting purposes. An overview of the potential health effects of HCN is given.

The EPA OTM-29 wet chemistry method and the instrumental FTIR technique are the two HCN monitoring techniques used in refineries. Currently applied abatement techniques for flue gas cleaning at FCCU's are not specifically designed for HCN emission control, but for particulate matter, NOx, SOx and CO reduction.

Emission factors for each mode of operation of an FCCU were developed using measurements undertaken on 10 FCCU's in European refineries together with data reported by the US EPA. The emission factors derived are: 0.58 kg HCN/t coke burn for full burn FCCU's, and 0.042 kg HCN/t coke burn for partial burn units. It is recommended that these be used for E-PRTR reporting purposes if measured values are not available.

A dispersion modelling assessment was conducted to establish the potential risk that HCN emissions from FCCU's could pose to human health. All runs showed that the predicted HCN ground-level concentrations were below the US EPA reference concentration (RfC) of 8×10^{-4} mg/m³ (0.8 µg/m³) for chronic inhalation exposure. This indicates that HCN emissions from the 10 European FCCU's tested are not considered a potential risk for human health.

KEYWORDS

Hydrogen Cyanide (HCN), Fluid Catalytic Cracking Unit (FCCU), Emission Factor (EF), US EPA, E-PRTR, Reference Concentration (RfC), Exposure, ADMS

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SUMMARY

This report provides an overview of the monitoring methods and abatement techniques available for hydrogen cyanide (HCN) emissions from fluid catalytic cracking units (FCCU's). Recommendations are given for emission factors (EF's) that can be used for E-PRTR reporting purposes to estimate HCN emissions from FCCU's (under different operating conditions) where measured data are not available. An overview is also given regarding the main toxicokinetic processes and the potential health effects of HCN. The chronic toxicological reference values derived by several organisations are summarised. Finally, the results of a dispersion modelling study undertaken to determine whether HCN ambient concentrations, from measured emissions from FCCU's in a number of European refineries, could be of potential health risk when compared against an exposure criterion derived from the health impact studies are provided.

The EPA OTM-29 wet chemistry method and the instrumental FTIR technique are the two HCN monitoring techniques mainly used in refineries. The EPA OTM-29 method is a revision of Conditional Test Method 33 (CTM-33) and specifically takes account of problems in the analytical procedures. EPA's Method 320 is a real-time FTIR method. In 2011, US EPA issued an Information Collection Request (ICR) to refineries that allowed the use of either OTM-29 or Method 320 for the FCCU's that were required to perform HCN testing. In late 2015, when US EPA published the final Refinery Sector Rule, it contained a requirement for each US refinery to complete and submit a one-time FCCU HCN test using Method 320 (ASTM D6348 was an acceptable alternative), indicating a preference by EPA for FTIR methods. In the EU, there is no such requirement to test HCN, and the EPA preference for FTIR does not mean that HCN must be measured by FTIR in the EU.

Currently applied abatement techniques for flue gas cleaning at FCCU's are not specifically designed for HCN emission control, but for particulate matter, NOx, SOx and CO reduction. Alkaline wet scrubbers with an aqueous solution of NaOH are usually applied for the removal of HCN from gas stream in other industrial sectors. However, the use of wet scrubbers for HCN reduction in FCCU flue gas has a very high investment and operational cost due to multi-staging and the consumption of very large quantities of chemical scrubbing solution. Recent patented developments for HCN abatement propose to optimize catalyst injection and the use of additives. The HCN reduction process by catalyst injection is being further investigated and optimised under laboratory conditions at the time of publication of this report.

FCCU's have two main operating modes. Full burn units run with an excess of air to the regenerator and have low CO emissions. Partial burn units run with a deficit of air to the regenerator to produce CO which is subsequently burned in a CO boiler. In order to estimate HCN emissions from FCCU's, EPA launched a data collection in 2011. However, the data collected to derive emission factors were not sufficient to differentiate between full burn and partial burn operation of FCCU regenerators, and a single emission factor for all types of FCCU operations was proposed by US EPA in 2015. Concawe considered that the use of the same emission factor for both operating modes does not provide reasonable and reliable emission estimates.

To address this concern and in order to develop more representative emission factors for HCN emitted from FCCU's, Concawe analysed HCN data from measurements made at a number of European refineries. Useable data were obtained from tests on 10 FCCU's (half were full burn, and half were partial burn). Statistical analyses were undertaken on both the full burn and partial burn data sets to identify any outliers. An emission factor for each mode of operation was developed using the combined US EPA and European refineries data sets. The emission factors developed are: 0.58 kg

HCN/t coke burn for full burn FCCU’s and 0.042 kg HCN/t coke burn for partial burn units. These are recommended to be used for E-PRTR reporting purposes if measured values are not available.

Regarding its health effects, HCN is rapidly and extensively absorbed via the oral and inhalation route, and more slowly absorbed by dermal exposure. The major metabolic pathway for cyanide is conversion to thiocyanate which accounts for 60-80% of a cyanide dose. Cyanide is primarily excreted in the urine as thiocyanate, following both inhalation and oral exposure.

- The principal features of the toxicity profile for cyanide are its high acute inhalation toxicity with a very steep dose–effect curve and chronic toxicity, probably mediated through the main metabolite and detoxification product, thiocyanate.
- The primary targets for chronic cyanide toxicity are the central nervous system and the endocrine system. The latter is expressed by thyroid toxicity that is caused by thiocyanate.
- HCN is not classified as a carcinogen or mutagen. Several bodies have derived chronic toxicological reference values, below which harmful effects of HCN are not anticipated.

The US EPA has adopted the value of 8×10^{-4} mg/m³ given in El Ghawabi et al. (1975) study as the reference concentration (RfC) to represent a safe concentration for lifetime exposure of the general public to HCN pollutants in ambient air. The study of El Ghawabi et al. (1975) has been chosen as the principal study due to the extended durations of HCN exposure (5-15 years) used in the study, the collection of individual breathing zone measurements of HCN exposure from the participants and the conclusion that low-level exposure to cyanide was associated with thyroid enlargement and altered iodine uptake in humans. This study was also considered to be the best available study considering the limited availability of studies in the HCN database.

In order to assess the potential risk that HCN emission from FCCU’s can pose to human health, a dispersion modelling assessment was conducted. The risk for non-cancer effects is determined from the hazard quotient (HQ) which is the ratio of estimated exposure to a reference level. Exposures at or below the reference level are deemed not likely to cause adverse health effects. The reference concentration (RfC) of 8×10^{-4} mg/m³ derived by US EPA for risk assessment of HCN was used in this study as the most relevant exposure value. All runs showed that the predicted HCN ground-level concentrations were below the RfC (i.e. HQ<1) indicating that HCN from the 10 FCCU’s tested are not considered to pose a potential risk for human health. It should be noted that the US EPA, which performed a similar risk characterisation during the 2011 Refinery Information Collection Request, also concluded that HCN emissions from FCCU’s are not projected to result in a hazard quotient exceeding 1.

1. INTRODUCTION

The establishment of the European Pollutant Release and Transfer Register (E-PRTR) [1] database in 2006 pointed out the need for reliable and consistent emissions data among the different sectors.

The E-PRTR regulation requires that annual emissions of key species are reported when those emissions exceed a minimum threshold. The EU Guidance Document on E-PRTR Implementation [1] provides indicative lists of the pollutants likely to be emitted on a sector specific “activity” basis. For hydrogen cyanide (HCN), the E-PRTR reporting threshold is 200 kg/year and it has not been listed in the refining sector specific indicative list because until recently there were no data showing that it can be produced in significant quantities. However, information available from the 2011 US EPA Refinery Information Collection Request [2] indicated that annual HCN emissions from some fluid catalytic cracking units (FCCU’s) might exceed the yearly E-PRTR reporting threshold of 200 kg/year.

The objectives of this report are:

- to provide a brief background on HCN formation within FCCU’s and the major factors influencing HCN formation,
- to review the available monitoring methods and the potential abatement techniques available for HCN emissions from FCCU’s,
- to develop reliable emission factors to estimate HCN emissions from FCCU’s under different operating conditions (i.e. full burn and partial burn) where data are not available,
- to assess the potential human health effects from HCN exposure and to assess whether the HCN ground level concentrations resulting from FCCU emissions are expected to be a potential concern.

This document uses information provided in two literature reviews carried out by VITO on behalf of Concawe:

- HCN emissions from FCCU’s: Part 1 Monitoring and Abatement Techniques [3]
- Hydrogen cyanide: evaluation of health effects and preliminary assessment of the health impact and a review of atmospheric processes influencing HCN dispersion [4].

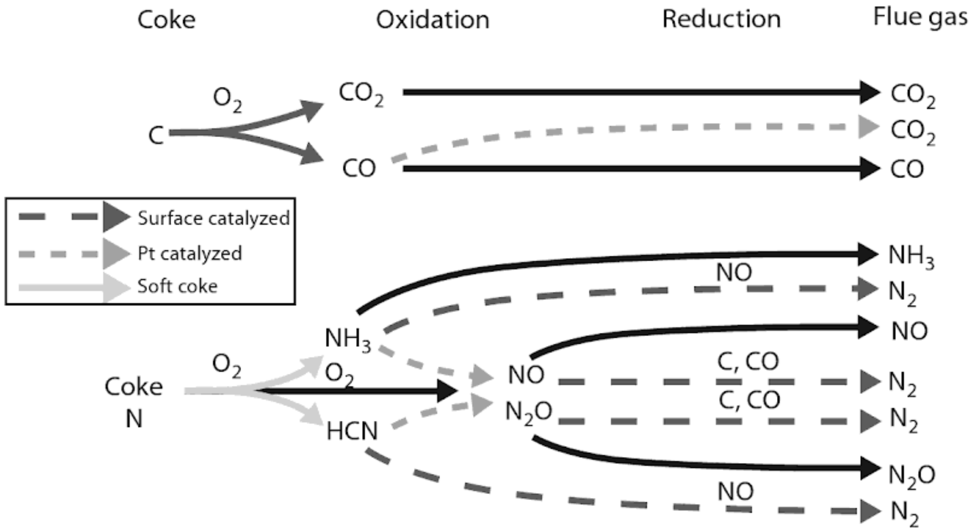
Emission factors were developed from the measured HCN emissions from 10 FCCU’s in European refineries, a project initiated by Concawe in 2016, and HCN emission measurements undertaken by refineries in the United States for the US EPA during the 2011 Refinery Information Collection Request (ICR) [2]. A dispersion modelling assessment was conducted to evaluate worse-case HCN ground-level concentrations using as inputs the measured HCN emissions from the European FCCU’s. These were then compared with a criterion concentration to assess whether the predicted HCN concentrations at ground level may pose a potential risk for human health.

