

# **CHAPTER 3**

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## **CHEMICAL INDUSTRY EMISSIONS**

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## 3 CHEMICAL INDUSTRY EMISSIONS

### 3.1 INTRODUCTION

The following Sections 3.2 through 3.10 give guidance for estimating greenhouse gas emissions that result from the production of various inorganic and organic chemicals for which experience by a number of countries has confirmed significant contributions to global or individual national greenhouse gas emission levels.

- Section 3.2 covers emissions from ammonia production;
- Section 3.3 covers emissions from nitric acid production;
- Section 3.4 covers emissions from adipic acid production;
- Section 3.5 covers emissions from the production of caprolactam, glyoxal, and glyoxylic acid;
- Section 3.6 covers emissions from the production of carbide;
- Section 3.7 deals with emissions from the production of titanium dioxide;
- Section 3.8 deals with emissions from the production of soda ash;
- Section 3.9 covers emissions from key processes in the petrochemical and carbon black production, i.e., methanol, ethylene and propylene, ethylene dichloride, ethylene oxide, acrylonitrile, and carbon black;
- Section 3.10 deals with emissions from fluorochemical production i.e., HFC-23 from the production of HCFC-22 and fugitive and by-product emissions from the production of other fluorinated compounds including hydrofluorocarbons (HFCs), sulphur hexafluoride (SF<sub>6</sub>) and uranium hexafluoride (UF<sub>6</sub>).

Care should be exercised to avoid double counting of carbon dioxide (CO<sub>2</sub>) emissions in both this chapter and in Volume 2 on Energy Sector, or, in omitting CO<sub>2</sub> emissions since CO<sub>2</sub> emissions resulting from carbon's role as process reactant and as a heat source to drive the chemical reactions involved in the chemical processes can be closely related. Should CO<sub>2</sub> capture technology be installed at a chemical plant, the CO<sub>2</sub> captured should be deducted in a higher tier emissions calculation. Respective guidance on the capture and subsequent destruction or use of HFC-23 or other fluorochemicals is given in section 3.10. Any methodology taking into account CO<sub>2</sub> capture should consider that CO<sub>2</sub> emissions captured in the process may be both combustion and process-related. In cases where combustion and process emissions are to be reported separately, e.g., in the petrochemical industry, inventory compilers should ensure that the same quantities of CO<sub>2</sub> are not double counted. In these cases the total amount of CO<sub>2</sub> captured should preferably be reported in the corresponding energy combustion and IPPU categories in proportion to the amounts of CO<sub>2</sub> generated in these source categories. The default assumption is that there is no CO<sub>2</sub> capture and storage (CCS) taking place. For additional information on CO<sub>2</sub> capture and storage refer to Volume 3, Section 1.2.2 and for more details to Volume 2, Section 2.3.4.

## 3.2 AMMONIA PRODUCTION

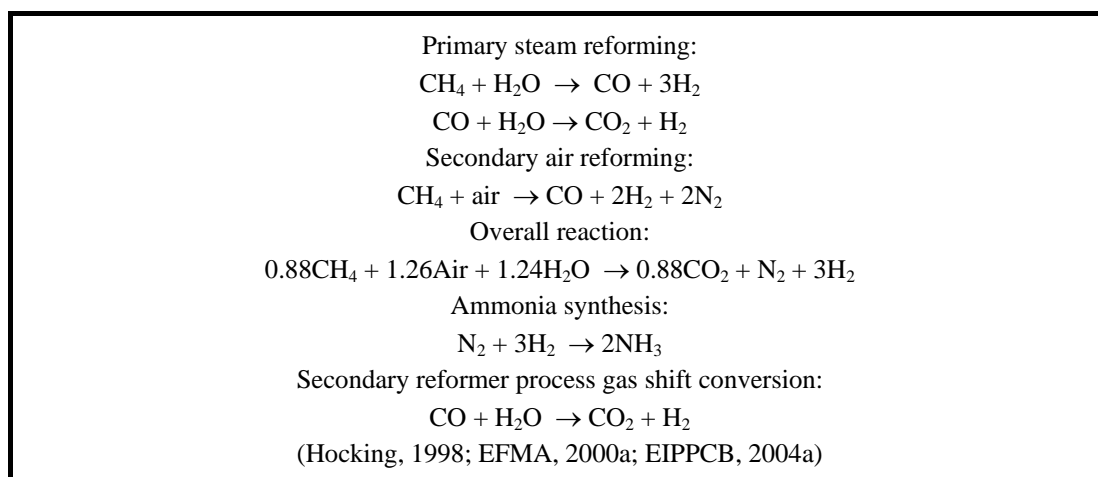
### 3.2.1 Introduction

Ammonia (NH<sub>3</sub>) is a major industrial chemical and the most important nitrogenous material produced. Ammonia gas is used directly as a fertiliser, in heat treating, paper pulping, nitric acid and nitrates manufacture, nitric acid ester and nitro compound manufacture, explosives of various types, and as a refrigerant. Amines, amides, and miscellaneous other organic compounds, such as urea, are made from ammonia (Austin, 1984; p.303).

Ammonia production requires a source of nitrogen (N) and hydrogen (H). Nitrogen is obtained from air through liquid air distillation or an oxidative process where air is burnt and the residual nitrogen is recovered. Most ammonia is produced from natural gas (chiefly methane (CH<sub>4</sub>)), although H can be obtained from other hydrocarbons (coal (indirectly), oil), and water (Hocking, 1998; p.317). A small number of plants continue to use fuel oil as the fuel input and H source in the partial oxidation process. The carbon (C) content of the hydrocarbon is eliminated from the process at the primary steam reforming stage and shift conversion stage through conversion to carbon dioxide (CO<sub>2</sub>) which is the main potential direct greenhouse gas emission. Plants using hydrogen rather than natural gas to produce ammonia do not release CO<sub>2</sub> from the synthesis process.

### 3.2.2 Methodological issues

The chemistry to obtain ammonia feedstocks is similar irrespective of the hydrocarbon used – CH<sub>4</sub> or other fossil fuels (Hocking, 1998; p.319). Because the industry uses predominantly natural gas, the following outline of the process and sources of greenhouse emissions (CO<sub>2</sub>) is based on production using natural gas. Anhydrous ammonia produced by catalytic steam reforming of natural gas (mostly CH<sub>4</sub>) involves the following reactions with carbon dioxide produced as a by-product.



The processes that affect CO<sub>2</sub> emissions associated with ammonia production are:

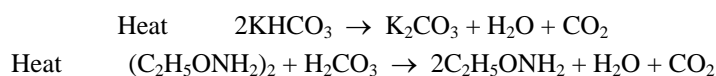
- carbon monoxide shift at two temperatures using iron oxide, copper oxide and/or chromium oxide catalyst for conversion to carbon dioxide;
- carbon dioxide absorption by a scrubber solution of hot potassium carbonate, monoethanolamine (MEA), Sulfinol (alkanol amine and tetrahydrothiophene dioxide) or others;
- methanation of residual CO<sub>2</sub> to methane with nickel catalysts to purify the synthesis gas.

The production of ammonia represents a significant non-energy industrial source of CO<sub>2</sub> emissions. The primary release of CO<sub>2</sub> at plants using the natural gas catalytic steam reforming process occurs during regeneration of the CO<sub>2</sub> scrubbing solution with lesser emissions resulting from condensate stripping.

Should CO<sub>2</sub> capture technology be installed and used at a plant, it is *good practice* to deduct the CO<sub>2</sub> captured in a higher tier emissions calculation. The default assumption is that there is no CO<sub>2</sub> capture and storage (CCS). In most cases, methodologies that account for CO<sub>2</sub> capture should consider that CO<sub>2</sub> emissions captured in the process may be both combustion and process-related. However, in the case of ammonia production no distinction is made between fuel and feedstock emissions with all emissions accounted for in the IPPU Sector. Similarly, all CO<sub>2</sub> captured should be accounted for in the IPPU Sector. For additional information on CO<sub>2</sub> capture and storage refer to Volume 3, Section 1.2.2 and for more details on capture and storage to Volume 2, Section 2.3.4.

## CARBON DIOXIDE REGENERATOR

After absorption of CO<sub>2</sub> from the process gas, the saturated scrubbing solutions (e.g., potassium carbonate, MEA, etc.) are regenerated (i.e., for re-use) with steam stripping and/or boiling to release CO<sub>2</sub> from the bicarbonates according to the following reactions:



The stripping gas, containing CO<sub>2</sub> and other impurities, may be directed to a urea plant (where operational), to a liquid carbonic acid plant, or vented to the atmosphere (Environment Canada, 1987).

## CONDENSATE STRIPPER

Cooling the synthesis gas after low temperature shift conversion forms a condensate containing small quantities of CO<sub>2</sub> and other process impurities. The condensate is stripped by steam, whereby the components may be vented to the atmosphere, but normally recycled to the process together with the process stream (U.S. EPA, 1985).

### 3.2.2.1 CHOICE OF METHOD

The choice of method will depend on national circumstances as shown in the decision tree, Figure 3.1. Emissions are estimated from the total fuel requirement, or values derived from estimates of the total fuel requirement, used in the production of NH<sub>3</sub>. The fuel energy requirement is not accounted for separately. Note that values reported in energy units (or volume units) need to be converted to mass units when estimating emissions.

Methods are classified according to the extent of plant-level data that are available. The Tier 1 method is based on default values and national statistics; the Tier 2 method is based on complete plant-level output data distinguished by fuel input type and process type, and default values; and the Tier 3 method is based entirely on plant-level input data.

The Tier 3 method uses plant-level output data and plant-level fuel input per unit of output to derive the total fuel requirement. Similarly, Tier 3 can also use plant-level emission factors per unit of output provided that the source of these factors is plant-level detailed data on the fuel inputs per unit of output.

### TIER 1 METHOD

The Tier 1 method uses ammonia production to derive emissions as follows:

$$\begin{array}{c} \text{EQUATION 3.1} \\ \text{CO}_2 \text{ EMISSIONS FROM AMMONIA PRODUCTION – TIER 1} \\ E_{\text{CO}_2} = AP \cdot FR \cdot CCF \cdot COF \cdot 44/12 - R_{\text{CO}_2} \end{array}$$

Where:

$E_{\text{CO}_2}$  = emissions of CO<sub>2</sub>, kg

AP = ammonia production, tonnes

FR = fuel requirement per unit of output, GJ/tonne ammonia produced

CCF = carbon content factor of the fuel, kg C/GJ

COF = carbon oxidation factor of the fuel, fraction

$R_{\text{CO}_2}$  = CO<sub>2</sub> recovered for downstream use (urea production), kg

Ammonia production and emission factors can be obtained from national statistics and the emission factor can be determined from default values shown in Table 3.1. Where no information is available on the fuel type and/or process type, it is *good practice* to use the highest emission factor shown in Table 3.1. CO<sub>2</sub> recovered for downstream use can be estimated from the quantity of urea produced where CO<sub>2</sub> is estimated by multiplying urea production by 44/60, the stoichiometric ratio of CO<sub>2</sub> to urea. When a deduction is made for CO<sub>2</sub> used in urea production it is *good practice* to ensure that emissions from urea use are included elsewhere in the inventory. If data are not available on urea production it is *good practice* to assume that CO<sub>2</sub> recovered is zero.

## TIER 2 METHOD

The initial step is to determine the total fuel requirement. For the Tier 2 method the total fuel requirement for each fuel type is estimated as follows:

$$\text{EQUATION 3.2}$$

$$\text{TOTAL FUEL REQUIREMENT FOR AMMONIA PRODUCTION – TIER 2}$$

$$TFR_i = \sum_j (AP_{ij} \cdot FR_{ij})$$

Where:

$TFR_i$  = total fuel requirement for fuel type  $i$ , GJ

$AP_{ij}$  = ammonia production using fuel type  $i$  in process type  $j$ , tonnes

$FR_{ij}$  = fuel requirement per unit of output for fuel type  $i$  in process type  $j$ , GJ/tonne ammonia produced

Ammonia production, the fuel type and process type can be obtained from producers, and the fuel requirement per unit of output (FR) can be determined from the default values shown in Table 3.1. Emissions are derived according to Equation 3.3:

$$\text{EQUATION 3.3}$$

$$\text{CO}_2 \text{ EMISSIONS FROM AMMONIA PRODUCTION – TIER 2 AND 3}$$

$$E_{CO_2} = \sum_i (TFR_i \cdot CCF_i \cdot COF_i \cdot 44/12) - R_{CO_2}$$

Where:

$E_{CO_2}$  = emissions of CO<sub>2</sub>, kg

$TFR_i$  = total fuel requirement for fuel type  $i$ , GJ

$CCF_i$  = carbon content factor of the fuel type  $i$ , kg C/GJ

$COF_i$  = carbon oxidation factor of the fuel type  $i$ , fraction

$R_{CO_2}$  = CO<sub>2</sub> recovered for downstream use (urea production, CO<sub>2</sub> capture and storage (CCS)), kg

When using the Tier 2 method, the C content of the fuel (CCF) and C oxidation factor (COF) may be obtained from the default values shown in Table 3.1 or country specific Energy Sector information. Data on CO<sub>2</sub> recovered for urea production and CCS should be obtained from producers.

## TIER 3 METHOD

The Tier 3 method requires that the fuel requirement be obtained from producers. The total fuel requirement is the sum of the total fuel requirements reported by each NH<sub>3</sub> production plant. That is:

$$\text{EQUATION 3.4}$$

$$\text{TOTAL FUEL REQUIREMENT FOR AMMONIA PRODUCTION – TIER 3}$$

$$TFR_i = \sum_n TFR_{in}$$

Where:

$TFR_i$  = total fuel requirement for fuel type  $i$ , GJ

$TFR_{in}$  = total fuel requirement for fuel type  $i$  used by plant  $n$ , GJ

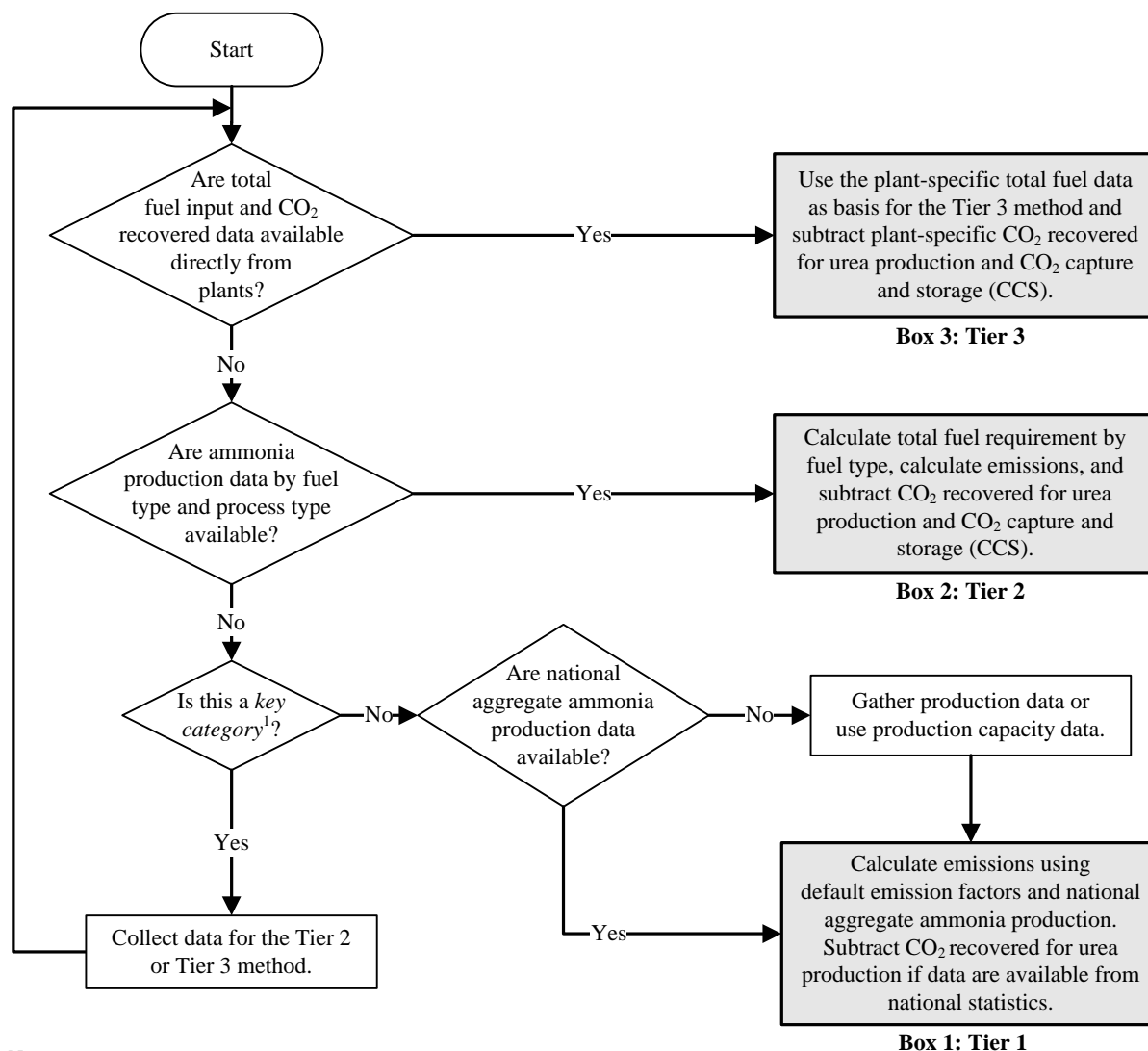
Once data on total fuel requirements are collected and collated, CO<sub>2</sub> emissions can be estimated using Equation 3.3. When using the Tier 3 method, it is *good practice* to obtain information on the CCF and COF from producers or to use country specific energy sector information. As with the Tier 2 method, data on CO<sub>2</sub> recovered for urea production (if any) and CCS (if undertaken) should be obtained from producers.

Although data on ammonia production is not used in the calculation under the Tier 3 method it also needs to be collected from producers for reporting purposes.

**BOX 3.1**  
**CO<sub>2</sub> RECOVERED FOR INDUSTRIAL GAS**

CO<sub>2</sub> recovered for industrial gas applications is not accounted for separately as this is a relatively low volume short term use and it is assumed that all industrial gas carbon will be emitted to the atmosphere in the producing country. For example, industrial CO<sub>2</sub> used in freezing applications is assumed to be released in the producing country.

**Figure 3.1** Decision tree for estimation of CO<sub>2</sub> emissions from ammonia production



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

### 3.2.2.2 CHOICE OF EMISSION FACTORS

#### TIER 1 METHOD

If plant-level information is not available, it is *good practice* to use default factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. Default factors by production process are provided in Table 3.1, and should be used only in cases where plant-specific data are not available. The default factors are estimates of total fuel requirements per unit of output expressed in energy units. They can be converted to mass units based on C content of the fuel and the C oxidation factor in Volume 2: Energy of these *Guidelines*. These values are also included in Table 3.1 as are emission factors of tonnes of CO<sub>2</sub> per tonne of NH<sub>3</sub> derived using these values.