2. HCN FORMATION IN FCCU'S

The FCCU (fluid catalytic cracking unit) is a major conversion unit in refineries throughout the world. The role of the FCCU is to convert high molecular weight feed into lighter and more valuable products in a catalytic cracking process. Some of the feed (5-6 %w) is converted to coke as a by-product. Nitrogen and sulphur are feed impurities which, together with coke, deposit on the catalyst during the cracking process, reducing its activity.

A regenerator unit (FCC regenerator) is used to burn off the coke and reactivate the catalyst by the addition of oxygen. During combustion in the regenerator, a wide range of gaseous sulphur and nitrogen species (SO_2, SO_3, COS, H_2S, N_2, NO, N_2O, NO_2, NH_3 and HCN) are formed, alongside CO and CO_2. The composition of the flue gas depends upon the detailed reaction conditions in the regenerator. The selectivity of competing reaction pathways to form the various N-species depends on both equilibrium and kinetic criteria. These reaction pathways are illustrated in **Figure 1**.

Figure 1 FCC NOx chemistry (reproduced from Occelli M.L., 2010 [5]).



2.1. FORMATION MECHANISM BASED ON LABORATORY EXPERIMENTS

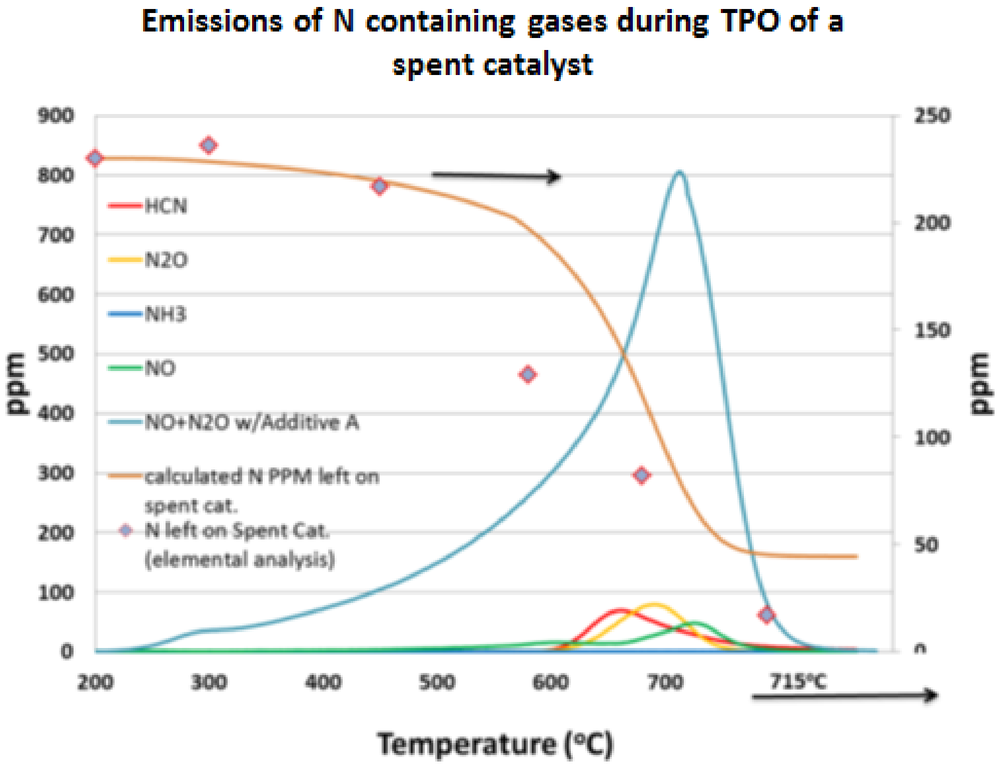
Mo et al. [6,7] (Johnson Matthey company) investigated HCN formation during coke combustion by temperature programmed oxidation experiments where coked catalyst (deactivated spent FCC catalyst) was heated under inert atmosphere initially and then switched to oxygen containing combustion gas while the temperature was ramped. Combustion flue gases were continuously monitored by infrared and mass spectroscopy.

The main results are summarized below and shown in **Figure 2**.

- The formation of N-containing species starts around a temperature of 300°C.

- The composition of N-species in the flue gas is different when a Pt-based CO combustion promoter is used.
- Without a Pt-based CO combustion promoter, HCN is observed in addition to N_2O and NO, the highest HCN concentrations are found in the 600-715°C temperature range.
- HCN generation starts at temperatures where the conversion of HCN to the thermodynamically more stable N species NO and N_2 is relatively slow. A peak in HCN concentration was observed around 600-650 °C, at further increasing temperatures the HCN concentration decreases rapidly. HCN is not stable enough at temperatures above 600-650 °C and is converted into NO or N_2.

Figure 2 Emission of N-containing gases during a temperature programmed oxidation experiment (reproduced from Mo et al. [7]) of spent FCC catalyst (3% O_2/N_2, 2% H_2O, 50 mL/min, 15 °C/min). Flue gas composition is shown without the addition of Pt-based CO combustion promoter and with the addition of CO combustion promoter (NO+N_2O w/Additive A).



Additional experiments involving HCN conversion in temperature programmed oxidation experiments showed that, even with an excess of O_2, HCN can survive FCC regenerator conditions indicating that HCN conversion is under kinetic control [7].

2.2. FORMATION MECHANISM IN INDUSTRIAL FCCU REGENERATORS

Recent information provided by Johnson Matthey Process Technologies, Inc., in the US Patent 20140241969 A1 “Process of removing HCN from flue gas” explains the formation of HCN in industrial FCCU regenerators.

Approximately 50% of the N-content of the feed is contained in the coke and burned off during the catalyst regeneration process in an FCCU. The regeneration process occurs over a temperature gradient, from typically 500-540°C at the entrance of the regenerator up to approximately 720-750°C further away from the entrance of the regenerator bed. In the low temperature area, HCN is formed. At higher temperatures, NOx and N_2 are mainly formed, and only a very limited amount of HCN. In these high temperature areas, HCN is not stable and is converted into NO or N_2.

2.3. FULL BURN VERSUS PARTIAL BURN FCCU'S

A good introduction on the principal modes of FCCU operation is found in Concawe report No. 4/09 [8].

To understand the reactions between the various nitrogen species in a FCCU regenerator, it is essential to distinguish between the two possible modes of operation: full burn and partial burn.

In full burn regeneration conditions the oxygen supply is greater than the stoichiometric requirement for coke combustion, in order to minimize CO in the flue gas. The main species leaving the regenerator are CO_2, H_2O, SO_2, SO_3, N_2 and NO. However, recent stack measurements in several full burn units indicate the presence of HCN at ppm levels (see Chapter 5). The presence of HCN can only be explained if conditions in the regenerator are not at reaction equilibrium, as HCN is not stable at the regeneration exhaust temperature (typically above 720°C). HCN is formed inside the regenerator, at the entry point of the colder catalyst. Local conditions (e.g. temperature around 600°C and oxygen depletion) favour the conversion of coke nitrogen to HCN and N_2O. Given the short residence time of the FCC catalyst in the regenerator (a few seconds) these species are not fully converted to the more oxidized forms of nitrogen, and are emitted as such at the stack.

Under partial burn regeneration conditions, the oxygen supply is less than the stoichiometric requirement for coke combustion, and the concentration of CO is higher in the flue gas (typically in the range 3-7% w). Partial combustion inhibits the formation of NOx and favours the formation of N_2 and of more reduced S and N species such as COS, H_2S, NH_3 and HCN. [5]

Partial burn FCC units require a CO boiler downstream of the regenerator to convert the CO to CO_2. This boiler usually has supplementary fuel firing. Recent stack measurements at several partial burn units, all equipped with a downstream CO boiler, indicate lower HCN levels than those measured at full burn units (see Chapter 5). This can be explained by the longer flue gas residence time in the CO boiler, where the conditions (high temperature, excess of oxygen) allow the conversion of the intermediate S and N species to more oxidized forms:

$COS, H_2S \rightarrow SO_2, SO_3$ and

$NH_3, HCN \rightarrow N_2, NO, N_2O, NO_2$

3. MONITORING TECHNIQUES

A literature review and available measurements (EPA data collection in 2011 [2], and Concawe data collection in 2016, see Chapter 5) indicate that two techniques are mainly used for HCN monitoring in refineries: 1) the EPA OTM-29 wet chemistry method [9], and 2) the use of the instrumental FTIR technique [10].

The EPA OTM-29 method specifically addresses the problems in the analytical procedures which were encountered with the earlier versions. FTIR is EPA's method of choice and in EPA's final rule [11] Method 320 (or alternatively, ASTM D6348) was required where HCN measurements have to be undertaken on FCCU stacks.

Tunable diode lasers (TDL) are in use on some FCCU's to monitor CO and O_2 content and are also available for the measurement of HCN, but they have not been validated. Some other techniques could be used, but they have not been developed.

Only the two main methods will be discussed further.

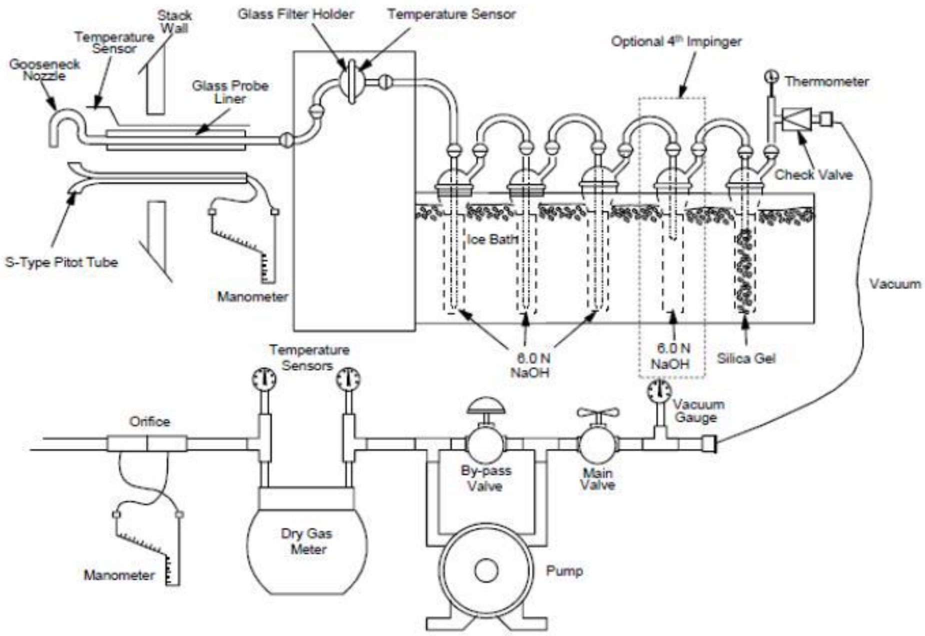
3.1. EPA WET CHEMISTRY METHOD OTHER TEST METHOD 29 (OTM-29)

The EPA OTM-29 [9] is a suitable wet chemistry method for HCN FCCU emission measurements. OTM-29 is applicable to the collection and analysis of gaseous cyanide (as HCN) in the gas phase and in suspended water droplets. Total gaseous cyanide includes hydrogen cyanide (HCN) and cyanogen $(CN)_2$. This method does not quantify total cyanide compound emissions, which include particulate bound cyanide where formal dissociation of CN- may occur.

3.1.1. Method summary

Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multi-component sampling train. The primary components of the sampling train are shown in **Figure 3** and include a heated probe, a heated filter, three impingers containing sodium hydroxide (NaOH) solution, and an impinger containing silica gel. Hydrogen cyanide present in the stack gas stream reacts with the NaOH to form a cyanide ion, which is retained in the alkaline solution until analysed by ion chromatography (IC). Particulate cyanide salts are retained on the filter and are not analysed during routine execution of the method. Sampling is conducted isokinetically because of the significant solubility of HCN in water droplets which may be present in combustion stacks, especially those equipped with wet gas scrubber systems.

Figure 3 OTM-29 sampling train [9].



3.1.2. Attention points when using this method

High concentrations of acidic gases, including carbon dioxide (CO_2), may lower the pH of the sodium hydroxide impinger solution during testing, decreasing the ability of the impinger to retain hydrogen cyanide. It is therefore important to maintain a high pH (≥ 12) in the impingers. For a measurement to be valid, the pH in the last NaOH impinger must be ≥ 12 at the end of the test run. OTM-29 specifically accounts for problems in the analytical determination of HCN emissions in catalytic cracking units mainly by using a 6N NaOH absorption solution to keep the pH above 12 and thus preventing the loss of gaseous HCN from the solution. Other methods that do not necessarily maintain the pH level at or above 12 because they use a lower concentrated NaOH solution such as CARB Method 426 ‘Determination of Cyanide Emissions from Stationary Sources’ [12] and EPA CTM-33 [13] should not be used given the composition of a FCCU gas matrix.

The NaOH solution used will absorb some of the CO_2 from the flue gas. The amount of CO_2 removed needs to be added back into the sample volume and therefore the CO_2 concentration in the stack and at the outlet of the sampling must be measured continuously. This ‘double’ measurement of the CO_2 concentration adds to the complexity of the sampling as two CO_2 analyzers need to be deployed.

The sodium carbonate precipitate that is formed in the impingers during sampling can at a given point in time inhibit further sampling and will necessitate a sampling stop that adversely affects the detection limit. Chances for this sampling stop increase in a partial burn FCCU when oxygen is added to the CO boiler resulting in elevated CO_2 levels and hence in more sodium carbonate precipitate. Prior to analysis the sodium carbonate precipitate needs to be dissolved which is difficult to achieve at room temperature. At 30°C dissolution is faster but the risk for HCN loss might increase.

3.2. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) AS USED ON FCCU’S

The only instrumental measurement technique being used for HCN FCCU emission measurements is the Fourier Transform Infrared (FTIR) spectroscopy. An FTIR-analyser gives a continuous measurement. A first option is its use in short-term periodical measurements. A second option is its use as an AMS (Automated Measurement System) or CEMS (Continuous Emissions Monitoring System).

FTIR was used under the US EPA “2011 Refinery Information Collection Request (ICR)” [2] on two FCCU’s and by Lenaers et al. [10] on three FCCU’s. Additional information on use of FTIR for HCN emission measurements on a FCCU can be found in [10].

It should be noted, however, that to-date in Europe, no FTIR instrument has been approved as an AMS (Automated Monitoring System) according to the EU CEMS standards (QAL1, QAL2, QAL3).

3.2.1. EPA method 320

EPA Method 320 ‘Measurement of vapor phase organic and inorganic emissions by extractive Fourier Transform Infrared (FTIR) spectroscopy’ and accompanying protocol [14] is a general (non-specific to HCN) FTIR method for measuring a wide range of organic and inorganic pollutants. It is a “self-validating” method, and sample results are valid provided that the quality assurance criteria defined in the method are met during the validation procedures and HCN quality assurance (QA) spikes.

EPA method 320 is comparable to the ASTM D 6348 test method [15]. In Europe within CEN TC 264 the Working Group WG36 is developing an EN standard for periodical FTIR measurements. This standard will build on the UK Technical Guidance Note TGN M22 [16] and the US EPA method 320.

In April 2011, EPA sent an Information Collection Request (ICR) to facilities in the Petroleum Refining industry. Emissions testing reports were collected for FCCU’s including results for HCN. The HCN FTIR measurements on two FCCU’s under the ICR were conducted according to the EPA method 320.

EPA for reasons of quality assurance specifically asked for the validation procedure to be followed as given in the standard. The HCN FTIR results together with those determined through OTM-29 were used in EPA’s “Review of Emissions Test Reports for Emissions Factors Development for Flares and Certain Refinery Operations” [17] in section 3.3 on FCCU’s.

3.2.2. Developing FTIR for HCN measurement in FCCU

There is limited literature for the use of FTIR on FCCU’s for the measurement of HCN. The recommendations below are based on the work carried out by VITO [10], who conducted laboratory experiments to investigate if FTIR was a potential alternative method to OTM-29. The HCN concentration range covered by this work is 5 to 150 mg/Nm^3. FTIR validation tests with known HCN concentrations were performed in the laboratory in a first phase. In a second phase, simultaneous stack measurements with FTIR and OTM-29 were performed, OTM-29 serving as reference method to validate the FTIR.

An FTIR analyzer allows for simultaneous monitoring of several pollutants besides HCN. This includes most of the pollutants emitted by an FCCU: CO, SO_2, NO_2, NO,

CO_2 and water. The first step is to make sure that the analyzer is capable of measuring HCN at the emitted range within the flue gas matrix and that the signal is linear.

An FTIR uses a library file (that is normally delivered by the FTIR supplier) consisting of the components present in the gas matrix, the list of interfering components per component, the selected and (according to the interferences) optimized infrared areas for analysis per component, and advanced corrections for cross interferences. The quality of this library file influences the measurements and the best results will be obtained with a matrix-specific library file. This might need matrix generation experiments in the laboratory before the start of the measurements. For a given matrix, however, this needs to be executed only once. As most FCCU's will have comparable composition of their stack gases, only minor adjustments might be necessary when switching from one FCCU to the other. However, care has to be taken for the differences in gas matrix composition between full and partial burn FCCU's especially if oxygen is added to the CO boiler of a partial burn FCCU. An interesting feature of FTIR is that the recorded data of a measurement (interferogram) can be re-analysed at any time with another library file.

A particle filter is needed to prevent particles from entering the analyser during sampling but there is no need to remove water in a gas cooler as is the case with most classical analysers. However, the analyser needs to be heated to prevent condensation.

Before starting a FTIR measurement a background spectrum is taken that is subtracted from the measured spectrum. When using a FTIR with an open interferometer, optimal performance, i.e. low and smooth background, will require a continuous purge of the interferometer with dry air to remove most of the water traces. For periodical measurements it is advised to start the purge a day ahead of the measurements.

4. ABATEMENT TECHNIQUES

For many refineries, the FCCU represents the largest air emission source of particulate, NOx and SOx emissions [18,19]. Emission control technologies have been implemented to reduce emissions for compliance with regulatory emission limits. Emission control technologies are focused on specific (regulated) pollutants: particulates, SOx, NOx and CO.

The BAT Reference Document for the Refining of Mineral Oil and Gas [20] gives a comprehensive overview of emission reduction techniques for FCC units, based on primary process technologies or secondary end-of-pipe technologies. However, the BREF does not include documentation about techniques specifically for the reduction of HCN emissions to the air.

This chapter provides a short overview on how FCC unit design features may affect HCN emissions. It then covers how changes in operating conditions may reduce HCN, including the use of catalyst additives. It finally lists end-of-pipe abatement methods from other industrial processes, which could be applied to FCCU’s.

4.1. FCCU DESIGN AND IMPACT ON HCN EMISSIONS

4.1.1. Full burn and partial burn regenerator

As explained in Chapter 3, the configuration of these two types of units is quite different.

The EPA report [17] summarizes HCN emission data from 11 FCCU’s submitted as part of the 2011 EPA Information Collection Request (ICR).

The study conjectured that there might be a difference in HCN emissions between FCC units of full burn and partial burn design but, because there were only two partial burn units in the survey, this was an insufficient number to draw a conclusion. The normalised HCN emissions from the partial burn units were however less than the average of the group, both on a coke burned and on a FCCU feed basis.

In the data analysis of HCN emissions from 10 European FCCU’s collected by Concawe in 2016 and presented in Chapter 5, half were full burn and half partial burn with a CO boiler. The HCN emitted data showed a greater differentiation between the HCN emission factors for the two types of units than shown by the US EPA data (see also Chapter 5).

It should be noted that the choice of unit configuration (e.g. partial burn or full burn) is made at initial design or possibly during a major retrofit, and is based on a series of local considerations and site integration (e.g., steam balance, product slate, etc.).

4.1.2. Installed end-of-pipe treatment for other pollutants

Statistical analyses were carried out on the US EPA dataset [17] to see if a downstream scrubber (7 FCCU) or electrostatic precipitator (4 FCCU) accounted for some of the variability in emission factors but no evidence was found from this small sample.

No statistical analyses relating to abatement methods were undertaken on the data from the European FCCU’s.

4.1.3. Recent developments in unit design features

Recent studies investigated the impact of unit design parameters on the nitrogen dynamics. The primary focus is hereby on the reduction of NOx emissions [21,22].

Afterburn control in catalyst regeneration, i.e. regulation of the regeneration bed temperature in relation to the exothermic oxidation of CO to CO_2, showed a dramatic effect on the concentration of nitrogen compounds [23]. When afterburn was suppressed, HCN was most abundant, with lesser amounts of NH_3, N_2O and NOx (N_2 was not measured). When afterburning was enabled, almost no HCN or NH_3 were found.