For the Tier 1 method it is *good practice* to use the highest total fuel requirement per tonne of ammonia. If no information on fuel type is available, it is *good practice* to use the average value shown in Table 3.1 for partial oxidation.

| <b>TABLE 3.1</b><br><b>DEFAULT TOTAL FUEL REQUIREMENTS (FUEL PLUS FEEDSTOCK) AND EMISSION FACTORS FOR AMMONIA PRODUCTION</b><br><b>(PER TONNE NH<sub>3</sub>)</b>  |  |  |   |   |
|--|--|--|---|---|
| <b>Production Process</b>  | <b>Total fuel requirement<br/>(GJ(NCV)/tonne NH<sub>3</sub>)<br/>± Uncertainty (%)</b> | <b>Carbon content<br/>factor [CCF]<sup>1</sup><br/>(kg/GJ)</b> | <b>Carbon oxidation<br/>factor [COF]<sup>1</sup><br/>(fraction)</b> | <b>CO<sub>2</sub> emission<br/>factor<br/>(tonnes CO<sub>2</sub><br/>/tonne NH<sub>3</sub>)</b> |
| <b>Modern plants – Europe</b><br>Conventional reforming –<br>natural gas   | 30.2 (± 6%)  | 15.3   | 1   | 1.694   |
| Excess air reforming –<br>natural gas  | 29.7 (± 6%)  | 15.3   | 1   | 1.666   |
| Autothermal reforming –<br>natural gas   | 30.2 (± 6%)  | 15.3   | 1   | 1.694   |
| Partial oxidation  | 36.0 (± 6%)  | 21.0   | 1   | 2.772   |
| <b>Derived from European<br/>average values for specific<br/>energy consumption (Mix of<br/>modern and older plants)</b><br>Average value – natural gas  | 37.5 (± 7%)  | 15.3   | 1   | 2.104   |
| Average value –<br>partial oxidation   | 42.5 (± 7%)  | 21.0   | 1   | 3.273   |
| NCV – Net Calorific Value.   |  |  |   |   |
| <sup>1</sup> Values from Energy, Vol. 2, Chapter.1, Tables 1.3 and 1.4.  |  |  |   |   |
| Source: Adapted from EFMA (2000b; p.21); de Beer, Phylipsen and Bates (2001; p.21); for modern plants default factors can be derived using C content based on natural gas (dry basis) and partial oxidation default factors can be derived using C content based on residual fuel oil. |  |  |   |   |

## TIER 2 METHOD

The total fuel requirement values per unit of output in Table 3.1 can be used in conjunction with data on NH<sub>3</sub> production by fuel type and process type, along with either default or country specific data on the C content factor and carbon oxidation factor of the fuels.

## TIER 3 METHOD

Plant-level data on total fuel requirement provide the most rigorous data for calculating CO<sub>2</sub> emissions from ammonia production. It is *good practice* to obtain information on the CCF and COF from producers or use country-specific Energy Sector data. The CCF is the key emission factor variable for deriving the quantity of CO<sub>2</sub> emissions. Derivation of emissions using plant-level ammonia production depends on an accurate estimate of the fuel requirement per unit of output, along with information on the other variables.

### 3.2.2.3 CHOICE OF ACTIVITY DATA

#### TIER 1 METHOD

The Tier 1 method requires data on national production of NH<sub>3</sub>. If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent) if the inventory compiler can document that utilisation for a year was below capacity. The same capacity utilisation factor should be applied to each year of the time-series.

#### TIER 2 METHOD

The Tier 2 method requires plant level data on ammonia production classified by fuel type and production process. In addition, plant level data on CO<sub>2</sub> recovered for downstream use or other application are required.

## TIER 3 METHOD

The plant-level activity data required for the Tier 3 approach are total fuel requirement classified by fuel type, CO<sub>2</sub> recovered for downstream use or other applications, ammonia production. Although ammonia production is not used in the Tier 3 calculation, collection of all activity data that influence the estimation of emissions allows changes over time and any misreporting of activity data to be identified. Where plant-level fuel requirement per unit of output is used, collection of plant-level production data is required.

### BOX 3.2 DOUBLE COUNTING

In order to avoid double counting, the total quantities of oil or gas used (fuel plus feedstock) in ammonia production must be subtracted from the quantity reported under energy use in the **Energy Sector**.

In addition, the quantity of CO<sub>2</sub> recovered for downstream use in **urea production** must be subtracted from the total quantity of CO<sub>2</sub> generated to derive CO<sub>2</sub> emitted. Emissions of CO<sub>2</sub> from urea use should be accounted for in the corresponding sectors. In particular, emissions from **urea use** as fertiliser should be included in the **Agriculture Forestry and Other Land Use (AFOLU) Sector** (see Volume 4). Emissions from urea use in automobile catalytic converters should be accounted for in the Energy Sector (Volume 2). Emissions from any other chemical products manufactured using CO<sub>2</sub> recovered from the process (e.g., emissions from carbonic acid use) are covered by methodology suggested in this section and should not be accounted for in other IPPU sections or in other sectors.

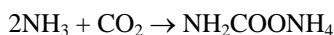
### BOX 3.3 UREA PRODUCTION

Urea (CO(NH<sub>2</sub>)<sub>2</sub>) (carbonyl amide or carbamide) is an important nitrogenous fertiliser with the highest nitrogen content available in a solid fertiliser. Urea is also used as a protein food supplement for ruminants, in melamine production, as an ingredient in the manufacture of resins, plastics, adhesives, coatings, textile anti-shrink agents, and ion-exchange resins (Austin, 1984; pp.311-312). A developing use is as a reducing agent in selective catalytic reduction of NO<sub>x</sub> in exhaust gases originating from diesel or gasoline direct injection engines. Emissions from urea applications should be accounted for in the appropriate application sectors.

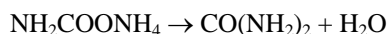
Urea production is a downstream process associated with ammonia production plants. The process uses the by-product CO<sub>2</sub> stream from an ammonia synthesis plant along with ammonia.

Urea is produced by the reaction of NH<sub>3</sub> and CO<sub>2</sub> to produce ammonium carbamate which is then dehydrated to urea according to the reactions:

Ammonium carbamate production:



Dehydration of ammonium carbamate to urea:



Assuming complete conversion of NH<sub>3</sub> and CO<sub>2</sub> to urea, 0.733 tonnes of CO<sub>2</sub> are required per tonne of urea produced. Greenhouse gas emissions from modern plants are likely to be small. Excess NH<sub>3</sub> and CO<sub>2</sub> are contained in the process water which is formed during the reaction. Water treatment is designed to recover these substances from the process water to enable recycling of the gases to the synthesis (EIPPCB, 2004a; p.118). Based on typical inputs for modern plants (EIPPCB, 2004a; p.121), the input values imply that emissions of CO<sub>2</sub> range from 2 to 7kg per tonne of urea. For a plant of 1 000 tonnes of urea per day and assuming capacity utilisation of around 90 percent, this would imply annual emissions of CO<sub>2</sub> of slightly in excess of 2Gg.

Although emissions from urea production are unlikely to be significant in well-managed modern plants, it is *good practice* to obtain plant-level information on urea production and to account for any significant emissions.



### 3.2.2.4 COMPLETENESS

In countries where only a subset of plants report data for the Tier 3 method or where there is a transition from Tier 2 to Tier 3, it may not be possible to report emissions using Tier 3 for all facilities during the transition. Where data for the Tier 3 method are not available for all plants, Tier 2 could be used for the remaining plants. Also, where data for the Tier 2 method are reported by only a subset of plants or where there is a transition from Tier 1 to Tier 2, it may be possible to determine the share of production represented by non-reporting plants and use this information to estimate the remaining emissions using Tier 1 in order to ensure completeness during the transition period.

Complete coverage for ammonia production requires accounting for all emissions from all sources. CO<sub>2</sub> emissions are straightforward. Completeness can be improved by ensuring that emissions of any fugitive CH<sub>4</sub> either from the primary reformer stage or catalytic methanation of CO<sub>2</sub> process are included. In order to include emissions of NO<sub>x</sub>, CO and SO<sub>2</sub> from the primary reformer stage, see guidance provided in Chapter 7 of Volume 1: General Guidance and Reporting.

### 3.2.2.5 DEVELOPING A CONSISTENT TIME SERIES

CO<sub>2</sub> emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available, including plant-specific production data and data for downstream use, for all years in the time series, it will be necessary to consider how current plant data can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.2.3 Uncertainty assessment

### 3.2.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values shown in Table 3.1 are estimates based on data from EFMA (2000a; p.21) and de Beer, Phylipsen and Bates (2001; p.21). In general, default emission factors for gaseous inputs and outputs have higher uncertainties than for solid or liquid inputs and outputs. Mass values for gaseous substances are influenced by temperature and pressure variations and gases are more easily lost through process leaks. It is *good practice* to obtain uncertainty estimates at the plant level, which should be lower than uncertainty values associated with default values. Default emission factor uncertainties reflect variations between plants across different locations.

### 3.2.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. These activity data are likely to be highly accurate (i.e., with uncertainty as low as  $\pm 2$  percent). This will include uncertainty estimates for fuel use, uncertainty estimates for ammonia production and CO<sub>2</sub> recovered. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of ammonia production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of  $\pm 5$  percent can be used.

## 3.2.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation

### 3.2.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable, if higher tier methods are used to determine

emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

### **Comparison of emission factors**

Inventory compilers should check if the estimated emission factors are within the range of default emission factors provided for the Tier 1 method, and also ensure that the emission factors are consistent with the values derived from analysis of the process chemistry. For example, the CO<sub>2</sub> generation rate based on natural gas should not be less than 1.14 tonnes of CO<sub>2</sub> per tonne of ammonia produced. If the emission factors are outside of the estimated ranges, it is *good practice* to assess and document the plant-specific conditions that account for the differences.

### **Plant-specific data check**

The following plant-specific data are required for adequate auditing of emissions estimates:

- Activity data comprising input and output data (input data should be total fuel requirement – fuel energy input plus feedstock input);
- Calculations and estimation method;
- List of assumptions;
- Documentation of any plant-specific measurement method, and measurement results.

If emission measurements from individual plants are collected, inventory compilers should ensure that the measurements were made according to recognised national or international standards. QC procedures in use at the site should be directly referenced and included in the QC plan. If the measurement practices were not consistent with QC standards, the inventory compiler should reconsider the use of these data.

## **3.2.4.2 REPORTING AND DOCUMENTATION**

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced.

Much of the production and process data are considered proprietary by operators, especially where there are only a small number of plants within a country. It is *good practice* to apply appropriate techniques, including aggregation of data, to ensure protection of confidential data. Guidance on managing confidential data is provided in Section 2.2, Volume 1.

## 3.3 NITRIC ACID PRODUCTION

### 3.3.1 Introduction

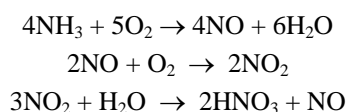
Nitric acid is used as a raw material mainly in the manufacture of nitrogenous-based fertiliser. Nitric acid may also be used in the production of adipic acid and explosives (e.g., dynamite), for metal etching and in the processing of ferrous metals.

During the production of nitric acid (HNO<sub>3</sub>), nitrous oxide (N<sub>2</sub>O) is generated as an unintended by-product of the high temperature catalytic oxidation of ammonia (NH<sub>3</sub>). The amount of N<sub>2</sub>O formed depends, inter alia, on combustion conditions (pressure, temperature), catalyst composition and age, and burner design (EFMA, 2000b; p.15). In addition, some NO<sub>x</sub> is produced. Formation of NO<sub>x</sub> is most pronounced at start-up and shut-down when the process is least stable (EFMA, 2000b; p.15). N<sub>2</sub>O is also generated in other industrial processes that use nitrogen oxides or nitric acid as feedstocks (e.g. the manufacture of caprolactam, glyoxal, and nuclear fuel reprocessing). Nitric acid is a significant source of atmospheric N<sub>2</sub>O if not abated and is the major source of N<sub>2</sub>O emissions in the chemical industry. While, unlike other emissions from nitric acid production, there are no mature technologies specifically designed for the destruction of N<sub>2</sub>O (Perez-Ramirez *et al.*, 2003) a number of technologies for N<sub>2</sub>O mitigation during nitric acid manufacture have been developed in recent years. Examples include a tail-gas process where both N<sub>2</sub>O and NO emissions can be simultaneously reduced (requiring addition of ammonia to the tail-gas), a process-gas option involving direct catalytic decomposition right after the platinum gauzes, and a full-scale catalyst decomposition option.

There are two types of nitric acid plants, single pressure plants and dual pressure plants. In single pressure plants the oxidation and absorption take place at essentially the same pressure, and in dual pressure plants absorption takes place at a higher pressure than the oxidation stage.

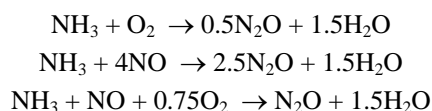
### 3.3.2 Methodological issues

Nitric acid production involves three distinct chemical reactions that can be summarised as follows:



Nitrous oxide generation during the production of nitric acid is not well documented. Nitrogen oxidation steps under overall reducing conditions are considered to be potential sources of N<sub>2</sub>O. Nitric oxide (NO), an intermediate in the production of nitric acid, is also documented to readily decompose to N<sub>2</sub>O and nitrogen dioxide (NO<sub>2</sub>) at high pressures for a temperature range of 30 to 50°C (Cotton and Wilkinson, 1988).

Perez-Ramirez *et al.* (2003; p.123) specify three intermediate reactions during the oxidation of ammonia that might result in the formation of N<sub>2</sub>O:



Reactions that lead to the formation of N<sub>2</sub>O or N<sub>2</sub> are undesirable in that they decrease the conversion efficiency of NH<sub>3</sub> and reduce the yield of the desired product, NO (Perez-Ramirez *et al.*, 2003; p.124). It is not possible to define a precise relationship between NH<sub>3</sub> input and N<sub>2</sub>O formation because in general, 'the amount of N<sub>2</sub>O formed depends on combustion conditions, catalyst composition and state (age), and burner design' (Perez-Ramirez *et al.*, 2003; p.123). Emissions of N<sub>2</sub>O depend on the amount generated in the production process and the amount destroyed in any subsequent abatement process. Abatement of N<sub>2</sub>O can be intentional, through installation of equipment designed to destroy N<sub>2</sub>O, or unintentional in systems designed to abate other emissions such as nitrogen oxides (NO<sub>x</sub>).

Perez-Ramirez *et al.* (2003; p.126) classify abatement approaches as follows and abatement measures associated with each approach are outlined in Table 3.2:

- Primary abatement measures aim at preventing N<sub>2</sub>O being formed in the ammonia burner. This involves modification of the ammonia oxidation process and/or catalyst.
- Secondary abatement measures remove N<sub>2</sub>O from the valuable intermediate stream, i.e. from the NO<sub>x</sub> gases between the ammonia converter and the absorption column. Usually this will mean intervening at the highest temperature, immediately downstream of the ammonia oxidation catalyst.
- Tertiary abatement measures involve treating the tail-gas leaving the absorption column to destroy N<sub>2</sub>O. The most promising position for N<sub>2</sub>O abatement is upstream of the tail-gas expansion turbine.
- Quaternary abatement measures are the pure end-of-pipe solution, where the tail-gas is treated downstream of the expander on its way to the stack.

| Abatement approaches                                     | Abatement measures  |
|--|---|
| Primary abatement  | <ul style="list-style-type: none"> <li>• Optimal oxidation process</li> <li>• Modification of platinum-rhodium gauzes</li> <li>• Oxide-based combustion catalysts</li> </ul>  |
| Secondary abatement                                      | <ul style="list-style-type: none"> <li>• Homogeneous decomposition in the burner</li> <li>• Catalytic decomposition in the burner (process gas catalytic decomposition)</li> <li>• Catalytic decomposition downstream of the burner (before the absorption column)</li> </ul> |
| Tertiary abatement                                       | <ul style="list-style-type: none"> <li>• Thermal decomposition</li> <li>• Non-selective catalytic reduction (NSCR)</li> <li>• Tail-gas catalytic decomposition</li> <li>• Selective catalytic reduction (SCR)</li> </ul>  |
| Quaternary abatement                                     | <ul style="list-style-type: none"> <li>• Non-selective catalytic reduction (NSCR)</li> <li>• Catalytic decomposition</li> <li>• Selective catalytic reduction (SCR)</li> </ul>  |
| Source: Adapted from Perez-Ramirez <i>et al.</i> (2003). |   |

The abatement achieved will depend on the technology implemented with tertiary measures stated as, ‘enabling the achievement of high levels of N<sub>2</sub>O removal (>99 percent)’ (Perez-Ramirez *et al.*, 2003; p.136). Additionally, it is noted that although NSCR is a proven technology for N<sub>2</sub>O reduction, the replacement of NSCR systems by SCR systems for NO<sub>x</sub> reduction has a negative side-effect on its application for N<sub>2</sub>O reduction. Further, ‘NSCR is most likely not a viable option anymore, due to the high fuel consumption levels and high secondary emissions’ (Perez-Ramirez *et al.*, 2003; p.137).

Future adoption of technologies will depend on cost-effectiveness and the stringency of any emissions regulation. More cost-effective options are available for new plants than for existing plants. Tail-gas options are appealing since they do not interfere with the process. Direct N<sub>2</sub>O decomposition is a very attractive and cost effective option in plants with tail-gas temperatures greater than 723 K. However, two-thirds of the nitric acid plants in Europe have low-temperature tail-gases. To this end, preheating or using reductants (light hydrocarbons or ammonia) is required, making the after-treatment prohibitive. The most elegant and cost-effective option is the in process-gas catalytic decomposition, located in the heart of the plant (the ammonia burner). Concerns with this abatement option are chemical and mechanical stability of the catalyst as well as the possible NO loss. Several catalyst manufacturers and nitric acid producers have addressed this problem and catalysts are in the early stages of commercialisation. Advantageously, and contrary to the tail-gas option, this technology can be retrospectively applied to all existing plants. Further discussion of options is provided in Perez-Ramirez *et al.* (2003).

### 3.3.2.1 CHOICE OF METHOD

The choice of *good practice* method depends on national circumstances. The decision tree in Figure 3.2 describes *good practice* in adapting the methods to national circumstances. Emissions can be estimated from:

- continuous emissions monitoring (CEM) where emissions are directly measured at all times;

- periodic emissions monitoring that is undertaken over a period(s) that is reflective of the usual pattern of operation of the plant to derive an emission factor that is multiplied by output (100 percent HNO<sub>3</sub>) to derive emissions;
- irregular sampling to derive an emission factor that is multiplied by output (100 percent HNO<sub>3</sub>) to derive emissions;
- by multiplying a default emission factor by output (100 percent HNO<sub>3</sub>).

Methods are classified according to the extent of plant-level data that are available. Both Tier 2 and Tier 3 are based on plant-level activity data.