4.2. PROCESS CONDITIONS CHANGES AND IMPACT ON HCN

HCN emission measurements from experiments at the regeneration unit of one full burn FCCU are summarised below. These data are based on a document of VOKA to the Flemish Minister of Environment, Nature and Culture 2010 [24]. This test program was developed to gain further insight on HCN emissions. During the tests, the HCN emissions were continuously measured with FTIR. Tests were performed in October 2009, February 2010 and March-June, 2010.

Some new developments on additives are also listed in this section.

4.2.1. Information provided in the VOKA report

In October 2009 the first tests were performed in which HCN concentrations in the range of 35 – 50 mg/Nm^3 were measured. The tests were designed to assess the reduction potential of HCN emissions by altering operational conditions. The main results are provided below:

- An increased regenerator temperature at low oxygen surplus results in increased HCN emissions;
- Increasing oxygen surplus at average regenerator temperature results in a small reduction of HCN emissions;
- Operating the regenerator in a combination of high temperature and high oxygen surplus reduced the HCN emissions to lower values (10 – 20 mg/Nm^3);
- This situation is only feasible when throughput is reduced by 10 – 15% compared to the average, leading to significant economic loss;
- Situations with increased oxygen surplus result in increased emissions of NOx and particulate matter above the limit values.

In February 2010 a second series of tests were performed to investigate the effect of the nitrogen content of the FCCU feed and the injection of extra steam in the regenerator, the theory behind this operation being the hydrolysis of HCN to NH_3. These tests did not result in measurable changes in HCN reduction.

From March to June 2010, a third series of extensive testing took place where different additives were applied in the regenerator. One part of the test was to replace the Pt-based CO-promoter by a non-Pt based additive to promote the oxidation of CO to CO_2. Small amounts of this promoter resulted in a decreased NOx concentration and an increased concentration of HCN and NH_3. Another part of the test was to add a NOx reducing additive (chemical reduction of NOx). The effect of this addition was minimal. Only when large amounts were added was some reduction possible. It should also be noted that the use of such large quantities is not sustainable in the longer term, as it results in a significant economic debit.

Furthermore, the report states that adaptations of the FCCU process could increase the emissions of other pollutants (e.g. NOx and particulate matter).

4.2.2. Recent developments in catalyst additives

The HCN reduction process described in US Patent 20140241969 A1 is being further investigated and optimised at the present time. The technology has not yet been applied at any FCCU. The research activities are focusing on the optimisation of catalyst injection and optimising the contact between HCN in flue gas and catalyst. Experiments with catalyst coating of a bag filter showed very high reduction efficiencies.

The methodology for HCN (and NOx) emission control that is proposed by Johnson Matthey Process Technologies, Inc. would include three steps:

1) Eliminate the use of Pt and use non-Pt promoters to avoid NOx formation during regeneration in the FCCU process;
2) Apply catalytic additives and other N-species such as NH_3 to convert HCN to N_2 and NOx to N_2 in the flue gas;
3) Apply catalyst either in the regeneration bed or further downstream (in the flue gas line) to reduce HCN and NOx emissions

4.3. END-OF-PIPE ABATEMENT TECHNIQUES FOR HCN FROM OTHER INDUSTRIAL PROCESSES

Some other industries, outside the refining sector, have implemented techniques to reduce HCN, when it was emitted in significant quantities. Two types of techniques have been used: combustion (flare, oxidiser or boiler) and scrubbing. The use of fabric filters (carbon black production) is only possible in cold applications (temperature < 170°C).

The tables presented in the Appendix of VITO report [3], illustrate the techniques used by other industry sectors and evaluate their applicability to FCCU regenerators. This information is either extracted from the Report EPA-454/R-93-041 [26] or from the Best Available Technique reference documents of other sectors and industries (BREFs, JRC IPTS, http://eippcb.jrc.ec.europa.eu/reference/).

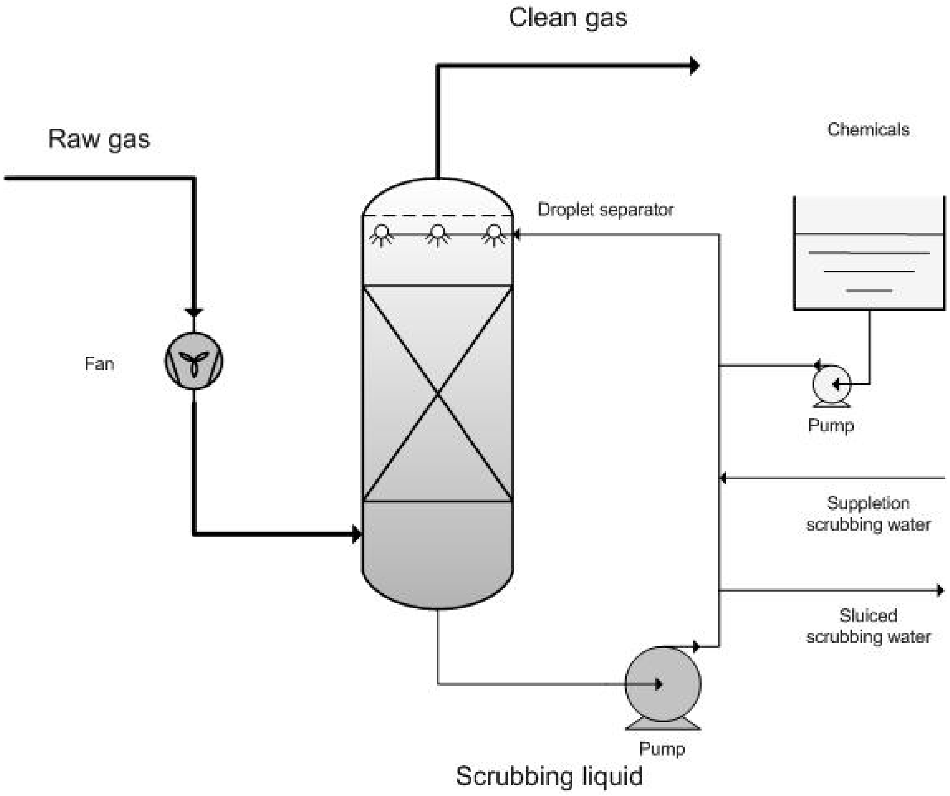
More information about scrubbing is provided in the section below. While flue gas scrubbing is a technique already used in some FCCU's for the abatement of some other pollutants (SOx and PM), adapting it for HCN removal is not straight-forward.

4.3.1. Flue gas scrubbing in FCCU for HCN removal

Wet scrubbers are installations where flue gases are intensively mixed with an aqueous solution to dissolve (or capture) pollutants into the liquid. Henry's law holds for the solubility of gases at low concentration in the aqueous solution and can be used to determine the flow rate of the solution. Equilibrium concentration in the vapour phase at a given concentration in the liquid phase is directly proportional to temperature. Lower temperatures result in higher reduction efficiencies.

A multitude of wet scrubbers with different characteristic designs exist: counter-current, co-current, cross-current. A schematic diagram of a wet gas scrubber installation is given in **Figure 4**.

Figure 4 Diagram of a wet gas scrubber.



Another classification of wet scrubbers is by the way the scrubbing solution is injected into the gas stream. Injections can be realised from the outer side of the scrubber (without built-in components) or by an injection component that is situated inside the gas stream (built-in components). Examples of the former systems are scrubbing towers or venturi scrubbers; examples of the latter are dynamic scrubbers with rotating elements for the dispersion of scrubbing solution.

The efficiency of a wet scrubber depends on the chemical compound to be reduced, the scrubbing solution and the design of the scrubber. Addition of chemicals into the water of the wet scrubber further increases its efficiency. Reduction efficiencies higher than 99% are reached for certain gaseous components and odours. Environmental aspects related to the use of a wet scrubber are the generation of (acidic) drain water that needs to be treated.

In the industries where wet scrubbers are installed for HCN reduction, there are no or limited mixed contaminants involved. Hydrogen cyanide (HCN) is usually scrubbed with an aqueous solution of NaOH. Recovery as a usable by-product is not practical. Also, in some cases, the addition of NaOCl to the scrubbing solution is used to increase removal performance or to produce more desirable reaction products. One of the issues in FCCU application is the high level of CO_2 which would consume the majority of the caustic in the solution.

Additionally, current applications are for flow rates that are much lower compared to the gas flow rates from FCCU's. Based on indicative numbers of the FCCU flue gas composition and physical properties, a four stage scrubber installation was proposed by one vendor for treatment of 60 000 Nm³/h flue gas from an FCCU. The following stages were recommended:

- Stage 1 scrubber operated with water only;
- Stage 2 scrubber operated with water / NaOH solution
- Stage 3 scrubber operated with water / $NaClO_2$ solution
- Stage 4 scrubber operated with water / NaHS and NaOH solution.

In conclusion, wet scrubbers for HCN are used in other industrial processes where HCN is less mixed with other pollutants compared to HCN in FCCU flue gas. However, the use of wet scrubbers for HCN reduction in FCCU flue gas is not recommended as a suitable technique due to multi-staging and the consumption of very large quantities of chemical scrubbing solution, which implies a very high investment and operational cost.

5. EMISSION ESTIMATION

5.1. BACKGROUND

Concawe provides guidance to the refining sector on air pollutant emission estimation to meet the reporting requirements of the European Pollutant Release and Transfer Register (E-PRTR) [1]. This is in the form of a regularly updated compendium of recommended emission estimation algorithms. The latest edition of the guidance is Concawe Report No. 4/17 [27]. There are 60 air pollutants which must be reported under the E-PRTR requirements if their respective annual emission threshold values are exceeded at a facility. Report 4/17 provides emission estimation methods for 24 of those pollutants. These are for those pollutants which are included in the indicative lists of the pollutants likely to be emitted from the “mineral oil and gas refineries” and “thermal power stations and other combustion installations” sectors in the EU guidance document on E-PRTR implementation [28]. HCN is not listed in the refining sector specific indicative list because until recently there were no data showing that it can be produced in quantities exceeding the E-PRTR reporting threshold.

Emission factors for HCN were published by the US EPA in 2015 (see Section 5.2) but these did not differentiate between full burn and partial burn operation of FCCU regenerators. The aim of the Concawe guidance is to provide estimation methodologies that represent as accurately as possible the actual pollutant emissions. Although the factors indicate that annual emissions for some FCCU’s could exceed the E-PRTR reporting threshold of 200 kg [29], they were not included in Report 4/17 because it was considered that the use of the same emission factor for both modes of operation does not provide reasonable estimates.