### TIER 1 METHOD

Emissions are estimated as follows:

|  |
|--|
| <p><b>EQUATION 3.5</b></p> <p><b>N<sub>2</sub>O EMISSIONS FROM NITRIC ACID PRODUCTION – TIER 1</b></p> $E_{N_2O} = EF \cdot NAP$ |
|--|

Where:

$E_{N_2O}$  = N<sub>2</sub>O emissions, kg

EF = N<sub>2</sub>O emission factor (default), kg N<sub>2</sub>O/tonne nitric acid produced

NAP = nitric acid production, tonnes

When applying the Tier 1 method it is *good practice* to assume that there is no abatement of N<sub>2</sub>O emissions and to use the highest default emission factor based on technology type shown in Table 3.3.

### TIER 2 METHOD

There are a large number of nitric acid plants (estimates range from 255 to 600 plants according to Choe *et al.*, 1993; Bockman and Granli, 1994) with substantial variations in the N<sub>2</sub>O generation factors among plant types. Consequently, default factors may be needed more often for nitric acid N<sub>2</sub>O emissions estimates. Where default values are used to estimate emissions from nitric acid production, it is *good practice* to categorise plants according to type and to use an appropriate N<sub>2</sub>O generation factor.

The Tier 2 method uses plant-level production data disaggregated by technology type and default emission factors classified by technology type. Emissions are calculated as follows:

|   |
|---|
| <p><b>EQUATION 3.6</b></p> <p><b>N<sub>2</sub>O EMISSIONS FROM NITRIC ACID PRODUCTION – TIER 2</b></p> $E_{N_2O} = \sum_{i,j} [EF_i \cdot NAP_i \cdot (1 - DF_j \cdot ASUF_j)]$ |
|---|

Where:

$E_{N_2O}$  = emissions of N<sub>2</sub>O, kg

EF<sub>*i*</sub> = N<sub>2</sub>O emission factor for technology type *i*, kg N<sub>2</sub>O/tonne nitric acid produced

NAP<sub>*i*</sub> = nitric acid production from technology type *i*, tonnes

DF<sub>*j*</sub> = destruction factor for abatement technology type *j*, fraction

ASUF<sub>*j*</sub> = abatement system utilisation factor for abatement technology type *j*, fraction

Note that the default emission factors shown in Table 3.3 include the impact on emissions of abatement technology where relevant. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

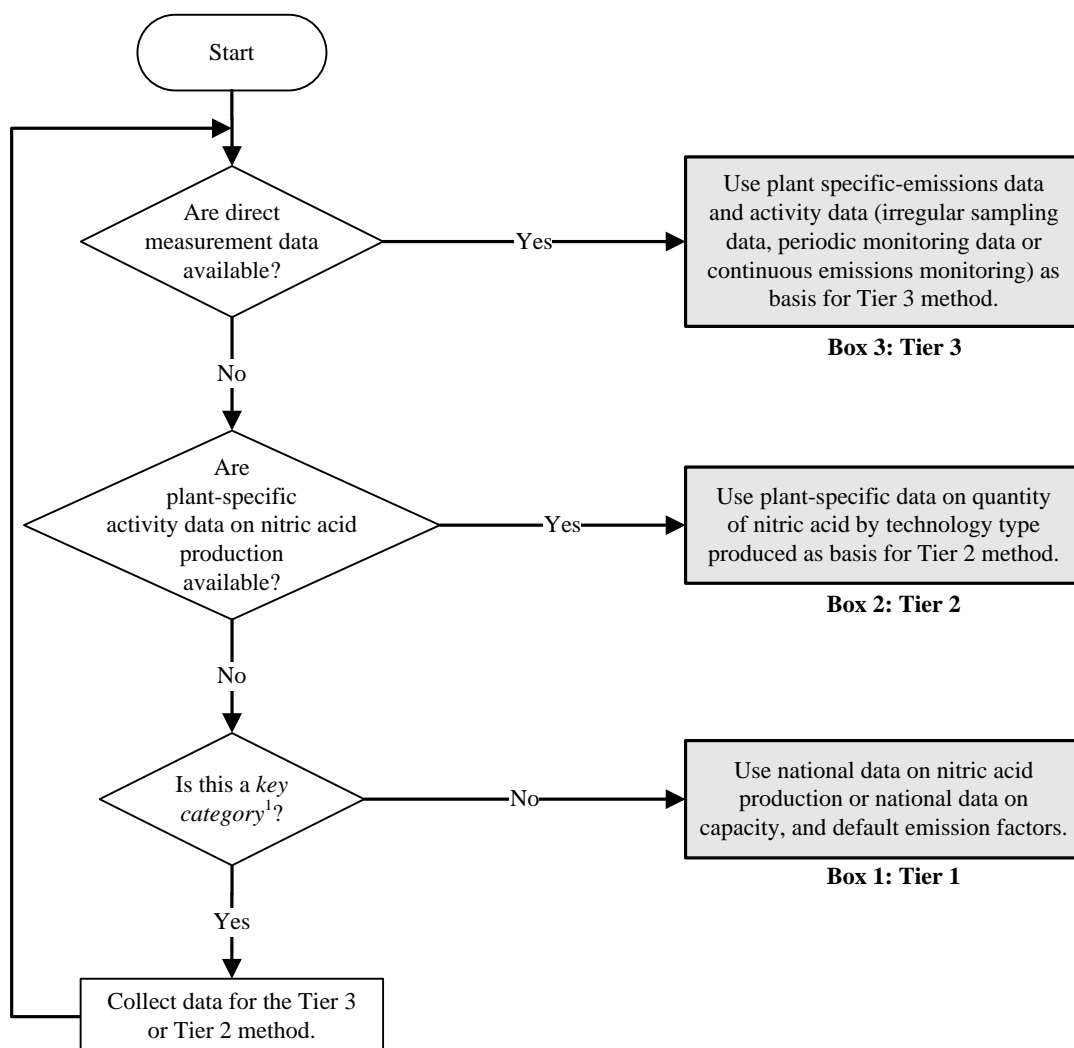
The basic equation for estimating N<sub>2</sub>O emissions includes additional terms that recognise the potential future use of N<sub>2</sub>O abatement technologies. The N<sub>2</sub>O destruction factor has to be multiplied by an abatement system utilisation factor in order to account for any down-time of the emission abatement equipment (i.e., time the equipment is not operating).

## TIER 3 METHOD – DIRECT MEASUREMENT

While the tier 2 approach applies technology specific emission factors reflecting the national technology mix. Tier 3 is based on real measurement data (e.g., CEMS). Plant-level production data disaggregated by technology type and plant level emission factors obtained from direct measurement of emissions. These may be derived from irregular sampling of emissions of N<sub>2</sub>O or periodic emissions monitoring of N<sub>2</sub>O undertaken over a period(s) that reflects the usual pattern of operation of the plant. Emissions can be derived using Equation 3.6.

Alternatively, the Tier 3 method uses the results of continuous emissions monitoring (CEM), although it is noted that most plants are unlikely to employ CEM due to the resource costs. Where CEM is employed, emissions can be estimated based on the sum of measured N<sub>2</sub>O emissions derived from the concentration of N<sub>2</sub>O in monitored emissions for each recorded monitoring interval.

**Figure 3.2 Decision tree for estimation of N<sub>2</sub>O emissions from nitric acid production**



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

### 3.3.2.2 CHOICE OF EMISSION FACTORS

#### TIER 1 METHOD

It is *good practice* to use the highest emission factor based on the technology type shown in Table 3.3 and to assume that there is no abatement of N<sub>2</sub>O emissions.

#### TIER 2 METHOD

If plant-level factors are not available, it is *good practice* to use default factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they

represent a specific plant's emission rate is unknown. Default factors in Table 3.3 should be used only in cases where plant-specific measurements are not available.

Table 3.3 includes emission factors for N<sub>2</sub>O, and associated uncertainties. The factors listed in Table 3.3 for plants using non-selective catalytic reduction (NSCR), (a NO<sub>x</sub> abatement technology that can also be managed to abate N<sub>2</sub>O), already incorporate the effect of N<sub>2</sub>O abatement measures. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

### TIER 3 METHOD

Plant measurements provide the most rigorous data for calculating net emissions (i.e., N<sub>2</sub>O generation and destruction factors). Monitoring N<sub>2</sub>O emissions from nitric acid production is practical because these are point sources and there are a finite number of production plants. Given currently available technology, instrumentation for sampling and monitoring emission rates do not limit precision or accuracy of the overall measurement. Usually sampling frequency and timing is sufficient to avoid systematic errors and to achieve the desired level of accuracy.

As a general rule, it is *good practice* to conduct sampling and analysis whenever a plant makes any significant process changes that would affect the generation rate of N<sub>2</sub>O, and sufficiently often otherwise to ensure that operating conditions are constant. In addition, plant operators should be consulted annually to determine the specific destruction technologies employed and confirm their use, since technologies may change over time. Precise measurement of the emissions rate and abatement efficiencies requires measurement of both the exit stream and the uncontrolled stream. Where measurement data are available only on the exit stream, *good practice* is to base emissions on these data. In this case, any available estimates of abatement efficiency should be provided only for information purposes and are not used to calculate emissions.

| <b>Production Process</b>  | <b>N<sub>2</sub>O Emission Factor<br/>(relating to 100 percent pure acid)</b> |
|--|---|
| Plants with NSCR <sup>a</sup> (all processes)  | 2 kg N <sub>2</sub> O/tonne nitric acid ±10%                                  |
| Plants with process-integrated or tailgas N <sub>2</sub> O destruction               | 2.5 kg N <sub>2</sub> O/tonne nitric acid ±10%                                |
| Atmospheric pressure plants (low pressure)   | 5 kg N <sub>2</sub> O/tonne nitric acid ±10%                                  |
| Medium pressure combustion plants  | 7 kg N <sub>2</sub> O/tonne nitric acid ±20%                                  |
| High pressure plants   | 9 kg N <sub>2</sub> O/tonne nitric acid ±40%                                  |
| <sup>a</sup> Non-Selective Catalytic Reduction (NSCR).<br>Source: van Balken (2005). |   |

### 3.3.2.3 CHOICE OF ACTIVITY DATA

It is *good practice* to compile production data at a level of detail that allows the use of a Tier 2 or Tier 3 method, where possible. Activity data should be based on 100 percent HNO<sub>3</sub>, - it is *good practice* to ensure that all production data reported are for 100 percent HNO<sub>3</sub>.

#### TIER 1 METHOD

The Tier 1 method requires data on national production of nitric acid. National nitric acid statistics may omit a substantial proportion of the national total (see details in Section 3.3.2.4 Completeness). If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

#### TIER 2 METHOD

The Tier 2 method requires plant-level production data disaggregated by technology type and abatement system type. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Typical plant-level production data is assumed to have an uncertainty of ±2 percent due to the economic value of having accurate information.

## TIER 3 METHOD

As with the Tier 2 method, plant-level production data disaggregated by technology and abatement system type are required. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Although production data are not used in the estimation of emissions where the estimate is based on CEM, these data should be collected and reported to ensure that changes in variables that influence emissions can be monitored over time. Typical plant-level production data is assumed to have an uncertainty of  $\pm 2$  percent due to the economic value of having accurate information.

### 3.3.2.4 COMPLETENESS

Nationally compiled nitric acid production statistics could underestimate production. Studies that compare global statistics compiled from national data on nitric acid production with industry estimates of global production suggest that the national statistics account for only 50 to 70 percent of the total (Bouwman *et al.*, 1995; Olivier, 1999). This is probably due to nitric acid production that is integrated as part of larger production processes, where the nitric acid never enters into commerce and is not counted in the national statistics. It is *good practice* to account for these sources by methods such as identifying them through national registries of NO<sub>x</sub> emissions, another unintended by-product of nitric acid production.

NSCR and SCR systems designed to abate N<sub>2</sub>O can give rise to additional emissions of CO, CO<sub>2</sub> and hydrocarbons (CH<sub>4</sub> and NMVOCs). These emissions will depend on the hydrocarbon reducing agent that is used (methane (CH<sub>4</sub>), propane (C<sub>3</sub>H<sub>8</sub>), propene (C<sub>3</sub>H<sub>6</sub>), LPG). Emissions can be estimated based on the quantity of reducing agent used and the completeness of combustion. Plant-level information will be required to enable emissions estimation. Over time default values could be developed as more information becomes available, however, at present there are no default values. Methods for estimating these emissions are not included in these *Guidelines*, however, inventory compilers are encouraged to investigate these emission sources and to develop appropriate methodologies.

There will usually be few nitric acid plants in a country, and it is suggested that emissions are calculated from plant specific data. In countries where only a subset of plants report data for the Tier 3 method or where there is a transition from Tier 2 to Tier 3, it may not be possible to report emissions using Tier 3 for all facilities during the transition. Where data for the Tier 3 method are not available for all plants, Tier 2 could be used for the remaining plants. Also, where data for the Tier 2 method are reported by only a subset of plants or where there is a transition from Tier 1 to Tier 2, it may be possible to determine the share of production represented by non-reporting plants and use this information to estimate the remaining emissions using Tier 1 in order to ensure completeness during the transition period.

### 3.3.2.5 DEVELOPING A CONSISTENT TIME SERIES

N<sub>2</sub>O emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available for all years in the time series, it will be necessary to consider how current plant measurements can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Such a recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.3.3 Uncertainty assessment

### 3.3.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values shown in Table 3.3 are estimates based on expert judgment. In general, default emission factors for gaseous substances have higher uncertainties because mass values for gaseous substances are influenced by temperature and pressure variations and gases are more easily lost through process leaks. The default values for nitric acid production have a relatively high level of uncertainty for two reasons. First, N<sub>2</sub>O may be generated in the gauze reactor section of nitric acid production as an unintended reaction by-product (Cook, 1999). Second, the exhaust gas may or may not be treated for NO<sub>x</sub> control, and the NO<sub>x</sub>



abatement system may or may not reduce (or may even increase) the N<sub>2</sub>O concentration of the treated gas<sup>1</sup>. It is *good practice* to obtain uncertainty estimates at the plant-level which should be lower than uncertainty values associated with default values.

### 3.3.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of nitric acid production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of  $\pm 2$  percent can be used. To reduce uncertainty it is *good practice* to ensure that all activity data are for 100 percent HNO<sub>3</sub>.

## 3.3.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation

### 3.3.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable if higher tier methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### Comparison of emissions estimates using different approaches

If emissions are calculated using data from individual nitric acid plants (bottom-up approach), inventory compilers should compare the estimate to emissions calculated using national production data (top-down approach). They should record the results and investigate any unexplained discrepancies.

Since industrial N<sub>2</sub>O source categories are relatively small compared to other anthropogenic and natural sources, it is not feasible to compare emissions with measured trends in atmospheric N<sub>2</sub>O concentrations.

#### Plant-level data

Inventory compilers should archive sufficient information to allow an independent review of the time series of emissions beginning in the base year, and to explain trends in emissions when making historical comparisons. This is particularly important in cases where recalculations are necessary, for example, when an inventory compiler changes from using default values to actual values determined at the plant level.

#### Revision of direct emission measurements

If plant-level N<sub>2</sub>O measurements are available, inventory compilers should confirm that internationally recognised, standard methods were used. If the measurement practices fail this criterion, then they should evaluate the use of these emissions data. In addition, they should reconsider the uncertainty estimates in light of the QA/QC results.

Inventory compilers should compare plant-based factors to the IPCC defaults to ensure that the plant-specific factors are reasonable. They should explain and document any differences between plant-specific factors and default factors, particularly any differences in plant characteristics that might lead to these differences.

### 3.3.4.2 REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

---

<sup>1</sup> In some cases, processes designed to reduce NO<sub>x</sub> emissions may result in additional N<sub>2</sub>O generation. Increased N<sub>2</sub>O concentrations due to NO<sub>x</sub> abatement technology have been measured at various power plants that employ non-catalytic reduction for NO<sub>x</sub> (Cook, 1999). From at least one nitric acid plant, it is known that NO<sub>x</sub> control resulted in increased N<sub>2</sub>O emissions (Burtscher, 1999).

- Description of the method used;
- Number of nitric acid plants;
- Emission factors;
- Production data;
- Production capacity;
- Number of plants using abatement technology;
- Type of abatement technology, destruction efficiency, and utilisation;
- Any other assumptions.

Plant operators should supply this information to the inventory compiler for compilation, and also archive the information at the site. Plant operators should also log and archive the measurement frequencies and instrumental calibration records where actual plant measurements are made.

Where there are only one or two producers in a country, activity data may be considered confidential. In this case, operators and the inventory compiler should determine the level of aggregation at which information can be reported while still protecting confidentiality. Detailed information including instrumentation records should still be archived at the plant level.

It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced.

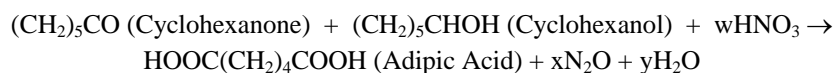
## 3.4 ADIPIC ACID PRODUCTION

### 3.4.1 Introduction

Adipic acid is used in the manufacture of a large number of products including synthetic fibres, coatings, plastics, urethane foams, elastomers and synthetic lubricants. The production of Nylon 6.6 accounts for the bulk of adipic acid use. As noted by Hocking (1998; p.657), 'A large fraction of this consumption is direct, as adipic acid in the production of nylon 6.6, but a substantial fraction of the adipic acid is further processed to give hexamethylene diamine, the other monomer required. A further small fraction of the adipic acid is converted into di-octyl (di-2-ethylhexyl) or di-hexyl esters for use as plasticizers in flexible grades of PVC, etc., or as a high boiling point component of synthetic motor oils'.

### 3.4.2 Methodological issues

Adipic acid is a dicarboxylic acid manufactured from a cyclohexanone/cyclohexanol mixture which is oxidised by nitric acid in the presence of a catalyst to form adipic acid. Nitrous oxide (N<sub>2</sub>O) is generated as an unintended by-product of the nitric acid oxidation stage:



Adipic acid is a significant source of atmospheric N<sub>2</sub>O if not abated. Emissions of N<sub>2</sub>O depend on the amount generated in the production process and the amount destroyed in any subsequent abatement process. Abatement of N<sub>2</sub>O can be intentional through installation of equipment specifically designed to destroy N<sub>2</sub>O in adipic acid plants. Adipic acid production also results in the emissions of NMVOC, CO and NO<sub>x</sub>. Process emissions from the production of adipic acid vary substantially with the level of emission control employed.

#### 3.4.2.1 CHOICE OF METHOD

The decision tree in Figure 3.3 describes *good practice* in adapting the methods to national circumstances. Emissions can be estimated from continuous emissions monitoring (CEM) where emissions are directly measured at all times, periodic emissions monitoring that is undertaken over a period(s) that is reflective of the usual pattern of operation of the plant to derive an emission factor that is multiplied by output to derive emissions, irregular sampling to derive an emission factor that is multiplied by output to derive emissions, or by multiplying a default emission factor by output.

Methods are classified according to the extent of plant-level data that are available. Both Tier 2 and Tier 3 require plant-level activity data.

#### TIER 1 METHOD

Emissions are estimated as follows:

$$\begin{aligned} &\text{EQUATION 3.7} \\ &\text{N}_2\text{O EMISSIONS FROM ADIPIC ACID PRODUCTION – TIER 1} \\ &E_{\text{N}_2\text{O}} = EF \cdot \text{AAP} \end{aligned}$$

Where:

$E_{\text{N}_2\text{O}}$  = N<sub>2</sub>O emissions, kg

EF = N<sub>2</sub>O emission factor (default), kg N<sub>2</sub>O/tonne adipic acid produced

AAP = adipic acid production, tonnes

When applying the Tier 1 method it is *good practice* to assume that there is no abatement of N<sub>2</sub>O emissions and to use the highest default emission factor shown in Table 3.4.

## TIER 2 METHOD

The Tier 2 method uses plant-level production data and default emission factors. Where default values are used to estimate emissions, it is *good practice* to categorise plants according to the abatement technology type employed and the utilisation factor of the abatement technology. Emissions are calculated as follows:

**EQUATION 3.8**  
**N<sub>2</sub>O EMISSIONS FROM ADIPIC ACID PRODUCTION – TIER 2**

$$E_{N_2O} = \sum_{i,j} [EF_i \cdot AAP_i \cdot (1 - DF_j \cdot ASUF_j)]$$

Where:

$E_{N_2O}$  = emissions of N<sub>2</sub>O, kg

$EF_i$  = N<sub>2</sub>O emission factor for technology type  $i$ , kg N<sub>2</sub>O/tonne adipic acid produced

$AAP_i$  = adipic acid production from technology type  $i$ , tonnes

$DF_j$  = destruction factor for abatement technology type  $j$ , fraction

$ASUF_j$  = abatement system utilisation factor for abatement technology type  $j$ , fraction

The basic equation for estimating N<sub>2</sub>O emissions includes additional terms that recognise the use of N<sub>2</sub>O abatement technologies. The N<sub>2</sub>O destruction factor has to be multiplied by an abatement system utilisation factor in order to account for any down-time of the emission abatement equipment (i.e., time the equipment is not operating).

To achieve the highest accuracy, *good practice* is to apply this equation at the plant-level using N<sub>2</sub>O generation and destruction factors developed from plant-specific measurement data. In this case, the national total is equal to the sum of plant totals. Where plant-level information is not available, *good practice* provides default N<sub>2</sub>O generation factors and destruction factors as shown in Table 3.4, Default Factors for Adipic Acid Production, based on abatement technologies implemented. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

## TIER 3 METHOD – DIRECT MEASUREMENT

The Tier 3 method uses plant level production data and plant-level emission factors obtained from direct measurement of emissions. These may be derived from irregular sampling of emissions of N<sub>2</sub>O or periodic emissions monitoring of N<sub>2</sub>O undertaken over a period(s) that reflects the usual pattern of operation of the plant. Emissions can be derived using Equation 3.8. To achieve the highest accuracy, *good practice* is to apply this equation at the plant-level using N<sub>2</sub>O generation and destruction factors developed from plant-specific measurement data where relevant. Given the relatively small number of adipic acid plants (about 23 globally, Choe *et al.*, 1993), obtaining plant-specific information requires few additional resources.

Alternatively, the Tier 3 method uses the results of continuous emissions monitoring (CEM), although it is noted that most plants are unlikely to employ CEM due to the resource costs. Where CEM is employed, emissions can be estimated based on the sum of measured N<sub>2</sub>O emissions derived from the concentration of N<sub>2</sub>O in monitored emissions for each recorded monitoring interval.

### 3.4.2.2 CHOICE OF EMISSION FACTORS

#### TIER 1 METHOD

It is *good practice* to use the default emission factor shown in Table 3.4 and to assume that there is no abatement of N<sub>2</sub>O emissions.

#### TIER 2 METHOD

If plant-level factors are not available, it is *good practice* to use default factors. The Tier 2 method is based on default emission factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. Default factors in Table 3.4 should be used only in cases where plant-specific measurements are not available.

Also included in Table 3.4 are default N<sub>2</sub>O destruction factors for commonly used abatement technologies, and associated uncertainties. To use these factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year. Failure to determine if abatement technologies

are being used can result in overestimation of emissions. Determination of the appropriate values requires that plants be classified according to the abatement technology implemented.

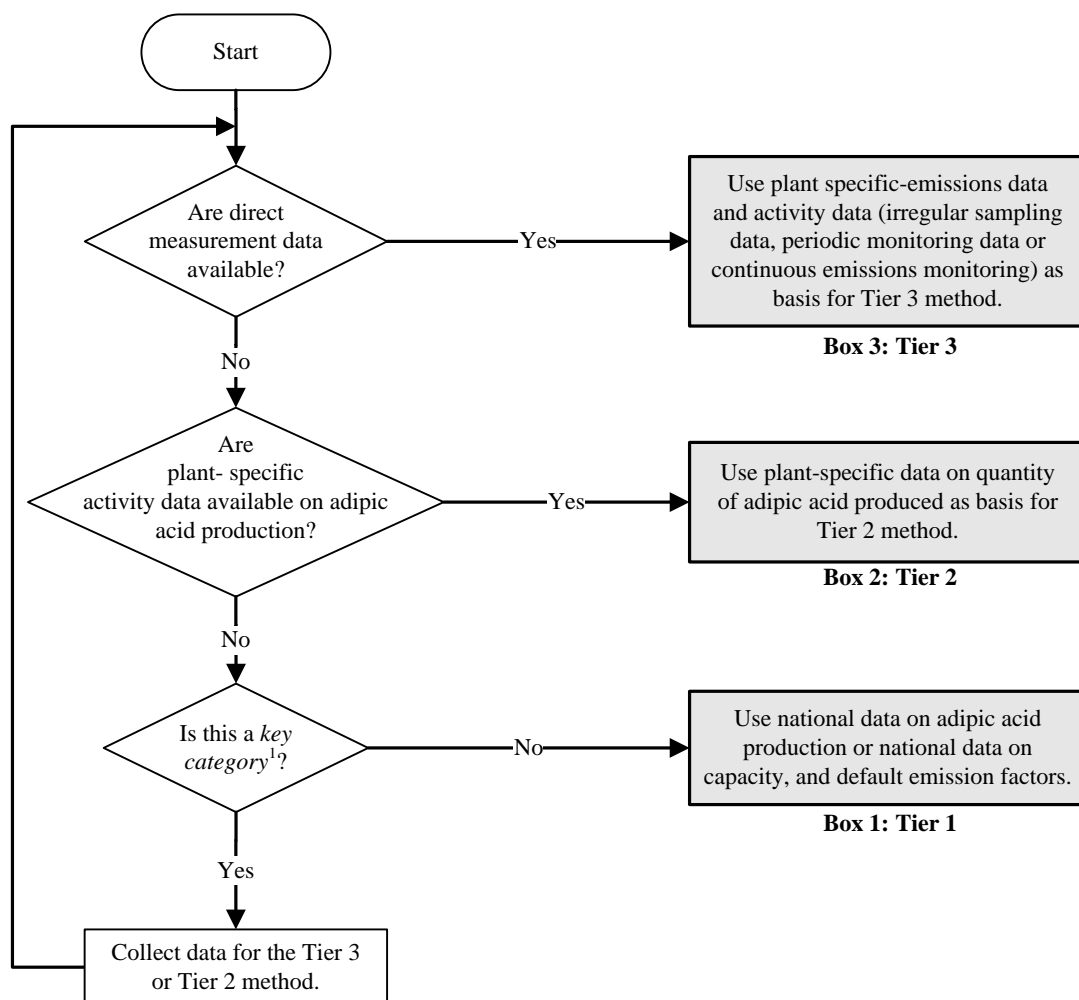
### TIER 3 METHOD

The Tier 3 method requires plant measurements. If the N<sub>2</sub>O abatement system is in use, plant measurements provide the most rigorous data for calculating net emissions (i.e., N<sub>2</sub>O generation and destruction factors). Monitoring N<sub>2</sub>O emissions from adipic acid production is practical because these are point sources and there are a finite number of production plants. Given currently available technology, instrumentation for sampling and monitoring emission rates do not limit precision or accuracy of the overall measurement. Usually sampling frequency and timing is sufficient to avoid systematic errors and to achieve the desired level of accuracy.

Where the N<sub>2</sub>O abatement system is not in use, a plant-specific emission factor can be obtained from periodic monitoring of emissions which is multiplied by the production level to estimate plant-level emissions.

As a general rule, it is *good practice* to conduct sampling and analysis whenever a plant makes any significant process changes that would affect the generation rate of N<sub>2</sub>O, and sufficiently often otherwise to ensure that operating conditions are constant. In addition, plant operators should be consulted annually to determine the specific destruction technologies employed and confirm their use, since technologies may change over time. Precise measurement of the emissions rate and abatement efficiencies requires measurement of both the exit stream and the uncontrolled stream. Where measurement data are available only on the exit stream, *good practice* is to base emissions on these data. In this case, any available estimates of abatement efficiency should be provided only for information purposes and not used to calculate emissions.

**Figure 3.3** Decision tree for estimation of N<sub>2</sub>O emissions from adipic acid production



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

**TABLE 3.4**  
**DEFAULT FACTORS FOR ADIPIC ACID PRODUCTION**

| <b>Production Process</b>            | <b>N<sub>2</sub>O Generation Factor<sup>a,d</sup></b> | <b>Uncertainty Estimate</b>   |
|--------------------------------------|---|---|
| Nitric Acid Oxidation                | 300 kg/tonne adipic acid (uncontrolled)               | ± 10% (based on expert judgement). The range of 300 kg ± 10% encompasses the variability from pure ketone to pure alcohol feedstocks, with most manufacturers somewhere in the middle. <sup>a</sup> |
| <b>Abatement Technology</b>          | <b>N<sub>2</sub>O Destruction Factor<sup>b</sup></b>  | <b>Uncertainty Estimate</b>   |
| Catalytic Destruction                | 92.5%   | 90-95% (based on expert judgement). Manufacturers known to employ this technology include: BASF (Scott, 1998), and DuPont (Reimer, 1999b).  |
| Thermal Destruction                  | 98.5%   | 98-99% (based on expert judgement). Manufacturers known to employ this technology include: Asahi, DuPont, Bayer, and Solutia (Scott, 1998).   |
| Recycle to Nitric Acid               | 98.5%   | 98-99% (based on expert judgement). Manufacturers known to employ this technology include: Alsachemie (Scott, 1998).  |
| Recycle to feedstock for Adipic Acid | 94%   | 90-98% (based on expert judgement). Solutia implemented this technology around 2002.  |
| <b>Abatement System</b>              | <b>Utilisation Factor<sup>d</sup></b>                 | <b>Uncertainty Estimate</b>   |
| Catalytic Destruction                | 89%   | 80-98% (based on expert judgement) <sup>c</sup> .   |
| Thermal Destruction                  | 97%   | 95-99% (based on expert judgement) <sup>c</sup> .   |
| Recycle to Nitric Acid               | 94%   | 90-98% (based on expert judgement) <sup>c</sup> .   |
| Recycle to Adipic Acid               | 89%   | 80-98% (based on expert judgement) <sup>c</sup> .   |

<sup>a</sup> With regard to a value from the Japan Environment Agency (1995) (282 kg N<sub>2</sub>O/tonne adipic acid), it is believed that this manufacturer uses oxidation of pure cyclohexanol (alcohol), instead of a ketone-alcohol mixture (Reimer *et al.*, 1999). This is the only plant known to use this method.

<sup>b</sup> The destruction factor (that represents the technology abatement efficiency) should be multiplied by an abatement system utility factor.

<sup>c</sup> Note that these default values are based on expert judgement and not industry-supplied data or plant-specific measurements. In the first 1-5 years of the abatement technology implementation, the utilisation factor tends to be at the lower end of the range. Lower utility of the equipment typically results because of the need to learn how to operate the abatement system and because more maintenance problems occur during the initial phase. After 1-5 years, the operating experience improves and the utilisation factor would tend to be at the high end of the range.

Source:  
<sup>d</sup> Thiemans and Trogler (1991).  
<sup>e</sup> Reimer (1999b).

### 3.4.2.3 CHOICE OF ACTIVITY DATA

It is *good practice* to compile production data at a level of detail that allows the use of a Tier 2 or Tier 3 method.

#### TIER 1 METHOD

The Tier 1 method requires data on national production of adipic acid. If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

#### TIER 2 METHOD

The Tier 2 method requires plant-level production data disaggregated by abatement technology type. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Typical plant-level production data is accurate to ±2 percent due to the economic value of having accurate information.

## TIER 3 METHOD

As with the Tier 2 method, plant-level production data disaggregated by abatement technology type are required when emissions estimates are derived using data from irregular or periodic sampling of emissions. It is *good practice* to gather activity (production) data at a level of detail consistent with that of any generation and destruction data. Although production is not used in the estimation of emissions where the estimate is based on CEM, these data should be collected and reported to ensure that changes in variables that influence emissions can be monitored over time. Typical plant-level production data is accurate to  $\pm 2$  percent due to the economic value of having accurate information.

### 3.4.2.4 COMPLETENESS

Complete coverage for the adipic acid source category is straightforward because of the small number of readily identifiable plants.

### 3.4.2.5 DEVELOPING A CONSISTENT TIME SERIES

N<sub>2</sub>O emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available for all years in the time series, it will be necessary to consider how current plant measurements can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Such a recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.4.3 Uncertainty assessment

### 3.4.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values shown in Table 3.4 are estimates based on expert judgement. In general, adipic acid default emission factors are relatively certain because they are derived from the stoichiometry of an intended chemical reaction (nitric acid oxidation) and N<sub>2</sub>O-specific abatement systems. The uncertainty in the emission factor for adipic acid represents a variability in N<sub>2</sub>O generation due to differences in the composition of the cyclohexanone and cyclohexanol feedstock (i.e. ketone and alcohol) that are used by different manufacturers. Higher ketone content results in increased N<sub>2</sub>O generation, whereas higher alcohol content results in less N<sub>2</sub>O generation (Reimer, 1999a). Dependent on the process, based on nitric acid (HNO<sub>3</sub>) consumption an individual plant should be able to determine the production of N<sub>2</sub>O within 1 percent. Uncertainties for the default values are shown in Table 3.4.

### 3.4.3.2 ACTIVITY DATA UNCERTAINTIES

Potential N<sub>2</sub>O emissions per metric tonne produced are far greater for adipic acid production than for other industrial sources of N<sub>2</sub>O. Measurements obtained from a properly maintained and calibrated monitoring system can determine emissions using Equation 3.8 to within  $\pm 5$  percent at the 95 percent confidence level. Given the small number of adipic acid plants, the uncertainty in national production data (Tier 1) is the same as for plant-level data, namely,  $\pm 2$  percent.

## 3.4.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation

### 3.4.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1 and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this

source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this source category are outlined below.

### **Comparison of emissions estimates using different approaches**

If emissions are calculated using data from individual adipic acid plants (bottom-up approach), inventory compilers should compare the estimate to emissions calculated using national production data (top-down approach). They should record the results and investigate any unexplained discrepancies.

Since industrial N<sub>2</sub>O source categories are relatively small compared to other anthropogenic and natural sources, it is not feasible to compare emissions with measured trends in atmospheric N<sub>2</sub>O concentrations.

### **Plant-level data**

Inventory compilers should archive sufficient information to allow an independent review of the time series of emissions beginning in the base year, and to explain trends in emissions when making historical comparisons. This is particularly important in cases where recalculations are necessary, for example, when an inventory compiler changes from using default values to actual values determined at the plant level.

### **Revision of direct emission measurements**

If plant-level N<sub>2</sub>O measurements are available, it is suggested that inventory compilers confirm that internationally recognised, standard methods were used. If the measurement practices fail this criterion, then they should evaluate the use of these emissions data. In addition, they should reconsider the uncertainty estimates in light of the QA/QC results.

Inventory compilers are encouraged to compare plant-based factors to the IPCC defaults to ensure that the plant-specific factors are reasonable. They should explain and document any differences between plant-specific factors and default factors, particularly any differences in plant characteristics that might lead to these differences.

## **3.4.4.2 REPORTING AND DOCUMENTATION**

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

- Description of the method used;
- Number of adipic acid plants;
- Emission factors;
- Production data;
- Production capacity;
- Number of plants using abatement technology;
- Type of abatement technology, destruction efficiency, and utilisation;
- Any other assumptions.

Plant operators should supply this information to the inventory compiler for compilation, and also archive the information at the site. Plant operators should also log and archive the measurement frequencies and instrumental calibration records where actual plant measurements are made.

Where there are only one or two producers in a country, as could often be the case for adipic acid production, activity data may be considered confidential. In this case, operators and the inventory compiler should determine the level of aggregation at which information can be reported while still protecting confidentiality. Detailed information including instrumentation records should still be archived at the plant level.

It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced.



## 3.5 CAPROLACTAM, GLYOXAL AND GLYOXYLIC ACID PRODUCTION

### 3.5.1 Introduction

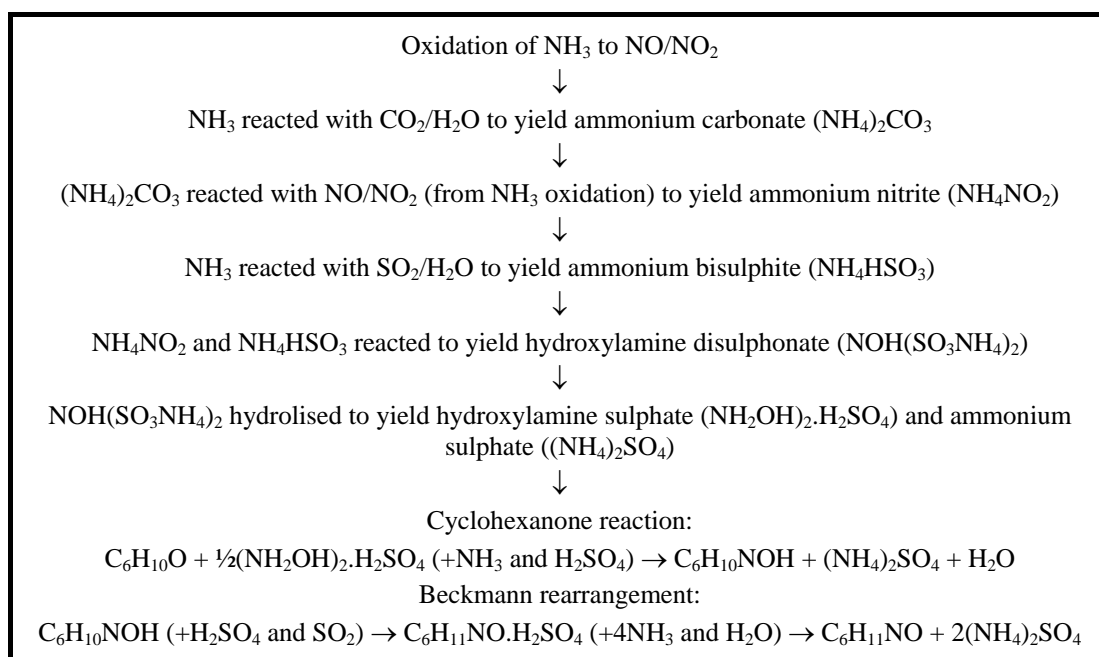
This section addresses the production of three chemicals - caprolactam, glyoxal, and glyoxylic acid - that are potentially important sources of nitrous oxide (N<sub>2</sub>O) emissions in the countries in which the chemicals are produced. The methodology for caprolactam is discussed in detail and is suitable for application to estimation of emissions from glyoxal and glyoxylic acid. In Section 3.5.3, the production processes for glyoxal and glyoxylic acid that give rise to emissions of N<sub>2</sub>O are outlined. Default generation factors, destruction factors, and emission factors are provided based on information from Clariant (France) (Babusiaux, 2005).