Instead Concawe initiated a project to develop more representative emission factors. This involved gathering data from HCN measurement campaigns at a number of European refineries. Section 5.3 provides information on that data and Section 5.4 on the development of emission factors for E-PRTR reporting purposes.

In the interim, Report 4/17 provides the recommended measurement methods if sites establish there is the potential for HCN to be released in excess of the E-PRTR reporting threshold.

5.2. EMISSION FACTORS DERIVED BY US EPA

HCN emission measurements were undertaken by refineries in the United States for the US EPA during the 2011 Refinery Information Collection Request (ICR). The US EPA subsequently developed emission factors for HCN from FCCU regenerators and published these in updates of their Publication AP-42: Compilation of Air Pollution Emission Factors [30] and their Emissions Estimation Protocol for Petroleum Refineries [31] in 2015.

The information provided to the US EPA contained useable data from HCN measurements on 12 FCCU’s [17]. Of these, 2 units operated in partial burn mode (with a CO boiler) and 10 in full burn mode, although one of the latter had retained its CO boiler after conversion from partial burn operation. Feed and coke burn data, however, were only available for 10 and 11 units respectively. Where such data were available the US EPA firstly developed emission factors for each individual FCCU related to feed and coke burn using their own recommended procedures [32].

Statistical analyses, as outlined in [32], to determine outliers were undertaken by the EPA on the complete data sets of the individual unit emission factors (EFunit) (i.e. 11 values related to coke burn and 10 related to feed rate) and none were found.

The US EPA also performed statistical analyses to establish if there was any impact on HCN emissions due to the abatement controls installed on the units to reduce other pollutant emissions. Seven FCCU's had scrubbers and four had electrostatic precipitators (ESPs) installed. CO boilers were installed on the 2 partial burn units (as an integral part of the unit) and one full burn unit. The analyses could not sub-categorise the data sets based on any of these three abatement control measures.

The US EPA state in [17] that because there were data for 9 full burn but only for 1 or 2 partial burn units (depending on which parameter the emissions factor is related to) they could not perform the statistical analysis to determine whether these units could be sub-categorised based on the type of regenerator.

The sets of individual unit emission factors, irrespective of mode of operation, were therefore averaged to provide the final published factors of 0.43 kg HCN/t coke burn and 20.0 kg HCN/kg*1000 unit feed.

The individual US unit emission factors are given in **Table 1** and the factors related to coke burn are shown in a scatter plot in **Figure 5**.

Table 1 Individual refinery FCCU emission factors for HCN developed by the US EPA.

Refinery Code	Operating mode F = Full burn P = Partial burn[1]	Individual unit emission factor (EF_{unit})	
		kg HCN/t coke burn	kg HCN/kg*1000 feed
US1	F[2]	0.18	8.83
US2	F	0.42	No data[3]
US3	F	0.0095	0.40
US4	F	1.20	42.7
US5	F	0.28	10.8
US6	F	0.22	8.26
US7	F	0.22	10.8
US8	F	0.77	39.9
US9	F	1.20	62.7
US10	F	No data[4]	13.4
US11	P	0.062	2.85
US12	P	0.063	No data[3]

Table notes:

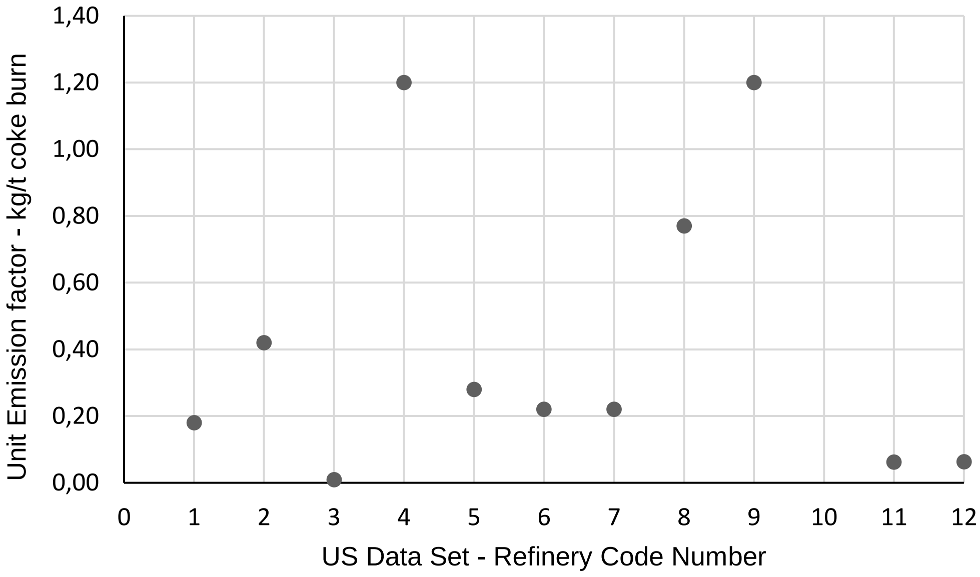
1 – With CO boiler as integral feature of partial burn unit design.

2 – Unit converted to full-burn from partial burn operation but the CO boiler retained.

3 – No feed data available.

4 – No coke burn data available.

Figure 5 Individual US refinery FCCU emission factors for HCN related to coke burn.



5.3. DEVELOPMENT OF UNIT EMISSION FACTORS FOR EUROPEAN FCCU'S

The values of EFunit determined for the US partial burn units are significantly less than the published emission factors derived from the complete data sets. In the case of the factor related to coke burn they are about a factor of 7 lower for both units (US11 and US12). However, statistical analyses show that there are no outliers in the complete data sets. The very low values of EFunit for one full burn unit (US3) impact the statistical reviews leading to the conclusion that the partial burn units cannot be sub-categorised. However, if outlier analyses are undertaken on the EFunit data sets for the full burn units (instead of on the complete data sets) the individual unit emission factors for refinery US3 are shown to be outliers. If US3 is removed from the data sets, then the use of common emission factors for both full and partial burn units is called into question.

To address that concern Concawe initiated an exercise to gather data from HCN measurement campaigns at European refineries. In addition to the HCN concentration and mass flow data, refineries were asked to complete a comprehensive questionnaire on the mode of operation of the regenerator, feed and coke burn data during the test periods, flue gas abatement methods installed, etc. Useable data were obtained from tests on 10 FCCU's.

Although both feed rate and coke burn data were supplied by all 10 refineries, the development of an emission factor has focussed on one related to coke burn. This is because HCN production is more closely related to coke burn rate than feed rate, and coke yield varies with feed characteristics.

From the data provided an emission factor (EFtest) was developed for each test. The US EPA recommended procedure ([32], Appendix C) was then used to identify any statistical outliers in the data sets of EFtest for each refinery. The procedure assumes that all emissions test data values follow log normal distributions. All values of EFtest in the data sets, therefore, were log transformed prior to conducting outlier tests. If there were 3 to 24 test values in the data set, the Dixon Q test was used to determine outliers. If there were 25 or more test values for analysis, the Rosner test was used to identify outliers. The ProUCL statistical software package available on the US EPA Site Characterization and Monitoring Technical Support Center website [33] was used for outlier identification in both the upper and lower tails. The US EPA procedure deems outliers to be those with a 5% or 95% significance level. Any points identified as outliers were removed from the respective EFtest data sets. The individual refinery emission factors (EFunit) were calculated as the mean of the remaining values in the EFtest data sets.

The individual unit emission factors related to coke burn for each of the 10 FCCU's are given in **Table 2** and shown in a scatter plot in **Figure 6**.

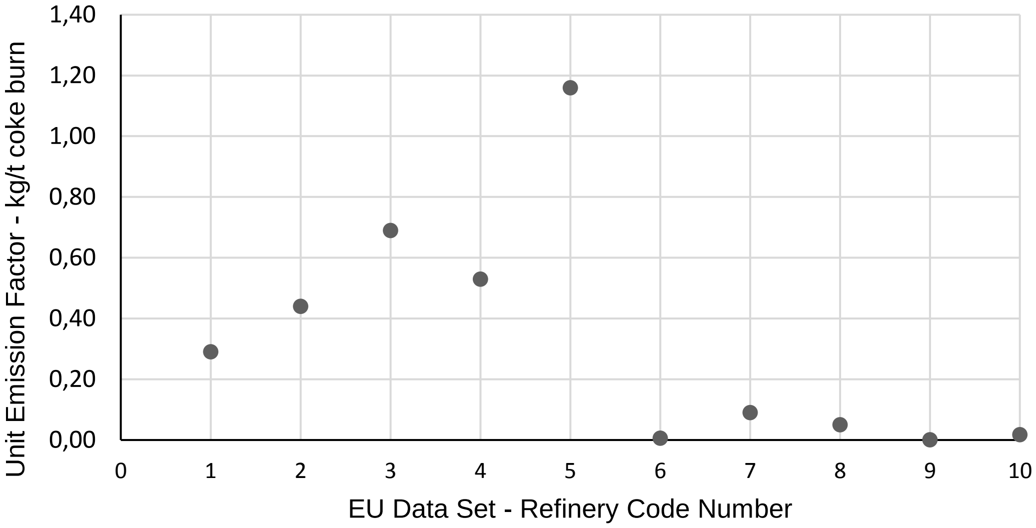
Table 2 Individual European refinery FCCU emission factors for HCN.

Refinery Code	Operating Mode F = Full burn P = Partial burn	Number of measurement campaign data points	Number of data points removed as outliers[1]	Individual unit emission factor (EF_{unit}) kg HCN/t coke burn
EU1	F	72	0	0.29
EU2	F	3	1	0.44
EU3	F	1	-	0.69
EU4	F	3	0	0.53
EU5	F	5	0	1.16
EU6	P	3	1	0.007
EU7	P	17	0	0.09
EU8	P	3	0	0.05
EU9	P	5	0	0.001
EU10	P	1	-	0.018

Table notes:

1 – Outlier analyses undertaken for data sets of 3 values or more.

Figure 6 Individual European refinery FCCU emission factors for HCN related to coke burn.



Review in Chapter 4 has shown the impact of scrubbers or ESP's installed in the regenerator vents on HCN emissions to be minimal, in line with the analyses undertaken by the US EPA. No statistical analyses were therefore undertaken on the data from the European FCCU's. CO boilers were installed only on the 5 partial burn units.

5.4. DEVELOPMENT OF EMISSION FACTORS FOR E-PRTR REPORTING PURPOSES

Figure 6 shows a greater differentiation between the HCN emission factors for the two types of unit than shown by the US EPA data in **Figure 5**. The average emission factor for the 5 full burn units (EU1 to EU5) is 0.62 kg/t. By comparison the average for the 5 partial burn units (EU6 to EU10) is 0.033 kg/t, giving a ratio between the average values of EFunit for full burn to partial burn of 19:1.