### 3.5.2 Caprolactam

Almost all of the annual production of caprolactam (C<sub>6</sub>H<sub>11</sub>NO) is consumed as the monomer for nylon-6 fibres and plastics (Kirk-Othmer, 1999; p.310), with a substantial proportion of the fibre used in carpet manufacturing. All commercial processes for the manufacture of caprolactam are based on either toluene or benzene.

#### 3.5.2.1 METHODOLOGICAL ISSUES

Where caprolactam is produced from benzene, the main process, the benzene is hydrogenated to cyclohexane which is then oxidised to produce cyclohexanone (C<sub>6</sub>H<sub>10</sub>O). The classical route (Raschig process) and basic reaction equations for production from cyclohexanone are (Reimschuessel, 1977; p.83: Lowenheim and Moran, 1975; p. 201):



Lowenheim and Moran (1975; p. 202) summarise the Raschig production process as follows. Caprolactam is produced via Beckmann rearrangement (conversion of a ketone oxime into an amide, usually using sulphuric acid as a catalyst) by the addition of hydroxylamine sulphate to cyclohexanone. Hydroxylamine sulphate is produced from ammonium nitrate and sulphur dioxide. Ammonia gas and air are fed to a converter where ammonia is converted to hydroxylamine disulphonate by contacting it with ammonium carbonate and sulphur dioxide in series. Ammonium carbonate is produced by dissolving ammonia and carbon dioxide in water, and sulphur dioxide by burning sulphur. The disulphonate is hydrolysed to hydroxylamine sulphate and ammonium sulphate. The addition of hydroxylamine sulphate to cyclohexanone produces cyclohexanone oxime which is converted to caprolactam by the Beckmann rearrangement.

Production of caprolactam can give rise to emissions of nitrous oxide (N<sub>2</sub>O) from the ammonia oxidation step, emissions of CO<sub>2</sub> from the ammonium carbonate step, emissions of sulphur dioxide (SO<sub>2</sub>) from the ammonium bisulphite step, and emissions of NMVOCs. Emissions of CO<sub>2</sub>, SO<sub>2</sub> and NMVOCs from the conventional process are unlikely to be significant in well-managed plants. The main greenhouse gas to be accounted for from caprolactam production is N<sub>2</sub>O. Modified caprolactam production processes are primarily concerned with elimination of the high volumes of ammonium sulphate that are produced as a by-product of the conventional process (Reimschuessel, 1977; p.84). NH<sub>3</sub> oxidation remains an integral part of all processes to obtain the NO/NO<sub>2</sub> required.

## CHOICE OF METHOD

Estimation of emissions of N<sub>2</sub>O from caprolactam production can be treated as analogous to estimation of emissions of N<sub>2</sub>O from nitric acid production. Both production processes involve an initial step of NH<sub>3</sub> oxidation which is the source of N<sub>2</sub>O formation and emissions.

The choice of *good practice* method depends on national circumstances. The decision tree in Figure 3.4 describes *good practice* in adapting the methods to national circumstances. Emissions can be estimated from continuous emissions monitoring (CEM) where emissions are directly measured at all times, periodic emissions monitoring that is undertaken over a period(s) that is reflective of the usual pattern of operation of the plant to derive an emission factor that is multiplied by output to derive emissions, irregular sampling to derive an emission factor that is multiplied by output to derive emissions, or by multiplying a default emission factor by output.

Methods are classified according to the extent of plant-level data that are available. Both Tier 2 and Tier 3 are require plant-level activity data.

### Tier 1 method

Emissions are estimated as follows:

|   |
|---|
| <p><b>EQUATION 3.9</b><br/> <b>N<sub>2</sub>O EMISSIONS FROM CAPROLACTAM PRODUCTION – TIER 1</b><br/> <math display="block">E_{N_2O} = EF \cdot CP</math></p> |
|---|

Where:

$E_{N_2O}$  = N<sub>2</sub>O emissions, kg

EF = N<sub>2</sub>O emission factor (default), kg N<sub>2</sub>O/tonne caprolactam produced

CP = caprolactam production, tonnes

When applying the Tier 1 method it is *good practice* to assume that there is no abatement of N<sub>2</sub>O emissions and to use the highest default emission factor shown in Table 3.5.

### Tier 2 method

Information on emissions arising from caprolactam production and control technologies is limited. Where plant-level information is not available, *good practice* provides default N<sub>2</sub>O generation factors as shown in Table 3.5. The default factors are based on N<sub>2</sub>O emissions from nitric acid plants because there is no information on caprolactam plants and the initial reaction step of oxidation of ammonia is similar for both processes. *Good practice* encourages the development of factors specific to caprolactam plants.

The number of caprolactam plants is relatively small (approximately 42 plants with around 19 plants using DSM (Stamicarbon) technology). It is unlikely that there are substantial variations in the N<sub>2</sub>O generation factors between plants. Where default values are used to estimate emissions from caprolactam production, it is *good practice* to ascertain the extent to which plant emissions vary according to type and to use an appropriate N<sub>2</sub>O generation factor.

The Tier 2 method uses plant-level production data disaggregated by technology type and default emission factors classified by technology type. Emissions are calculated as follows:

**EQUATION 3.10**  
**N<sub>2</sub>O EMISSIONS FROM CAPROLACTAM PRODUCTION – TIER 2**

$$E_{N_2O} = \sum_{i,j} [EF_i \cdot CP_i \cdot (1 - DF_j \cdot ASUF_j)]$$

Where:

$E_{N_2O}$  = emissions of N<sub>2</sub>O, kg

$EF_i$  = N<sub>2</sub>O emission factor for technology type  $i$ , kg N<sub>2</sub>O/tonne caprolactam produced

$CP_i$  = caprolactam production from technology type  $i$ , tonnes

$DF_j$  = destruction factor for abatement technology type  $j$ , fraction

$ASUF_j$  = abatement system utilisation factor for abatement technology type  $j$ , fraction

The basic equation for estimating N<sub>2</sub>O emissions includes additional terms that recognise current and the potential future use of N<sub>2</sub>O abatement technologies. The N<sub>2</sub>O destruction factor has to be multiplied by an abatement system utilisation factor in order to account for any down-time of the emission abatement equipment (i.e. time the equipment is not operating).

Where plant-level information is not available, *good practice* provides default N<sub>2</sub>O generation factors as shown in Table 3.5, Default Factors for Caprolactam Production, based on plant types classified by age. To achieve the highest accuracy, *good practice* is to apply Equation 3.10 at the plant-level taking into account N<sub>2</sub>O generation and destruction factors developed from plant-specific measurement data. In this case, the national total is equal to the sum of plant totals.

### **Tier 3 method – direct measurement**

The Tier 3 method uses plant level production data and plant-level emission factors obtained from direct measurement of emissions. These may be derived from irregular sampling of emissions of N<sub>2</sub>O or periodic emissions monitoring of N<sub>2</sub>O undertaken over a period(s) that reflects the usual pattern of operation of the plant. Emissions can be derived using Equation 3.10.

Alternatively, the Tier 3 method uses the results of continuous emissions monitoring (CEM), although it is noted that most plants are unlikely to employ CEM due to the resource costs. Where CEM is employed, emissions can be estimated based on the sum of measured N<sub>2</sub>O emissions derived from the concentration of N<sub>2</sub>O in monitored emissions for each recorded monitoring interval.

## **CHOICE OF EMISSION FACTORS**

### **Tier 1 method**

It is *good practice* to use the emission factor shown in Table 3.5 and to assume that there is no abatement of N<sub>2</sub>O emissions.

### **Tier 2 method**

If plant-level factors are not available, it is *good practice* to use default factors. The Tier 2 method uses a default factor. Default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. This is especially true for caprolactam production where the value is based on high pressure nitric acid plants. Default factor in Table 3.5 should be used only in cases where plant-specific measurements are not available.

### **Tier 3 method**

Plant measurements provide the most rigorous data for calculating net emissions (i.e., N<sub>2</sub>O generation and destruction factors). Monitoring N<sub>2</sub>O emissions from caprolactam production is practical because these are point sources and there are a finite number of production plants. Given currently available technology, instrumentation for sampling and monitoring emission rates do not limit precision or accuracy of the overall measurement. Usually sampling frequency and timing is sufficient to avoid systematic errors and to achieve the desired level of accuracy.

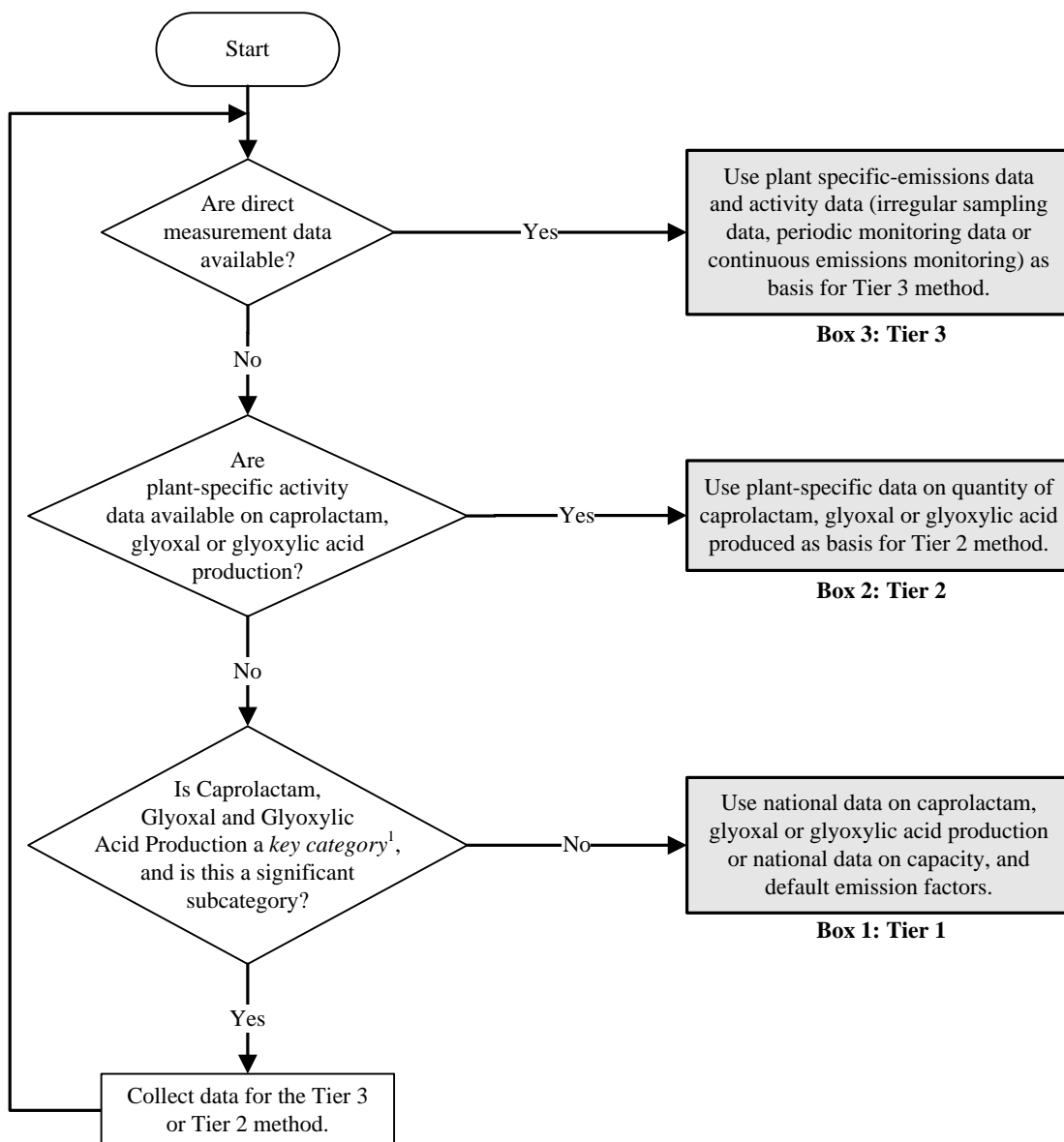
As a general rule, it is *good practice* to conduct sampling and analysis whenever a plant makes any significant process changes that would affect the generation rate of N<sub>2</sub>O, and sufficiently often otherwise to ensure that operating conditions are constant. In addition, plant operators should be consulted annually to determine the specific destruction technologies employed and confirm their use, since technologies may change over time. Precise measurement of the emissions rate and abatement efficiencies requires measurement of both the exit

stream and the uncontrolled stream. Where measurement data are available only on the exit stream, *good practice* is to base emissions on these data. In this case, any available estimates of abatement efficiency should be provided only for information purposes and not used to calculate emissions.

| TABLE 3.5<br>DEFAULT FACTOR FOR CAPROLACTAM PRODUCTION |   |             |
|--|---|-------------|
| Production Process                                     | N <sub>2</sub> O Emission Factor<br>(kg N <sub>2</sub> O/tonne caprolactam) | Uncertainty |
| Raschig  | 9.0 <sup>a</sup>  | ± 40%       |

<sup>a</sup> Based on high pressure plants for nitric acid production.  
Source: Default Factors for Nitric Acid Production. (See Table 3.3 in this chapter.)

**Figure 3.4** Decision tree for estimation of N<sub>2</sub>O emissions from caprolactam, glyoxal or glyoxylic acid production



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

## CHOICE OF ACTIVITY DATA

It is *good practice* to compile production data at a level of detail that allows the use of Tier 2 or Tier 3 method.

### Tier 1 method

The Tier 1 method requires data on national production of caprolactam. If national-level activity data are not available, information on production capacity can be used. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent  $\pm$  20 percent (i.e., a range of 60-100 percent).

### Tier 2 method

The Tier 2 method requires plant-level production data disaggregated by the age the plant. If additional information on technology type and abatement technology is available, it is *good practice* to collect this information and disaggregate production data according to the information obtained. That is, it is *good practice* to gather activity (production) data at a level of detail consistent with that of generation and destruction data. Where plant-level emission factors are used, *good practice* is to collect plant-level production data. Typical plant-level production data are accurate to  $\pm 2$  percent due to the economic value of having accurate information.

### Tier 3 method

The Tier 3 method require plant-level production data disaggregated by technology type when emissions estimates are derived using data from irregular or periodic sampling of emissions. It is *good practice* to collect activity (production) data at a level of detail consistent with that of any generation and destruction data. Although production is not used in the estimation of emissions where the estimate is based on CEM, these data should be collected and reported to ensure that changes in variables that influence emissions can be monitored over time. Typical plant-level production data are accurate to  $\pm 2$  percent due to the economic value of having accurate information.

## COMPLETENESS

Complete coverage requires accounting for all plants and emissions of all direct greenhouse gases. In addition to N<sub>2</sub>O, there may be non-combustion emissions of CO<sub>2</sub>, NO<sub>x</sub>, NMVOCs and SO<sub>2</sub>. In order to include emissions of the indirect greenhouse gases (NO<sub>x</sub>, NMVOCs and SO<sub>2</sub>), see guidance provided in Chapter 7 of Volume 1: General Guidance and Reporting. Plant-level information will be required to enable emissions estimation. Over time default values could be developed as more information becomes available.

There will be few caprolactam plants in a country, and it is suggested that emissions are calculated from plant specific data.

## DEVELOPING A CONSISTENT TIME SERIES

N<sub>2</sub>O emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available for all years in the time series, it will be necessary to consider how current plant measurements can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Such a recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

### 3.5.2.2 UNCERTAINTY ASSESSMENT

#### EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default value shown in Table 3.5 is an estimate based on default values for nitric acid plants. In general, default emission factors for gaseous substances have higher uncertainties because mass values for gaseous substances are influenced by temperature and pressure variations and gases are more easily lost through process leaks. The default values for caprolactam production have a relatively high level of uncertainty due to the limited information available. It is *good practice* to obtain uncertainty estimates at the plant-level which should be lower than uncertainty values associated with default values.

#### ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical

agencies collect data from the population of nitric acid production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of  $\pm 2$  percent can be used.

### **3.5.2.3 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION**

#### **QUALITY ASSURANCE/QUALITY CONTROL**

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable if higher tier methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### **Comparison of emissions estimates using different approaches**

If emissions are calculated using data from individual caprolactam plants (bottom-up approach), inventory compilers should compare the estimate to emissions calculated using national production data (top-down approach). They should record the results and investigate any unexplained discrepancies.

Since industrial N<sub>2</sub>O source categories are relatively small compared to other anthropogenic and natural sources, it is not feasible to compare emissions with measured trends in atmospheric N<sub>2</sub>O concentrations.

#### **Plant-level data**

Inventory compilers should archive sufficient information to allow an independent review of the time series of emissions beginning in the base year, and to explain trends in emissions when making historical comparisons. This is particularly important in cases where recalculations are necessary, for example, when an inventory compiler changes from using default values to actual values determined at the plant level.

#### **Revision of direct emission measurements**

If plant-level N<sub>2</sub>O measurements are available, inventory compilers should confirm that internationally recognised, standard methods were used. If the measurement practices fail this criterion, then they should evaluate the use of these emissions data. In addition, they should reconsider the uncertainty estimates in light of the QA/QC results.

Inventory compilers should compare plant-based factors to the IPCC defaults to ensure that the plant-specific factors are reasonable. They should explain and document any differences between plant-specific factors and default factors, particularly any differences in plant characteristics that might lead to these differences.

### **REPORTING AND DOCUMENTATION**

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

- Description of the method used;
- Number of caprolactam plants;
- Emission factors;
- Production data;
- Production capacity;
- Number of plants using abatement technology;
- Type of abatement technology, destruction efficiency, and utilisation;
- Any other assumptions.

Plant operators should supply this information to the inventory compiler for compilation, and also archive the information at the site. Plant operators should also log and archive the measurement frequencies and instrumental calibration records where actual plant measurements are made.

Where there are only one or two producers in a country as will be the case for caprolactam producers, activity data may be considered confidential. In this case, operators and the inventory compiler should determine the

level of aggregation at which information can be reported while still protecting confidentiality. Detailed information including instrumentation records should still be archived at the plant level.

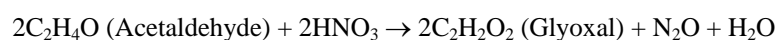
It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced.