The values of EFunit related to coke burn for the 5 European full burn units (0.29 kg/t to 1.16 kg/t) fall within the range of the 8 US units (0.18 kg/t to 1.2 kg/t, if the outlier value for US3 is removed). Similarly, the 2 values for the US partial burn units (0.062 kg/t and 0.063 kg/t) fall within the range of the 5 European partial burn factors (0.001 kg/t to 0.09 kg/t).

Development of emission factors for the two modes of operation, therefore, has been undertaken using the combined US and European data sets of EFunit. QA/QC checks were undertaken on the European refinery test data. Outlier analyses were then undertaken on both the full burn and partial burn data sets. The value of EFunit for the full burn unit at US refinery US3 was again identified as an outlier in the lower tail and it was removed from the dataset. No other outliers were identified. The remaining 13 values for full burn units are given in **Table 3** and shown in a scatter plot in **Figure 7**. The 7 values of EFunit for partial burn units are given in **Table 4** and **Figure 8**.

The lowest value of EFunit related to coke burn for a US full burn unit is for refinery US1 where a CO boiler has been retained. Due to the much lower CO concentration in the vent from a full burn FCCU this installation is now used as a waste heat boiler to generate steam. The value of EFunit for this FCCU is only 18% lower than the next lowest value (0.22 kg/t) for both refineries US6 and US7. The data point for US1 has therefore been included in the data set for full burn units in the development of the emission factors.

The overall emission factors are calculated as the mean values of the two data sets of EFunit. These are shown in **Table 5**. It is recommended that these values are used for E-PRTR reporting purposes.

Table 3 Individual refinery full burn FCCU emission factors for HCN.

Refinery Code	**Individual full burn unit emission factor (EF_{unit}) kg HCN/t coke burn**
1 (EU1)	0.29
2 (EU2)	0.44
3 (EU3)	0.69
4 (EU4)	0.53
5 (EU5)	1.16
6 (US1)	0.18
7 (US2)	0.42
8 (US4)	1.20
9 (US5)	0.28
10 (US6)	0.22
11 (US7)	0.22
12 (US8)	0.77
13 (US9)	1.20

Figure 7 Individual refinery full burn FCCU emission factors for HCN (kg/t coke burn.

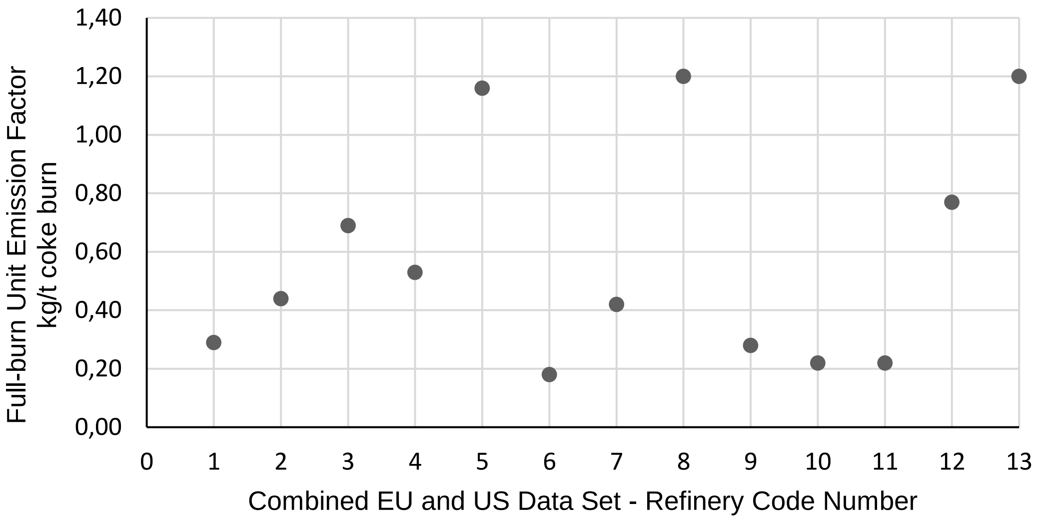


Table 4 Individual refinery partial burn FCCU emission factors for HCN.

Refinery Code	Individual partial burn unit emission factor (EF_{unit}) kg HCN/t coke burn
1 (EU6)	0.007
2 (EU7)	0.09
3 (EU8)	0.05
4 (EU9)	0.001
5 (EU10)	0.018
6 (US11)	0.062
7 (US12)	0.063

Figure 8 Individual refinery partial burn FCCU emission factors for HCN (kg/t coke burn).

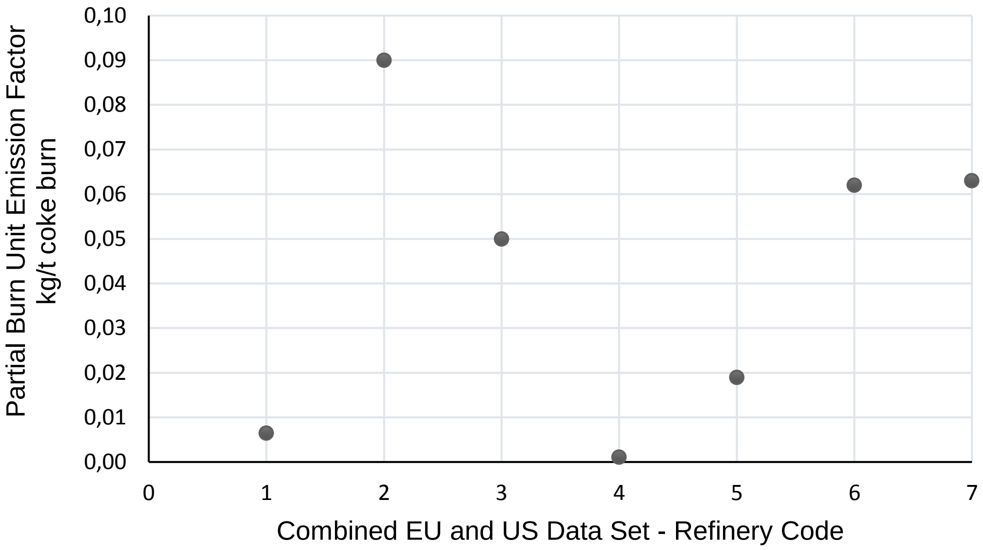


Table 5 FCCU emission factors for HCN.

FCCU regenerator mode of operation	Emission factor kg HCN/t coke burn
Full burn	0.58
Partial burn	0.042

6. HEALTH EFFECTS OF HCN

6.1. INTRODUCTION

HCN is a colourless or pale blue liquid or gas with a faint bitter almond-like odour. It is a weak acid and it is soluble in all proportions. HCN is lighter than water; the octanol-water partition coefficient (log Kow) is low, indicating a moderate lipid solubility.

The following sections provide an overview of the main toxicokinetics processes and the potential health effects of HCN. A summary of the chronic toxicological reference values derived by several organisations, below which harmful effects of HCN are not anticipated, is also given. The information provided in the report has been taken from a literature review on potential effects of HCN on human health that VITO carried out on behalf of Concawe [4].

6.2. TOXICOKINETICS PROCESSES

Cyanide is rapidly and extensively absorbed via the oral and inhalation route, and more slowly absorbed by dermal exposure [34,35]. Previous studies have estimated that oral absorption of HCN could range from 18-80% [34]. When inhaled or dermally absorbed, HCN enters the systemic circulation and distributes rapidly and uniformly throughout the body. Stomach contents immediately appear to contain the highest concentration of cyanide after oral exposure, while other tissues containing cyanide include the liver, brain, spleen, blood, kidneys, and lungs [36,37]. The major metabolic pathway for cyanide is conversion to thiocyanate, primarily by the mitochondrial enzyme rhodanese. Thiocyanate is less toxic than cyanide. Conversion to thiocyanate accounts for 60-80% of a cyanide dose. Minor pathways include incorporation in a 1-carbon metabolic pathway pool and conversion to 2-aminothiazoline-4-carboxylic acid. Small amounts of HCN are converted to carbon dioxide (CO_2) or exhaled unchanged. Cyanide is primarily excreted in the urine as thiocyanate, following both inhalation and oral exposure. Smaller amounts are excreted as urinary cyanide or as HCN or CO_2 in exhaled air.

6.3. EFFECTS OF HCN AFTER INHALATION

HCN is acutely toxic via inhalation. The emphasis of potential harmful effects of HCN is put on chronic exposure via inhalation because these are the exposure time and direct route of exposure to ambient air emissions.

6.3.1. Short term inhalation studies

Although acute oral doses of cyanide cause cardiovascular, respiratory, and neurophysiological changes, the brain appears to be the organ most sensitive to acute cyanide toxicity [38]. Death from cyanide poisoning is believed to result from central nervous system (CNS) depression, subsequent to inhibition of brain cytochrome oxidase activity [39]. Dizziness, weakness, and throbbing pulse were also reported as potential effects due to dermal absorption of HCN gas [35]. The symptoms persisted for several hours following exposure.

6.3.2. Systemic effects

Neurotoxicity

The central nervous system is a primary target for cyanide toxicity. Clinical symptoms related to neurological effects include headaches, weakness, changes in taste and smell, dizziness, disturbances of accommodation, and psychosis. In addition, several reports of occupationally exposed workers indicate that chronic exposure to low concentrations of cyanide can cause alterations of thyroid function and neurological symptoms [40,41,42].

Endocrine effects

Although thiocyanates are less harmful than cyanide in humans, they are known to affect the thyroid glands, affecting the ability of the gland to produce hormones that are necessary for the normal function of the body.

Enlargement of the thyroid gland and increased levels of thyroid stimulating hormone were observed in several past exposure studies where workers were exposed by inhalation to HCN concentrations ranging from 4-15 ppm [41,42].

Respiratory effects

HCN is noted for its systemic respiratory toxicity, which is expected to occur at concentrations below those at which any direct respiratory tract effects would be anticipated. Nasal irritation and congestion, dyspnea, cough, sore throat, altered sense of smell, epistaxis and hemoptysis were reported as potential respiratory effects due to exposure to HCN [41,42,43].

Cardiovascular effects

Chronic occupational exposure studies showed that HCN is related to cardiovascular effects like precordial pain, palpitations, and chest pain [41,42].

Gastro-intestinal effects

The gastrointestinal effects resulting from cyanide exposure are probably provoked by central nervous system effects and/or by irritation of the gastric mucosa in cases in which the gas is swallowed during breathing. Nausea and vomiting are the most common effects [41,42].