### 3.5.3 Glyoxal and glyoxylic acid production

Glyoxal (ethanedial) (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>) is produced from oxidation of acetaldehyde (ethanal) (C<sub>2</sub>H<sub>4</sub>O) with concentrated nitric acid (HNO<sub>3</sub>). Glyoxal can also be produced from catalytic oxidation of ethylene glycol (ethanediol) (CH<sub>2</sub>OHCH<sub>2</sub>OH). Glyoxal is used as a crosslinking agent for vinyl acetate/acrylic resins, disinfectant, gelatine hardening agent, textile finishing agent (permanent-press cotton, rayon fabrics), wet-resistance additive (paper coatings) (Ashford, 1994; p.454).

Glyoxylic acid is produced by nitric acid oxidation of glyoxal. Glyoxylic acid is used for the production of synthetic aromas, agrochemicals and pharmaceutical intermediates (Babusiaux, 2005; p.1).

The basic reaction equation for the production of glyoxal from acetaldehyde is:



The stoichiometric relationship indicates that complete reaction will result in 0.543 tonnes of N<sub>2</sub>O per tonne of glyoxal. Under commercial conditions, the yield of N<sub>2</sub>O per tonne of glyoxal is approximately 0.52 tonnes (Babusiaux, 2005; p.1).

Glyoxylic acid production is a batch process where nitric acid is reduced to NO and N<sub>2</sub>O with NO recovered as HNO<sub>3</sub> in the process. N<sub>2</sub>O arises in the production process through a secondary reaction where glyoxal is converted to oxalic acid (COOH)<sub>2</sub>.

Default factors for glyoxal and glyoxylic acid production are shown in Table 3.6. Emissions can be estimated using the same approach as described in the foregoing for caprolactam. To use default destruction factors, inventory compilers should verify that the abatement technology is installed at individual plants and operated throughout the year.

| <b>Product</b> | <b>N<sub>2</sub>O Generation Factor<br/>(tonnes N<sub>2</sub>O/tonne)</b> | <b>N<sub>2</sub>O Destruction Rate<br/>(%)</b> | <b>N<sub>2</sub>O Emission Factor<br/>(tonnes N<sub>2</sub>O/tonne)</b> | <b>Uncertainty<br/>(%)</b> |
|----------------|---|--|---|----------------------------|
| Glyoxal        | 0.52  | 80   | 0.10  | ±10                        |
| Glyoxylic acid | 0.10  | 80   | 0.02  | ±10                        |

Source: Babusiaux (2005)

## 3.6 CARBIDE PRODUCTION

### 3.6.1 Introduction

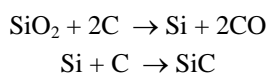
Greenhouse gas emissions are associated with production of silicon carbide (SiC) and calcium carbide (CaC<sub>2</sub>). The production of carbide can result in emissions of carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), carbon monoxide (CO) and sulphur dioxide (SO<sub>2</sub>). Silicon carbide is a significant artificial abrasive. It is produced from silica sand or quartz and petroleum coke. Calcium carbide is used in the production of acetylene, in the manufacture of cyanamide (a minor historical use), and as a reductant in electric arc steel furnaces. It is made from two carbon-containing raw materials: calcium carbonate (limestone) and petroleum coke.

Use of carbon-containing raw materials in the production processes result in emissions of CO<sub>2</sub> and CO. The presence of hydrogen-containing volatile compounds and sulphur (S) in the petroleum coke may cause formation and emission to the atmosphere of CH<sub>4</sub> and SO<sub>2</sub>.

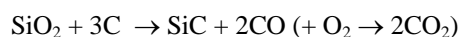
### 3.6.2 Methodological issues

#### CO<sub>2</sub> AND CH<sub>4</sub> FROM SILICON CARBIDE PRODUCTION

Silicon carbide is produced from silica sand or quartz and petroleum coke, which is used as a carbon source, according to the reactions (Austin, 1984; p. 262):



The formula describing the overall reaction is given below but in practice it does not proceed in the stoichiometric proportions indicated:



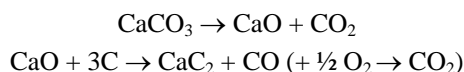
In the production process, silica sand and carbon are mixed in an approximate molar ratio of 1:3. Some carbon, about 35 percent, is contained in the product and the rest is converted to CO<sub>2</sub> in excess oxygen and released to the atmosphere as a process by-product.

The petroleum coke used in this process may contain volatile compounds, which will form methane. Some methane will escape to the atmosphere, particularly during start-up.

#### CO<sub>2</sub> FROM CALCIUM CARBIDE PRODUCTION

Calcium carbide (CaC<sub>2</sub>) is made by heating calcium carbonate (limestone) and subsequently reducing CaO with carbon e.g., petroleum coke. Both steps lead to emissions of CO<sub>2</sub>. Around 67 percent of the carbon from petroleum coke will be contained in the product.

The basic reactions are:



The CO gas will be used as an energy source in most plants.

#### BOX 3.4 DOUBLE COUNTING

To avoid double counting, CO<sub>2</sub> emission from combusting CO gas generated in the process of CaC<sub>2</sub> production should be accounted in the **IPPU Sector**, and should not be included in the **Energy Sector**. Petroleum coke used in the production process should be deducted from the **Energy Sector** as a non-energy use of petroleum coke.

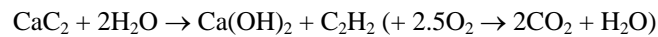
The most important application of calcium carbide is producing acetylene (C<sub>2</sub>H<sub>2</sub>) by reacting CaC<sub>2</sub> with water. A substantial use of acetylene is welding applications. Acetylene is also used in chemical synthesis for the



production of acetaldehyde, acetic acid, acetic anhydride, and as a feedstock to manufacture 'acetylene black', a form of carbon black. Frequently, acetylene is not produced within the same plant that produces CaC<sub>2</sub> and this needs to be taken into account when applying higher tier methods to estimating CO<sub>2</sub> emissions from CaC<sub>2</sub> use.

Use of acetylene in chemical synthesis and production of acetylene black results in carbon contained in the products reducing the total emissions of CO<sub>2</sub> that are related to CaC<sub>2</sub> use. Acetylene may be produced from partial oxidation of natural gas as well as from CaC<sub>2</sub>. The approach to accounting for acetylene in these uses is outlined in Section 3.9 of this volume.

Production and use of acetylene for welding applications is summarised by reaction:



Where acetylene is used in welding applications, emissions can be derived from the quantity of CaC<sub>2</sub> used in the production of this acetylene on the assumption that the acetylene will be used in a relatively short period of time after production.

#### BOX 3.5

##### ALLOCATION OF EMISSIONS FROM CaO PRODUCTION

CaO (lime) might be produced in-house or at a plant other than the carbide plant. In either case, the emissions from the CaO step should be reported as emissions from lime production (Section 2.3 of this volume) and only the emissions from reaction of CaO with petroleum coke and use of the product to produce acetylene for welding applications should be reported as emissions from calcium carbide.

### 3.6.2.1 CHOICE OF METHOD

Methods are classified according to the extent of plant-level data that are available. The Tier 1 method is based on default values and national statistics. Tier 2 is based on plant-level data on production and use of CaC<sub>2</sub> in acetylene production for welding applications. The Tier 3 method is based on plant-level data on petroleum coke input (including the carbon content factor (CCF) and carbon oxidation factor (COF) if available; alternatively, country specific Energy Sector values may be used), use of CaC<sub>2</sub> in acetylene production for welding applications, and plant-level emission factors where relevant.

Both Tier 2 and Tier 3 are based on plant-level activity data. The choice of method to estimate emissions of CO<sub>2</sub> and CH<sub>4</sub> depends on national circumstances as shown in Figure 3.5.

### CO<sub>2</sub> AND CH<sub>4</sub> FROM CARBIDE PRODUCTION

#### Tier 1 method

Emissions from carbide production can be estimated from activity data (AD) on petroleum coke consumption or carbide production, calcium carbide used in the production of acetylene used in welding applications, and default emission factors. Where AD on petroleum coke consumption are used the CCF and COF of the petroleum coke can be obtained from Volume 2, Chapter 1 and the result must be multiplied by 44/12 to convert C to CO<sub>2</sub>. The basic equation for estimating emissions is:

#### EQUATION 3.11

##### EMISSIONS FROM CARBIDE PRODUCTION

$$E_{\text{CO}_2} = \text{AD} \cdot \text{EF}$$

Where:

E<sub>CO<sub>2</sub></sub> = emissions of CO<sub>2</sub>, tonnes

AD = activity data on petroleum coke consumption or carbide production, tonnes raw material used or tonnes carbide produced

EF = CO<sub>2</sub> emission factor. There are two options as follows:

When carbide production is used as activity data, EF should be average CO<sub>2</sub> emissions per unit of output for carbide production, tonnes CO<sub>2</sub>/tonne carbide production.

When petroleum coke consumption is used as activity data, EF should be CCF (carbon content

factor) multiplied by COF (carbon oxidation factor) multiplied by 44/12 and adjusted to account for the C contained in the product, tonnes CO<sub>2</sub>/tonne material used

$$\text{Adjustment factor for SiC} = 0.35 \Rightarrow \text{Emission factor} = 0.65 \cdot \text{CCF} \cdot \text{COF} \cdot 44/12;$$

$$\text{Adjustment factor for CaC}_2 = 0.67 \Rightarrow \text{Emission factor} = 0.33 \cdot \text{CCF} \cdot \text{COF} \cdot 44/12.$$

Equation 3.11 can also be used to estimate CH<sub>4</sub> emissions, where EF is the appropriate emission factor for CH<sub>4</sub>.

Estimation of emissions from CaC<sub>2</sub> needs to include emissions of CO<sub>2</sub> indirectly attributable to CaC<sub>2</sub> that is used in acetylene production. Equation 3.11 can be applied where AD is the amount of CaC<sub>2</sub> used and EF is the emission factor associated with this use. Under the Tier 1 method it is *good practice* to assume that all CaC<sub>2</sub> used in acetylene production gives rise to CO<sub>2</sub> emissions.

### Tier 2 method

The Tier 2 method uses plant-level data on production of carbide and the amount of C contained in the product. For CaC<sub>2</sub>, data on the use of CaC<sub>2</sub> for the production of acetylene used in welding applications is also required. Emissions from production and use can be estimated with Equation 3.11 using default emission factors. Where acetylene is produced from CaC<sub>2</sub> at another location and the quantity of CaC<sub>2</sub> used for this purpose is not known, it is *good practice* to document this fact.

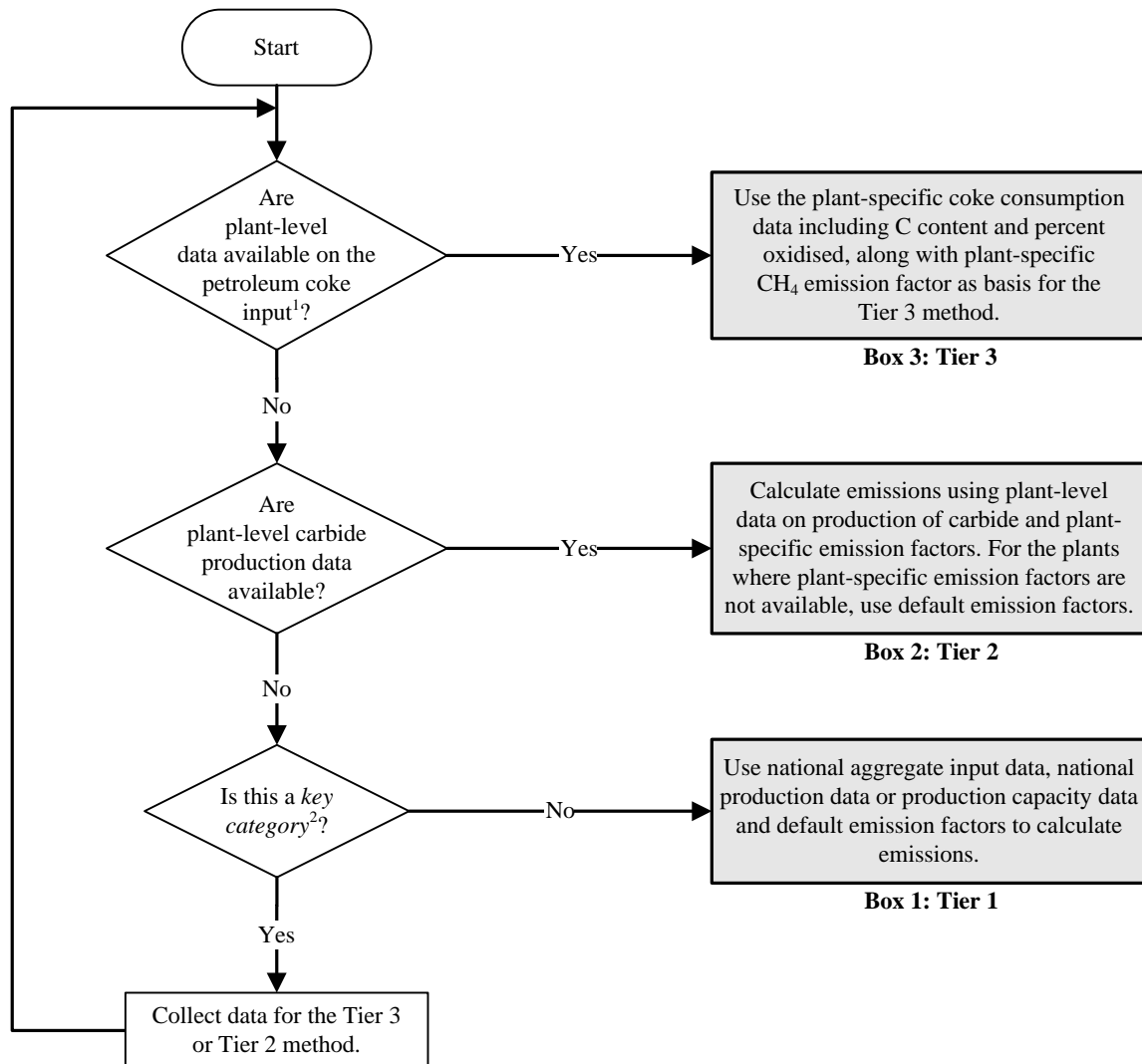
### Tier 3 method

The Tier 3 method requires plant-level data on the petroleum coke input along with the CCF and COF if available; alternatively, country specific Energy Sector values for CCF and COF may be used. Plant-level data on the amount of C contained in the product are also required.

In the case of CaC<sub>2</sub>, data on the use of CaC<sub>2</sub> for the production of acetylene used in welding applications are required, as are plant-level emission factors. Where acetylene is produced from CaC<sub>2</sub> at another location and the quantity of CaC<sub>2</sub> used for this purpose is not known, it is *good practice* to document this fact. In addition, plant-level emission factors for CH<sub>4</sub> need to be collected. Equation 3.11 can be applied to estimate emissions for each plant and total national emissions are the sum of these estimates.

Production data are not used in the calculation but should be collected for reporting purposes. Where acetylene production data cannot be disaggregated by use, national inventory compilers using the Tier 3 method are encouraged to account for any emissions at the point where they arise; for example, emissions from acetylene use in welding applications should be accounted for at the point of use of acetylene using a country specific emission factor. A similar approach should be followed for other uses of acetylene.

**Figure 3.5** Decision tree for estimation of CO<sub>2</sub> and CH<sub>4</sub> emissions from carbide production



Note:

1. "Input data" means raw material consumption data.
2. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

### 3.6.2.2 CHOICE OF EMISSION FACTORS

#### Tier 1 method

The Tier 1 method uses default values for CCF, COF and C contained in the product where petroleum coke is used in the estimation. Alternatively, where carbide production is used, the method uses default emission factors shown in Tables 3.7 and 3.8 where relevant. In both cases, the default factor for CaC<sub>2</sub> use is applied.

#### Tier 2 method

As for the Tier 1 method, the Tier 2 method uses default emission factor values except for the amount of C contained in the product, where plant-level data are required.

#### Tier 3 method

The Tier 3 method requires plant-level data for all variables except for CCF and COF of the petroleum coke where country specific Energy Sector values may be used. This includes plant-level emission factors for lime if it is produced in-house and plant-level emission factors for CaC<sub>2</sub> used to produce acetylene for welding applications.

### CO<sub>2</sub> from silicon carbide production

More carbon is needed in the silicon carbide production process than calculated from a stoichiometric reaction. The excess carbon is oxidised during the process, little is left as ash (Raanes, 1991). Typical default values for Norwegian plants for carbon content in coke are 97 percent and for carbon contained in product, 35 percent. This implies a typical emission factor of 2.3 tonnes CO<sub>2</sub>/tonne petroleum coke used (IPCC, 1997), or 2.62 tonnes CO<sub>2</sub>/tonne carbide produced.

### CH<sub>4</sub> from silicon carbide production

Measurements at Norwegian plants suggest emission factors of 10.2 kg CH<sub>4</sub>/tonne petroleum coke or 11.6 kg CH<sub>4</sub>/tonne carbide produced (IPCC, 1997).

| Process                       | Emission Factor<br>(tonnes CO <sub>2</sub> /tonne<br>raw material used) | Emission Factor<br>(kg CH <sub>4</sub> /tonne raw<br>material used) | Emission Factor<br>(tonnes CO <sub>2</sub> /tonne<br>carbide produced) | Emission Factor<br>(kg CH <sub>4</sub> /tonne<br>carbide produced) |
|-------------------------------|---|---|--|--|
| Silicon carbide<br>production | 2.30  | 10.2  | 2.62   | 11.6   |

Source: Revised 1996 IPCC National Greenhouse Gas Inventories, Vol.3, p.2.21 (IPCC, 1997)

### CO<sub>2</sub> from calcium carbide production

Emission factors may be derived from the use of raw materials (petroleum coke) and from carbide production using a mass-balance approach. Limestone used in carbide manufacture contains about 98 percent CaCO<sub>3</sub> and is accounted for elsewhere. 1 750 kg limestone (or 950 kg CaO), 640 kg of petroleum coke and 20 kg carbon electrodes are required to produce 1 tonne of carbide.

The default emission factors for estimating emissions are included in Table 3.8.

| Process            | Default Emission Factor<br>(tonnes CO <sub>2</sub> /tonne raw material used) | Default Emission Factor<br>(tonnes CO <sub>2</sub> /tonne carbide produced) |
|--------------------|--|---|
| Petroleum coke use | 1.70   | 1.090   |
| Use of product     | not relevant   | 1.100   |

Source: Revised 1996 IPCC National Greenhouse Gas Inventories, Vol.3, p.2.22 (IPCC, 1997)

The theoretical emission factor calculated from a stoichiometric reaction is lower for the petroleum coke step than that shown in the table. Excess carbon is oxidised in the process and the suggested emission factors were calculated from the actual use of raw materials in a Norwegian plant. The emission factor for acetylene use is calculated from the actual (not stoichiometric) carbon content of carbide.

The CO<sub>2</sub> emissions may be lowered by utilising the gas when producing dicyanodiamide from carbide (Olsen, 1991).