Haematological effects

Increased haemoglobin and high lymphocyte count are the most commonly reported haematological effects due to cyanide exposure [42]. In addition, punctate basophilia of erythrocytes, which indicates toxic poisoning, could be another potential effect.

Other effects

Other effects that could potentially reported due to exposure to HCN are eye irritation, lacrimation, dermal rash, loss of appetite and weight loss [41,42].

Carcinogenicity and genotoxicity

HCN is not classified as a carcinogen by the European Commission [44], IARC, the National Toxicology Program (NTP) or US EPA. US EPA explicitly classified HCN in group D, as not classifiable as human carcinogen.

Mutagens are substances that are genotoxic, meaning they can cause harm to the genetic information system (DNA). HCN is not classified for mutagenicity [44].

6.4. TOXICOLOGICAL REFERENCE VALUES FOR CHRONIC INHALATION EXPOSURE

Several bodies have derived chronic toxicological reference values. Below these values harmful effects of HCN are not anticipated. An overview of the reference values is presented in the following table (**Table 6**). The most relevant is considered to be the US EPA value of 8×10^{-4} mg/m^3 which was adopted by the study of El Ghawabi et al. (1975) [42]. This study has been chosen by US EPA as the best available study to represent a safe concentration for lifetime exposure of the general public to pollutants in ambient air. It is the only study that includes environmental exposure data based on breathing zone samples for the individual study participants, it uses extended durations on HCN exposure (5-15 years), while the results of this study indicate that chronic, low-level exposure to cyanide is associated with thyroid enlargement and altered iodine uptake in humans.

Table 6 Toxicological chronic reference values for non-carcinogenic effects of HCN (inhalation).

Organisation	Reference value for HCN	Point of departure	Critical effect	Study	Assessment factors	Reference
IRIS	RfC: 8×10^{-4} mg/m^3	LOAEL: 7.07 mg/m^3	thyroid enlargement and altered iodide uptake	epidemiological occupational study [21]	- exposure adjustment: 10m^3/20m^3 x 5d/7d - 10: deficiencies CN^- inhalation database - 10: lack of NOAEL - 10: intrahuman variability - 3: subchronic to chronic exposure	US EPA, 2010 [45]
ECHA-CHEM database	DNEL for general public: 0.13 mg/m^3	NOEL: 32 mg/m^3 (9.2 ppm) for acetone cyanohydrin	irritation and breathing effects	repeated dose toxicity study with rats	30	Consulted March 2016
California-OEHHA	Chronic REL: 9×10^{-3} mg/m^3 (0,008 ppm)	LOAEL 7.1 mg/m^3	CNS effects, thyroid enlargement, and hematological disorders	epidemiological occupational study [21]	- Exposure adjustment: 10m^3/20m^3 x 5d/7d - d10: lack of NOAEL - 10: intrahuman variability - 3: subchronic to chronic exposure:	OEHHA, 2000 [46]
Canada - Ontario	AAQC: 8×10^{-3} mg/m^3 (24-hr average)	-	CNS effects and thyroid effects	-	-	Ontario, 2012 [47]
Netherlands-RIVM,	Preliminary TCL 2×10^{-1} mg/m^3	lowest reported odour threshold	-	-	not applicable	Vermeire, 1991 [48]
WHO	Air Quality Guideline value	no data	-	-	-	-
ATSDR	MRL not derived	no adequate data	-	-	-	-

7. MODELLING ASSESSMENT OF HCN CONCENTRATIONS FROM FCCU'S

In order to get an indication whether the emitted HCN from FCCU's, as measured in the European refineries, could lead to ambient HCN concentrations in excess of reference values for human health, air dispersion modelling simulations were performed using ADMS [49].

ADMS [49] is an advanced, three-dimensional, steady state quasi-Gaussian dispersion model. It was used to predict ambient HCN concentrations resulting from the HCN emitted from FCCU's. A risk characterisation was performed to assess whether HCN levels are of potential risk for human health. The risk for non-cancer effects is determined from the hazard quotient (HQ) which is the ratio of estimated exposure, i.e. the predicted ADMS value in this study, to a reference level. Exposures at or below the reference level are deemed not likely to cause adverse health effects. The reference concentration (RfC) of 8×10^{-4} mg/m³ [45] derived by US EPA for risk assessment of HCN was used in this study as the most relevant exposure value. A similar risk characterisation has been performed by US EPA during the 2011 Refinery Information Collection Request [50].

7.1. ADMS – MODEL DESCRIPTION

ADMS [49] is an advanced, three-dimensional, steady state quasi-Gaussian dispersion model developed in the UK by CERC, that can be used for calculating concentrations of pollutants emitted both continuously from point, line, volume, and area sources, or discretely from point sources. The model includes algorithms which take into account the impact of buildings at the emissions site, topography data, the complexity of the terrain, dry and wet deposition characteristics, chemical transformation, as well as hourly meteorological data. It models concentrations of pollutants for specified averaging times at receptor points as well as short- and long-term averages of wet, dry and total deposition.

ADMS has a number of advanced features which set it apart from other Gaussian plume models and make it a well suited modelling tool for regulatory purposes. These comprise the following:

- an integral plume rise model, which takes account of a fully three-dimensional flow field;
- a building effects module, which calculates the impact of main site buildings on mean flow and turbulence and hence dispersion;
- a complex flow model, which calculates the impact of changes in terrain elevation and surface roughness on the mean flow and turbulence and hence dispersion;
- a dry deposition model, which may allow for spatial variation in the deposition velocity;
- a wet deposition model, including a falling drop method which explicitly calculates the rate at which the chemical species dissolve in raindrops;
- a condensed plume visibility model which calculates the in-plume water content and hence may be adapted for calculations of chemistry within droplets; and
- an in-plume chemistry model.

Table 7 summarises the input requirements for an ADMS simulation, and the main outputs.

Table 7 Overview of ADMS main input parameters and output data:

Model Inputs/Outputs	**ADMS Options**
Setup Screen	– General site details and modelling parameters to be used in the simulation
Source Type	– Point – Area – Volume – Line – Jet
Source Data	– Emission rate (g/s) – Heat capacity of the source material (J/°C/kg) – Molecular mass of the release pollutant (g) – Density of the release pollutant (kg/m^3) – Height of source (m) – Internal diameter of the source (m) – Exit velocity (m/s) – Volume flux (m^3/s), – Temperature of the release (^{o}C)
Meteorology	– Year/Day/Local time – Surface Roughness (m) – Surface heat flux (W/m^2) – Boundary layer height (m) – Surface Temperature (^{o}C) – Relative humidity (%) – Wind Speed (m/s) – Wind angle (^{o}) – Cloud Cover (octas)
Background Data	– Background concentrations of pollutants
Grid Data	– Coordinate System (Polar/Cartesian) – Receptor type (gridded/specified points)
Dry Deposition	– Deposition velocity (m/s) – Terminal velocity (m/s) (for particles only) – Particles diameter (m) – Particle density (kg/m^3)
Wet Deposition	– Washout Coefficient (s^{-1})
Building Effects	– Building dimensions and location
Terrain	– Terrain height (m) – Surface Roughness (m)
Receptor locations	– Discrete distances – Array option

Output Data	– Pollutant Name – Type of data (concentration, dry/wet deposition) – Averaging Time – Extra Conditions (maximum daily/exceedances, etc.) – Percentiles – Max 1-hour (simple terrain) – Max 24-hour (complex terrain) – Conversion to other averaging times using adjustment factors.

7.2. ADMS SIMULATION RESULTS - COMPARISON WITH CHRONIC EXPOSURE LIMIT VALUES

As mentioned previously, HCN measurement campaigns were performed at European refineries and useable data were obtained from tests on 10 FCCU's. In total, 113 measured HCN emission data points are available. From the full dataset of HCN emission measurements the following two cases were considered for ADMS simulations:

- Case 1: Use of the highest emission value of all measured data obtained from the 10 refineries (Emission rate = 6.65 g/s).
- Case 2: Use of the 2nd highest emission value of all measured data obtained from the 10 refineries (Emission rate = 3.86 g/s).

ADMS version 5.0 was used in both cases, and simulations were carried out for a FCC stack on a refinery (height 90 m, diameter 3.2 m) using normal operating conditions to define exit conditions (T 242 to 283 °C, volume flux around 100 m^3/s). The refinery was located in flat terrain. The ADMS simulations were conducted using the source factors in **Table 7**, and hourly meteorological data taken from a national meteorological service for one year (July 2008 – June 2009). The Flowstar model [51] was also used to take into account the variation of terrain and the roughness. The predicted annual mean HCN concentrations for both cases, are shown in the following contour maps.

Figure 9 ADMS predicted annual mean HCN concentrations – Case 1.