## 3.6.2.3 CHOICE OF ACTIVITY DATA

### Tier 1 method

The Tier 1 method requires data on petroleum coke used in carbide production or national production of carbide. These data may be obtained from national statistics or from industrial and trade organizations representing carbide and petroleum coke producers.

### Tier 2 method

Activity data required for the Tier 2 method comprise plant-level data on carbide produced and the amount of CaC<sub>2</sub> used in the production of acetylene for welding applications.

### Tier 3 method

The Tier 3 method requires plant-level activity data for all variables including the petroleum coke input and  $\text{CaC}_2$  used to produce acetylene for welding applications.

The Tier 2 methods require the collection of activity data from individual plants or companies. In Tier 1 the activity data provided by national statistics or by industrial and trade organizations associated with carbide and petroleum coke production should be used. However, if sufficient plant-specific or company-specific data are available, they may be used to estimate emissions.

#### 3.6.2.4 COMPLETENESS

Carbide production plants are generally known in each country. As a result, carbide production data may be available in national statistical databases, or could be collected, even if these data have not been published in national statistics. The petroleum coke consumption data may be obtained directly from carbide production plants, or from coke producers and traders. Activity data and emissions estimation is complicated by the fact that acetylene produced from  $\text{CaC}_2$  is not necessarily produced at the same plant that produces the  $\text{CaC}_2$ . This needs to be accounted for when using the higher tier methods, with emissions originating from the use of  $\text{CaC}_2$  accounted at the point where the emissions occur; for example, in the case of acetylene used in welding applications, where the acetylene is produced at a different location to the  $\text{CaC}_2$  emissions should be accounted for at the point of production of the acetylene on the assumption that it will be used in a short time after production.

Application of the Tier 2 and 3 methods assumes the bottom-up (plant by plant) estimation of emissions and plant-level data collection. In countries where only a subset of plants report data for the Tier 3 method or where there is a transition from Tier 2 to Tier 3, it may not be possible to report emissions using Tier 3 for all facilities during the transition. Where data for the Tier 3 method are not available for all plants, Tier 2 could be used for the remaining plants. Also, where data for the Tier 2 method are reported by only a subset of plants or where there is a transition from Tier 1 to Tier 2, it may be possible to determine the share of production represented by non-reporting plants and use this information to estimate the remaining emissions using Tier 1 in order to ensure completeness during the transition period.

#### 3.6.2.5 DEVELOPING A CONSISTENT TIME SERIES

It is *good practice* to estimate emissions from carbide production using the same method for every year in the time series. Where data are unavailable to support a more rigorous method for all years in the time series, it is *good practice* to recalculate these gaps according to the guidance provided in Volume 1, Chapter 5.

### 3.6.3 Uncertainty assessment

#### 3.6.3.1 EMISSION FACTOR UNCERTAINTIES

In general, the default  $\text{CO}_2$  emission factors are relatively uncertain because industrial-scale carbide production processes differ from the stoichiometry of theoretical chemical reactions. The uncertainty in the emission factors for  $\text{CH}_4$  is due to the possible variations in the hydrogen-containing volatile compounds in the raw material (petroleum coke) that are used by different manufacturers and due to the possible variations in production process parameters. Where uncertainty values are not available from other sources, a default value of  $\pm 10$  percent can be used.

It is *good practice* to obtain uncertainty estimates at the plant level which should be lower than uncertainties associated with default values.

#### 3.6.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained directly from plants, uncertainty estimates can be obtained from producers. This will include uncertainty estimates for petroleum coke and limestone used and for carbide production data. Data that are obtained from national statistical agencies or from industrial and trade organizations usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistic agencies collect carbide production data from production facilities, uncertainties in national statistics are not expected to differ from uncertainties estimated

from plant-level consultations. Where uncertainty values are not available from other sources, a default value of  $\pm 5$  percent can be used.

## **3.6.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation**

### **3.6.4.1 QUALITY ASSURANCE/QUALITY CONTROL**

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emission estimates. More extensive quality control checks and quality assurance procedures may be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance given in Volume 1, specific procedures of relevance to this source category are outlined below.

#### **Comparison of emission estimates using different approaches**

If the Tier 2 (plant-specific) method is used, then inventory compilers should compare the emission estimates to the estimates calculated using national level activity data (Tier 1). The inventory compilers are also encouraged to compare the emission estimates calculated using different modifications of the same methods.

The results of such comparison should be recorded for internal documentation, including explanation for any discrepancies.

#### **Review of emission factors**

Inventory compilers should compare aggregated national emission factors with the IPCC default emission factors in order to determine if the national factor is reasonable relative to the IPCC default. The same procedure (i.e., comparison with the IPCC default) should be applied to plant specific emission factors. Differences between national or plant specific factors and default factors should be explained and documented, particularly if they are representative of different circumstances.

#### **Plant-specific data check**

For plant-specific data, inventory compilers should review inconsistencies between plants to establish whether they reflect errors, different measurement techniques, or result from real differences in raw materials, operational conditions or technology.

Inventory compilers should ensure that activity data and emission factors are developed in accordance with internationally recognized and proven measurement methods. If any emission measurements from individual plants are collected inventory compilers should ensure that the measurements were made according to the recognised national or international standards. If the measurement practices fall this criterion, then the use of this emission factors and activity data should be carefully evaluated, uncertainty estimations reconsidered and qualifications documented.

#### **Expert review**

Inventory compilers are encouraged to include key industrial and trade organizations associated with carbide and petroleum coke production in a review process. This process should begin on the early stage of the inventory development to provide input to the development and review of methods and data acquisition.

Third party reviews may be also useful for this source category, particularly in relation of initial data collection, transcription, calculation and documentation.

### **3.6.4.2 REPORTING AND DOCUMENTATION**

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. Recalculation of previous years emissions also should be documented and archived.

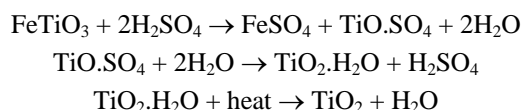
## 3.7 TITANIUM DIOXIDE PRODUCTION

### 3.7.1 Introduction

Titanium dioxide (TiO<sub>2</sub>) is one of the most commonly used white pigments. The main use is in paint manufacture followed by paper, plastics, rubber, ceramics, fabrics, floor covering, printing ink, and other miscellaneous uses (Austin, 1984; Lowenheim and Moran, 1975). Given production of around 4 million tonnes of TiO<sub>2</sub>, and the substantial use of the chloride route, carbon dioxide (CO<sub>2</sub>) emissions are likely to be significant and need to be accounted for in greenhouse gas inventories. Global production by the chloride route has increase approximately eight fold since 1970 whilst sulphate route production has been relatively stable (Kirk-Othmer, 1999; p. 2017). Note that in the discussion, titanium dioxide products are referred to generically as titanium dioxide unless there is a need to make a distinction between the products. The discussion applies to titanium slag, synthetic rutile (>90 percent TiO<sub>2</sub>) and rutile TiO<sub>2</sub>.

### 3.7.2 Methodological issues

TiO<sub>2</sub> is produced as anatase TiO<sub>2</sub> and rutile TiO<sub>2</sub>. The forms of TiO<sub>2</sub> differ in terms of the crystalline structure and purity of the final product. Anatase TiO<sub>2</sub> may be produced by digesting ilmenite (essentially ferrous titanate (FeO.TiO<sub>2</sub>)) with sulphuric acid, the sulphate process, or from titanium slag. Basic reaction equations for the acid digestion route are (Lowenheim and Moran, 1975; p. 814):



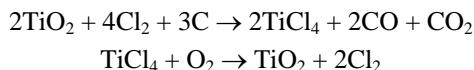
The sulphate route process does not give rise to process greenhouse gas emissions that are of significance.

There are three processes that are used in the production of TiO<sub>2</sub> that lead to process greenhouse gas emissions: titanium slag production in electric furnaces, synthetic rutile production using the Becher process, and rutile TiO<sub>2</sub> production via the chloride route.

Titanium slag used for production of anatase TiO<sub>2</sub> is produced from electric furnace smelting of ilmenite. Where titanium slag is used the acid reduction step is not required as the electric furnace smelting reduces the ferric iron contained as an impurity in ilmenite. Rutile TiO<sub>2</sub> may be produced by further processing of the anatase TiO<sub>2</sub>. Process emissions arise from the reductant used in the process.

Production of synthetic rutile can give rise to CO<sub>2</sub> emissions where the Becher process is used. This process reduces the iron oxide in ilmenite to metallic iron and then reoxidises it to iron oxide, and in the process separates out the titanium dioxide as synthetic rutile of about 91 to 93 percent purity (Chemlink, 1997). Black coal is used as the reductant and the CO<sub>2</sub> emissions arising should be treated as industrial process emissions.

The main route for the production of rutile TiO<sub>2</sub> is the chloride route. Rutile TiO<sub>2</sub> is produced through the carbothermal chlorination of rutile ore or synthetic rutile to produce titanium tetrachloride (TiCl<sub>4</sub>) and oxidation of the TiCl<sub>4</sub> vapours to TiO<sub>2</sub> according to the following reactions (Kirk-Othmer, 1999; p.2017):



Based on stoichiometry and assuming complete conversion of the input C to CO<sub>2</sub> through further conversion of CO in excess air, the CO<sub>2</sub> emission factor cannot be less than 0.826 tonnes of CO<sub>2</sub> per tonne of TiO<sub>2</sub> (based on 1.5 moles of CO<sub>2</sub> per mole of TiO<sub>2</sub>).

#### 3.7.2.1 CHOICE OF METHOD

The general approach for calculating CO<sub>2</sub> emissions from titanium dioxide production is the same irrespective of the product because the emissions are based on the quantity of reducing agent or carbothermal input. The choice of a *good practice* method depends on national circumstances as shown in the decision tree in Figure 3.6. Process emissions of carbon dioxide in TiO<sub>2</sub> production take place primarily as a result of anode carbon oxidation in the production of titanium slag, coal oxidation in the process of producing synthetic rutile using the Becher process, and petroleum coke oxidation in the process of producing rutile TiO<sub>2</sub> via the chloride route.

Methods are classified according to the extent of plant-level data that are available.

## TIER 1 METHOD

The Tier 1 method uses a default emission factor per unit of output multiplied by activity data obtained from national statistics. The basic equation for estimating CO<sub>2</sub> emissions is:

**EQUATION 3.12**  
**CO<sub>2</sub> EMISSIONS FROM TITANIUM SLAG, SYNTHETIC RUTILE AND RUTILE TiO<sub>2</sub> PRODUCTION – TIER 1**

$$E_{CO_2} = \sum_i (AD_i \cdot EF_i)$$

Where:

$E_{CO_2}$  = emissions of CO<sub>2</sub>, tonnes

$AD_i$  = production of titanium slag, synthetic rutile or rutile TiO<sub>2</sub> (product  $i$ ), tonnes

$EF_i$  = CO<sub>2</sub> emissions per unit of production of titanium slag, synthetic rutile or rutile TiO<sub>2</sub> (product  $i$ ), tonnes CO<sub>2</sub>/tonne product

## TIER 2 METHOD

Emissions can be calculated from the consumption of the reducing agent for electrode carbon (titanium slag), and coal (synthetic rutile) in the Becher process, and the carbothermal input (petroleum coke) for rutile TiO<sub>2</sub> from the chloride route process. The Tier 2 method uses plant-level data on the quantities of reducing agent and carbothermal input to derive emissions as follows:

**EQUATION 3.13**  
**CO<sub>2</sub> EMISSIONS FROM TITANIUM SLAG, SYNTHETIC RUTILE AND RUTILE TiO<sub>2</sub> PRODUCTION – TIER 2**

$$E_{CO_2} = \sum_i (AD_i \cdot CCF_i \cdot COF_i \cdot 44/12)$$

Where:

$E_{CO_2}$  = emissions of CO<sub>2</sub>, kg

$AD_i$  = amount of reducing agent or carbothermal input  $i$ , GJ

$CCF_i$  = carbon content factor of reducing agent or carbothermal input  $i$ , kg C/GJ

$COF_i$  = carbon oxidation factor for reducing agent or carbothermal input  $i$ , fraction

To achieve the highest accuracy, *good practice* is to apply Equation 3.13 at the plant-level with all data inputs obtained from plant operators.

Where plant-level information is not available, *good practice* provides default CO<sub>2</sub> emission factors for synthetic rutile and rutile TiO<sub>2</sub> as shown in Table 3.9. A default factor for titanium slag is not available because of the small number of plants.

**BOX 3.6**  
**DOUBLE COUNTING**

In order to avoid double counting, the quantities of electrode carbon, coal used as a reductant, and petroleum coke used in the chloride route process, must be subtracted from the quantity reported under energy and non-energy use in the **Energy Sector**.

### 3.7.2.2 CHOICE OF EMISSION FACTORS

#### TIER 1 METHOD

If plant-level information is not available, it is *good practice* to use default factors. These default values often represent midpoint or mean values of data sets (as determined by expert analysis). The extent to which they represent a specific plant's emission rate is unknown. Default factors by product are provided in Table 3.9, and should be used only in cases where plant-specific data are not available. The default factors are based on



estimates of reductant or carbothermal input per unit of output assuming complete conversion of the C content to CO<sub>2</sub>.

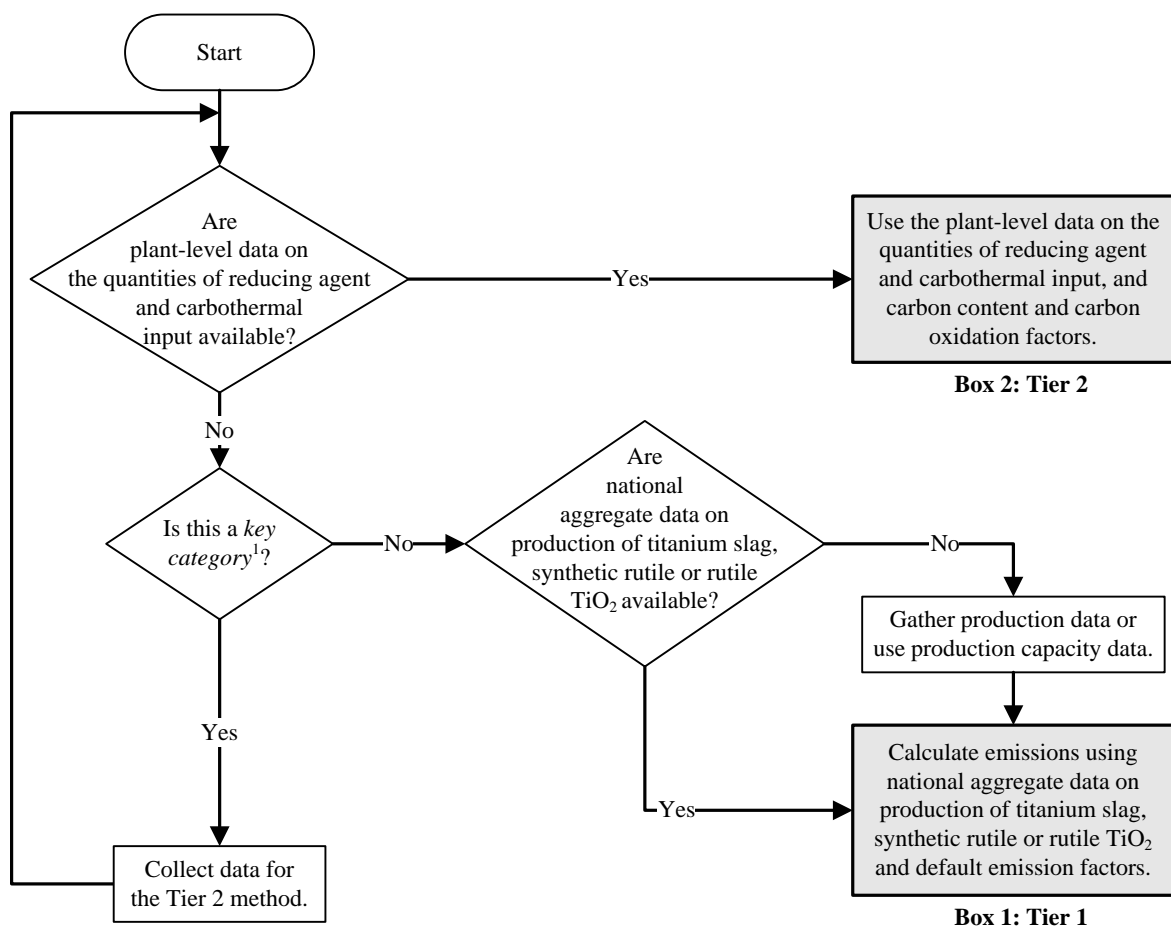
## TIER 2 METHOD

Plant-level data provides the most rigorous data for calculating CO<sub>2</sub> emissions from titanium dioxide production. For the Tier 3 method, C content of the reductant and carbothermal inputs along with the proportion of C oxidised are the key emission factor variables for deriving the quantity of CO<sub>2</sub> emitted.

| Product   | Emission factor and respective uncertainty<br>(tonnes CO <sub>2</sub> /tonne product) |
|---|---|
| Titanium slag <sup>1</sup>                            | Not available   |
| Synthetic rutile <sup>2</sup>                         | 1.43 (± 10%)  |
| Rutile titanium dioxide (chloride route) <sup>3</sup> | 1.34 (± 15%)  |

Source:  
<sup>1</sup> A default emission factor is not available because there are two plants only, Richards Bay in South Africa, and Allard Lake in Canada, and data are confidential. It is *good practice* for the respective countries to include plant specific estimates of emissions in their national greenhouse gas inventories.  
<sup>2</sup> Derived from data provided by Iluka Resources.  
<sup>3</sup> Adapted from EIPPCB (2004a; p.99).

**Figure 3.6** Decision tree for estimation of CO<sub>2</sub> emissions from titanium dioxide production



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

### 3.7.2.3 CHOICE OF ACTIVITY DATA

It is *good practice* to compile activity data at a level of detail that allows the use of the Tier 2 method. When applying the methods it is essential that a clear distinction is made between the products to avoid multiplying the incorrect emission factor by activity data.

#### TIER 1 METHOD

The Tier 1 method requires data on national production of titanium slag, synthetic rutile and rutile TiO<sub>2</sub>. If national-level activity data are not available, information on production capacity can be used with emissions estimated using a default emission factor. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent ± 10 percent (i.e., a range of 70-90 percent).

#### TIER 2 METHOD

The plant-level activity data required for the Tier 2 method are total reductant use, total carbon electrode consumption, and total carbothermal input. It is *good practice* to also collect data on total titanium slag production, total synthetic rutile production, and total rutile TiO<sub>2</sub> production. Collection of production data enables comparisons of inputs per unit of outputs over time and provides a sound basis for ensuring time series consistency. Where plant-level emission factors are used, *good practice* is to collect plant-level production data. Typical plant-level activity data is assumed to be accurate to ±2 percent due to the economic value of having accurate information. If plant-level data are not available, nationally compiled production data may be used.