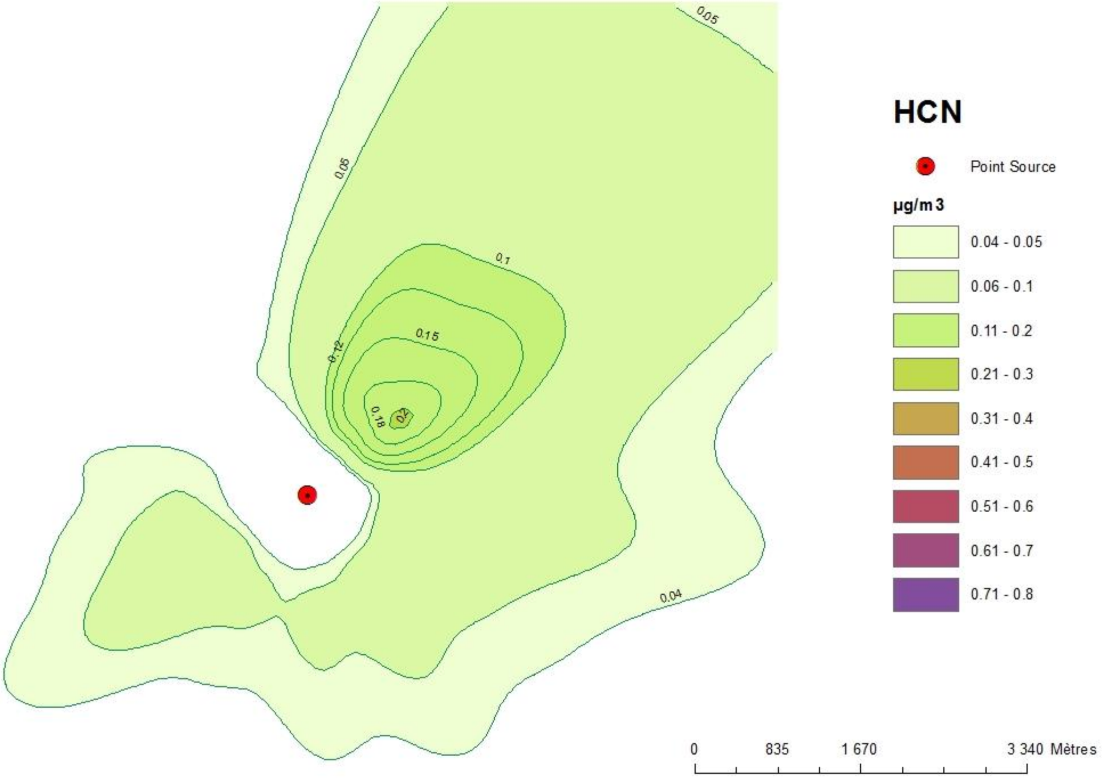
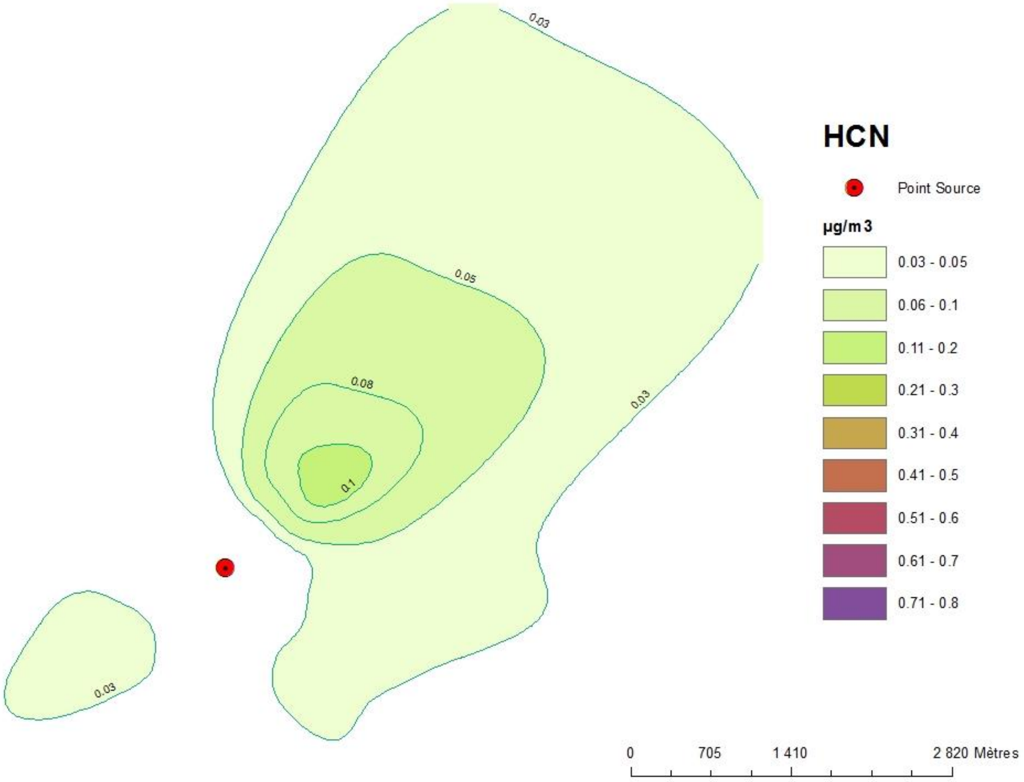


Figure 10 ADMS predicted annual mean HCN concentrations – Case 2.



The maximum predicted annual mean HCN concentrations were 0.25 µg/m^3 for Case 1, and 0.11 µg/m^3 for Case 2 respectively, and occurred at approximately 1 km away from the stack.

In order to assess whether the ambient HCN concentrations resulting from measured HCN emissions from FCCU's could be characterised of potential risk, the predicted ADMS results were compared with a reference value for human health.

The modelling has shown that the highest two HCN emissions values of all the 113 measured data points, gave HCN ground-level concentrations below the RfC (i.e. HQ<1). ADMS was applied to these two cases as they represent the maximum emissions values in the dataset and were therefore considered to result in the maximum predicted HCN concentrations at ground level. As an additional level of assurance, dispersion modelling using a less complex Gaussian model (SCREEN3) [52] was conducted for all other 111 data points, and all runs resulted in a predicted concentration below the RfC. Therefore, based on the screening and advanced dispersion modelling undertaken, HCN from the 10 FCCU's tested are not considered of potential risk for human health.

US EPA performed a similar risk characterisation during the 2011 Refinery Information Collection Request [50]. In their study, US EPA used their derived RfC of 8×10^{-4} mg/m^3 as the reference value for neurological effects, and considered this endpoint to be the driver of the chronic non-cancer risk. The US EPA study, also concluded that HCN emissions from FCCU's are not projected to result in a hazard quotient exceeding 1.

8. CONCLUSIONS

This report provides an overview of the monitoring methods and abatement techniques available for HCN emissions from fluid catalytic cracking units (FCCU's). It recommends emission factors that can be used to estimate HCN emissions from European FCCU's (under different operating conditions). An overview of the potential health effects of HCN is provided and the reference concentration identified which is the best available for this scenario for risk characterisation. An assessment of HCN concentrations at ground level has been carried out using dispersion modelling and compared with the reference concentration.

There are two main techniques employed for HCN monitoring in refineries: the EPA OTM-29 wet chemistry method and the use of the instrumental FTIR technique. The EPA OTM-29 method specifically identifies critical factors that have to be accounted for in the analytical procedures. FTIR is EPA's method of choice and in EPA's final rule Method 320 (or alternatively, ASTM D6348) was required for one-time testing of HCN emissions from FCCU stacks. The EPA mandating FTIR does not mean that HCN must be measured by FTIR in the EU. FTIR when used as AMS has currently no certification for HCN in the EU.

Currently applied abatement techniques for flue gas cleaning at FCCU's are not specifically designed for HCN emission control, but for particulate matter, NOx, SOx and CO reduction. Alkaline wet scrubbers with an aqueous solution of NaOH are usually applied for the removal of HCN from gas stream in other industrial sectors. However, the use of wet scrubbers for HCN reduction in FCCU flue gas has a very high investment and operational cost due to multi-staging and the consumption of very large quantities of chemical scrubbing solution. Recent patented developments for HCN abatement propose to optimize catalyst injection and the use of additives. The HCN reduction process by catalyst injection is being further investigated and optimised under laboratory conditions at the time of publication of this report.

The development of different HCN emissions factors for FCCU's operated under full burn and partial burn conditions is needed to provide reasonable and reliable emissions estimations. Emission factors for HCN were published by the US EPA in 2015 however, these did not differentiate between full burn and partial burn operation of FCCU regenerators. To address this concern, Concawe analysed HCN data which were measured in 10 FCCU's in European refineries, combined with HCN emission measurements undertaken by refineries in the United States for the US EPA, and emission factors for each mode of FCCU operation were developed. The emission factors developed are: 0.58 kg HCN/t coke burn for full burn FCCU's and 0.042 kg HCN/t coke burn for partial burn units. These are recommended to be used for E-PRTR reporting purposes where measurements have not been made.

Regarding its health effects, HCN is rapidly and extensively absorbed via the oral and inhalation route, and more slowly absorbed by dermal exposure. The major metabolic pathway for cyanide is conversion to thiocyanate. Cyanide is primarily excreted in the urine as thiocyanate, following both inhalation and oral exposure. The principal features of the toxicity profile for cyanide are its high acute inhalation toxicity and chronic toxicity, probably mediated through the main metabolite and detoxification product, thiocyanate. The primary targets for chronic cyanide toxicity are the central nervous system and the endocrine system. HCN is not classified as carcinogen or mutagen. Several bodies have derived chronic toxicological reference values, below which harmful effects of HCN are not anticipated.

To assess the potential risk that HCN emission from FCCU's can pose to human health, a dispersion modelling assessment was conducted. All runs resulted in predicted HCN ground-level concentrations below the RfC of 8 × 10^{-4} mg/m³ (0.8 µg/m^3 annual mean) derived by US-EPA for chronic inhalation exposure. This indicates that HCN from the 10 FCCU's tested are not considered of potential risk for human health.

These results are aligned with the findings by US EPA which performed a similar risk characterisation during the 2011 Refinery Information Collection Request [50]. In their study it was concluded that HCN emissions from FCCU's are not projected to result in a hazard quotient exceeding 1.

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10. GLOSSARY

AAQC	Ambient air quality criterion
ADMS	Atmospheric Dispersion Modelling System
AMS	Automated Measurement Systems
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BAT	Best Available Techniques
BREF	Best available techniques Reference document
CEMS	Continuous Emissions Monitoring System
$(CN)_2$	Cyanogen
CNS	Central nervous system
CO	Carbon monoxide
CO_2	Carbon dioxide
COS	Carbonyl Sulphide
CTM	Conditional Test Method
DNEL	Derived No Effect Level
ECHA	European Chemicals Agency
EFtest	Test Emission Factor
EFunit	Unit Emission Factor
E-PRTR	European Pollutant Release and Transfer Register
ESP	Electrostatic Precipitator
FCCU	Fluid Catalytic Cracking Unit
FTIR	Fourier Transform InfraRed
H_2S	Hydrogen Sulphide
HCN	Hydrogen Cyanide
HQ	Hazard Quotient
IARC	International Agency for Research on Cancer
IC	Ion Chromatography
ICR	Information Collection Request
IRIS	Integrated Risk Information System

LOAEL	Lowest Observed Adverse Effect Level
MRL	Minimal Risk Level
NaOH	Sodium Hydroxide
NOAEL	No Observed Adverse Effect Level
N_2	Nitrogen
N_2O	Nitrous Oxide
NH_3	Ammonia
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NOx	Nitrogen Oxides
NTP	National Toxicology Program
O_2	Oxygen
OEHHA	Office of Environmental Health Hazard Assessment
OTM	Other Test Method
REL	Reference Exposure Level
RfC	Reference Concentration
SO_2	Sulfur Dioxide
SO_3	Sulfur Trioxide
SOx	Sulphur Oxides
TCL	Tolerable Concentration Limit
US EPA	United States Environmental Protection Agency
VOKA	Vlaams netwerk van ondernemingen (Flanders' Chamber of Commerce and Industry
VLAREM	Vlaams reglement betreffende de milieuvergunning
WHO	World Health Organisation

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