### 3.7.2.4 COMPLETENESS

Complete coverage for titanium dioxide production requires accounting for all emissions from all sources including titanium slag, synthetic rutile and rutile TiO<sub>2</sub>. CO<sub>2</sub> emissions are the main process emissions. In order to include emissions of NO<sub>x</sub>, CO and SO<sub>2</sub> from this source category, see guidance provided in Chapter 7 of Volume 1: General Guidance and Reporting.

### 3.7.2.5 DEVELOPING A CONSISTENT TIME SERIES

CO<sub>2</sub> emissions should be recalculated for all years whenever emission calculation methods are changed (e.g., if the inventory compiler changes from the use of default values to actual values determined at the plant level). If plant-specific data are not available, including plant-specific production data, for all years in the time series, it will be necessary to consider how current plant data can be used to recalculate emissions for previous years. It may be possible to apply current plant-specific emission factors to production data from previous years, provided that plant operations have not changed substantially. Recalculation is required to ensure that any changes in emissions trends are real and not an artefact of changes in procedure. It is *good practice* to recalculate the time series according to the guidance provided in Volume 1, Chapter 5.

## 3.7.3 Uncertainty assessment

### 3.7.3.1 EMISSION FACTOR UNCERTAINTIES

Uncertainties for the default values are estimates based on expert judgement. It is *good practice* to obtain uncertainty estimates at the plant level which should be lower than uncertainty values associated with default values.

### 3.7.3.2 ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. This will include uncertainty estimates for reductant use, carbothermal inputs, and production data. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data from the population of titanium dioxide production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of ±5 percent can be used.

## 3.7.4 Quality Assurance/Quality Control (QA/QC), Reporting and Documentation

### 3.7.4.1 QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable, if higher tier methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### Comparison of emission factors

Inventory compilers should check if the estimated emission factors are within the range of default emission factors provided for the Tier 1 method, and also ensure that the emission factors are consistent with the values derived from analysis of the process chemistry. For example, the CO<sub>2</sub> generation rate for rutile TiO<sub>2</sub> from the chloride route process should not be less than 0.826 tonnes of CO<sub>2</sub> per tonne of rutile TiO<sub>2</sub> produced. If the emission factors are outside of the estimated ranges, it is *good practice* to assess and document the plant-specific conditions that account for the differences.

If emission measurements from individual plants are collected, inventory compilers should ensure that the measurements were made according to recognised national or international standards. QC procedures in use at the site should be directly referenced and included in the QC plan. If the measurement practices were not consistent with QC standards, the inventory compiler should reconsider the use of these data.

### 3.7.4.2 REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced.

#### Plant-specific data check

The following plant-specific data is required for adequate auditing of emissions estimates:

- Activity data comprising electrode carbon consumption (titanium slag), coal reductant use (synthetic rutile), carbothermal input (rutile TiO<sub>2</sub>), titanium slag production, synthetic rutile production, and rutile TiO<sub>2</sub> production;
- Emission factor data including the carbon content of the reductant (carbon electrode and coal) and carbothermal input (petroleum coke), and the proportion oxidised in the process;
- Calculations and estimation method;
- List of assumptions;
- Documentation of any plant-specific measurement method, and measurement results.

In general production and process data are considered proprietary by operators, especially where there are only a small number of plants within a country. It is *good practice* to apply appropriate techniques, including aggregation of data, to ensure protection of confidential data.

## 3.8 SODA ASH PRODUCTION

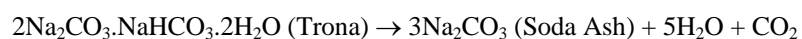
### 3.8.1 Introduction

Soda ash (sodium carbonate,  $\text{Na}_2\text{CO}_3$ ) is a white crystalline solid that is used as a raw material in a large number of industries including glass manufacture, soap and detergents, pulp and paper production and water treatment. Carbon dioxide ( $\text{CO}_2$ ) is emitted from the use of soda ash and these emissions are accounted for as a source under the relevant using industry as discussed in Volume 3, Chapter 2.  $\text{CO}_2$  is also emitted during production with the quantity emitted dependent on the industrial process used to manufacture soda ash.

Emissions of  $\text{CO}_2$  from the production of soda ash vary substantially with the manufacturing process. Four different processes may be used commercially to produce soda ash. Three of these processes, monohydrate, sodium sesquicarbonate (trona) and direct carbonation, are referred to as natural processes. The fourth, the Solvay process, is classified as a synthetic process. Calcium carbonate (limestone) is used as a source of  $\text{CO}_2$  in the Solvay process. Other uses of limestone and other carbonates are discussed in Volume 3, Chapter 2.

### 3.8.2 Natural soda ash production

About 25 percent of the world production is produced from natural sodium carbonate-bearing deposits referred to as natural processes. During the production process, Trona (the principal ore from which natural soda ash is made) is calcined in a rotary kiln and chemically transformed into a crude soda ash. Carbon dioxide and water are generated as by-products of this process. Carbon dioxide emissions can be estimated based on the following chemical reaction:



#### 3.8.2.1 METHODOLOGICAL ISSUES

##### CHOICE OF METHOD

The choice of method will depend on national circumstances. Emissions can be estimated using an output-based approach (emissions per unit of output), or an input-based approach (emissions per unit of input). However, it is *good practice* to use the input-based method where data are available.

Methods are classified according to the extent of plant-level data that are available. The Tier 1 method is based on default values and national statistics, and the Tier 2 method is based on complete plant-level input or output data and plant specific emission factors. If there is monitoring and direct measurement of  $\text{CO}_2$  emissions this would be equivalent to a Tier 3 method.

##### Tier 1 method

Natural soda ash production emits  $\text{CO}_2$  through the thermal decomposition (calcination) of the Trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) to produce soda ash. According to the chemical reaction presented above, it takes 10.27 tonnes of Trona to produce 1 tonne of carbon dioxide. Hence, for natural soda ash production using Trona, emissions of carbon dioxide can be calculated from the Trona input or natural soda ash output by the following formula:

$$\begin{aligned} &\text{EQUATION 3.14} \\ &\text{CO}_2 \text{ EMISSIONS FROM NATURAL SODA ASH PRODUCTION – TIER 1} \\ &E_{\text{CO}_2} = AD \cdot EF \end{aligned}$$

Where:

$E_{\text{CO}_2}$  = emissions of  $\text{CO}_2$ , tonnes

AD = quantity of Trona used or soda ash produced, tonnes of Trona used or tonnes natural soda ash produced

EF = emission factor per unit of Trona input or natural soda ash output, tonnes  $\text{CO}_2$ /tonne of Trona or tonnes  $\text{CO}_2$ /tonne natural soda ash produced:  $EF_{\text{Trona}} = 0.097$  tonnes  $\text{CO}_2$ /tonne of Trona,  $EF_{\text{Soda Ash}} = 0.138$  tonnes  $\text{CO}_2$ /tonnes natural soda ash produced.

It is *good practice* to assess the available national statistics for completeness. The choice of *good practice* methods depends on national circumstances, as shown in Figure 3.7: Decision Tree for Estimation of CO<sub>2</sub> Emissions from Natural Soda Ash Production. If no data are available for the purity of the Trona input, it is *good practice* to assume it is 90 percent and adjust the emission factor shown in Equation 3.14.

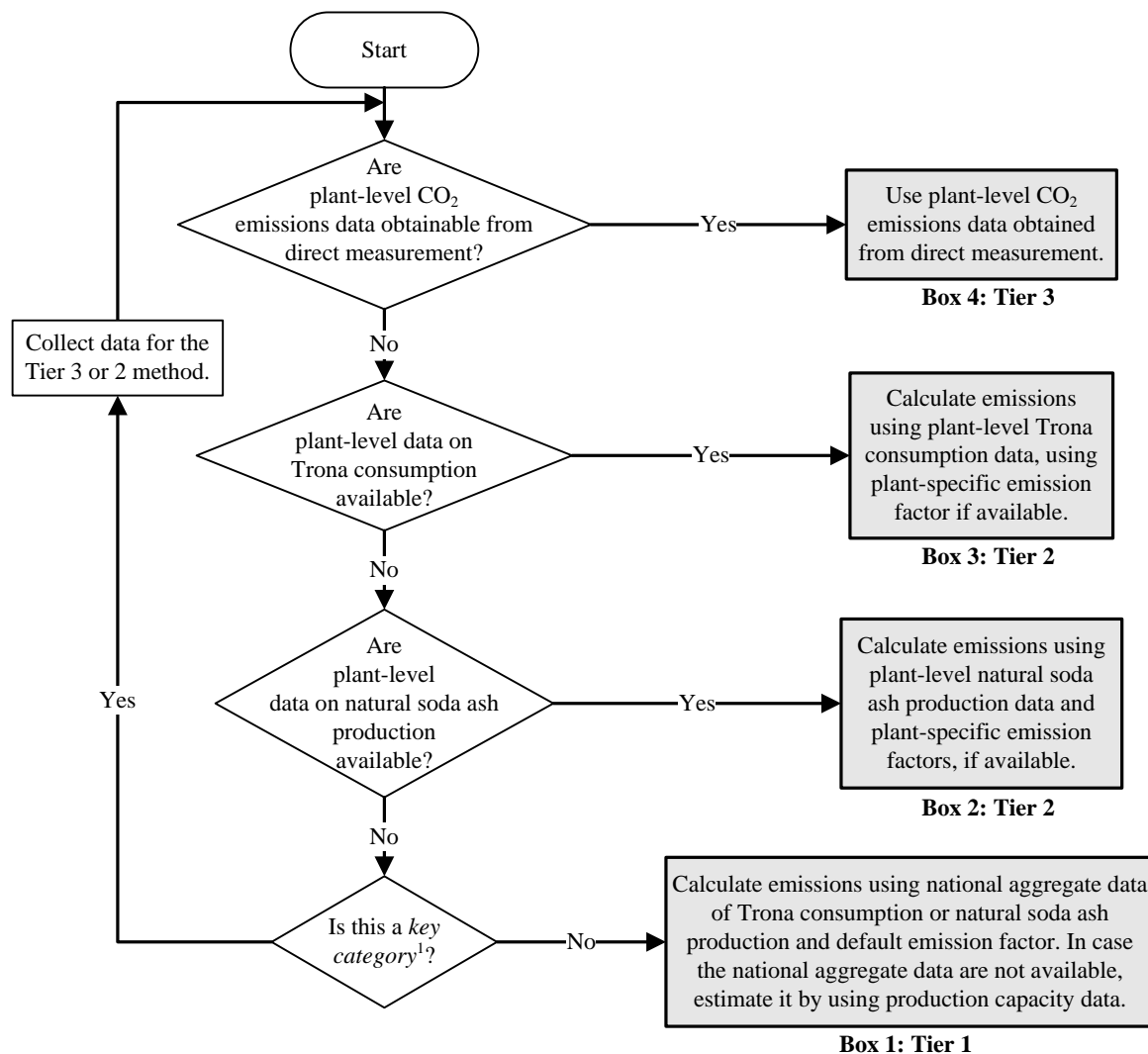
### Tier 2 method

To use the Tier 2 method, it is necessary to gather complete data on Trona consumption or natural soda ash production for each of the plants within the country along with plant-specific emission factors for the Trona input or soda ash output. The CO<sub>2</sub> emissions for each plant can be calculated using either variation of Equation 3.14. For plants where plant-specific emission factors are not available, the default emission factors provided in Equation 3.14 can be used. Total CO<sub>2</sub> emissions are the sum of the emissions from all plants.

### Tier 3 method

The Tier 3 method uses plant-level CO<sub>2</sub> emissions data obtained from direct measurement. Total emissions are the sum of emissions from all plants.

**Figure 3.7** Decision tree for estimation of CO<sub>2</sub> emissions from natural soda ash production



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

## CHOICE OF EMISSION FACTORS

### Tier 1 method

The Tier method uses the default emission factors presented in Equation 3.14. The default emission factors are derived from the stoichiometric ratio between soda ash produced and purified sodium sesquicarbonate obtained from Trona. They are based on the main natural production process that is used at present, where soda ash is produced by calcination of purified sodium sesquicarbonate.

### Tier 2 method

The Tier 2 method requires plant-level emission factors per unit of Trona input or per unit of natural soda ash output. Plant-level emission factors should reflect the fractional purities of the Trona input and natural soda ash output and it is *good practice* to ensure that these are taken into account in the derivation of plant-level emission factors.

## CHOICE OF ACTIVITY DATA

It is *good practice* to compile activity data at a level of detail that allows the use of the Tier 2 method. When applying the methods it is essential that a clear distinction is made between the products to avoid multiplying the incorrect emission factor by activity data.

### Tier 1 method

The Tier 1 method requires data on national consumption of Trona or national production of natural soda ash. If national-level activity data are not available, information on production capacity can be used with emissions estimated using a default emission factor. It is *good practice* to multiply the total national production capacity by a capacity utilisation factor of 80 percent  $\pm$  10 percent (i.e., a range of 70-90 percent).

### Tier 2 method

Activity data should be collected at the plant-level to use the Tier 2 method. The most important data are the amount of Trona used for soda ash production and the amount of natural soda ash produced at each plant. Although soda ash production is not used in the calculation if emissions are derived from Trona input, it is *good practice* to collect and report these data to enable comparisons of inputs per unit of outputs over time and provide a sound basis for ensuring time series consistency.

## COMPLETENESS

Completeness of the activity data (e.g., Trona utilisation) is a crucial attribute of *good practice*. Therefore, it is *good practice* to assess the available national statistics for completeness. If data are available at the plant-level, it is *good practice* to aggregate these data and check the result with the data available at a national level. This practice enables assessment of whether any significant soda ash producer is omitted, and ensures that all production processes within the country have been considered. If data at the plant-level are not available, it is *good practice* to use production capacity data along with national statistics to estimate the emissions for completeness purposes.

## DEVELOPING A CONSISTENT TIME SERIES

It is *good practice* to calculate emissions from soda ash using the same method for every year in the time series. Where data are unavailable to support a more rigorous method for all years in the time series, *good practice* is to recalculate these gaps according to the guidance provided in Volume 1, Chapter 5.

### 3.8.2.2 UNCERTAINTY ASSESSMENT

#### EMISSION FACTOR UNCERTAINTIES

The stoichiometric ratio is an exact number and assuming 100 percent purity of the input or output, the uncertainty of the default emission factor is negligible. However, the default factors do not take into account the fractional purities of either the Trona input or soda ash output and, in both cases, are expected to result in consistent over-estimation of emissions. As noted earlier, if no data are available for the purity of the Trona input, it is *good practice* to assume it is 90 percent and adjust the emission factor shown in Equation 3.14. It is *good practice* to develop uncertainty estimates based on plant-level data.

#### ACTIVITY DATA UNCERTAINTIES

Where activity data are obtained from plants, uncertainty estimates can be obtained from producers. This will include uncertainty estimates for Trona used and natural soda ash used. Data that are obtained from national statistical agencies usually do not include uncertainty estimates. It is *good practice* to consult with national statistical agencies to obtain information on any sampling errors. Where national statistical agencies collect data

from the population of soda ash production facilities, uncertainties in national statistics are not expected to differ from uncertainties established from plant-level consultations. Where uncertainty values are not available from other sources, a default value of  $\pm 5$  percent can be used.

### 3.8.2.3 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

#### QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### Comparison of the emissions estimates using different approaches

If the bottom-up approach is used, then inventory compilers should compare the emissions estimates to the estimate calculated using the top-down approach. The results of such comparisons should be recorded for internal documentation, including explanations for any discrepancies.

#### REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to data sources, and all the information needed to reproduce the estimate.

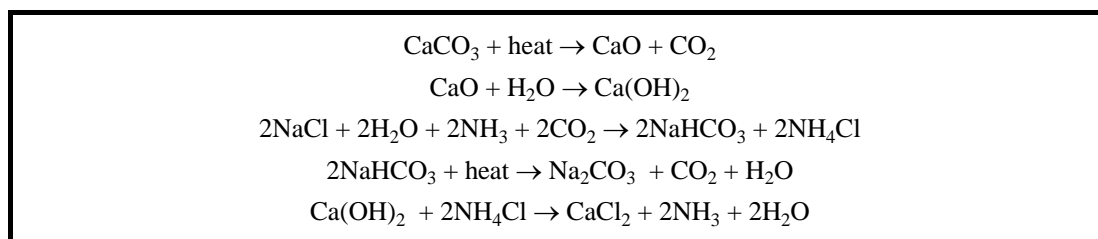
Besides the emissions, *good practice* is to report the activity data used in the calculation (Trona utilisation) and the corresponding emission factors along with all assumptions used in the derivation.

To preserve an internally consistent emission time series, whenever national methods change, *good practice* is to recalculate the entire time series. If confidentiality is an issue for any type of production, estimates may be aggregated to the minimum extent possible to maintain confidentiality.

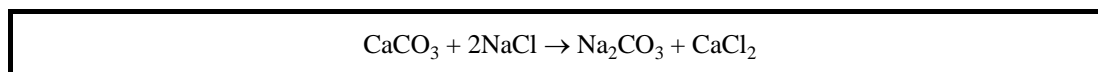
In addition, inventory compilers should document the QA/QC procedures.

### 3.8.3 Solvay soda ash production

About 75 percent of the world production of soda ash is synthetic ash made from sodium chloride. In the Solvay process, sodium chloride brine, limestone, metallurgical coke and ammonia are the raw materials used in a series of reactions leading to the production of soda ash. Ammonia, however, is recycled and only a small amount is lost. The series of reactions involved in the Solvay process may be described as follows:



The net overall reaction may be summarised as:



From the series of reactions presented above,  $\text{CO}_2$  is generated in two pyrolysis processes. The  $\text{CO}_2$  generated is captured, compressed and directed to Solvay precipitating towers for consumption in a mixture of brine (aqueous  $\text{NaCl}$ ) and ammonia. Although  $\text{CO}_2$  is generated as a by-product, the  $\text{CO}_2$  is recovered and recycled for use in the carbonation stage and in theory the process is neutral, i.e.,  $\text{CO}_2$  generation equals uptake.

In practice, some  $\text{CO}_2$  is emitted to the atmosphere during production by the Solvay process because more  $\text{CO}_2$  is produced than is stoichiometrically required. The excess  $\text{CO}_2$  arises from calcining the limestone with metallurgical grade coke. The limestone is combined with the coke at approximately 7 percent of limestone by weight.

The estimation of the CO<sub>2</sub> emissions from a stand alone soda ash plant should be based on an overall balance of CO<sub>2</sub> around the whole chemical process. For inventory purposes, a simplified version of the balance may be used assuming that the CO<sub>2</sub> emissions result from the stoichiometric oxidation of the coke carbon. The Solvay ammonia soda ash production process is a chemical industry activity and emissions should be reported under the Industrial Processes and Product Use (IPPU) Sector.

**BOX 3.7**  
**DOUBLE COUNTING**

In order to avoid double counting, CO<sub>2</sub> emissions generated in the process of soda ash production should be accounted in the **IPPU Sector**, and should not be included in the **Energy Sector**. Coke used in the production process should be deducted from the **Energy Sector** as a non-energy use of coke.

### **3.8.3.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION**

The allocation of emissions from the use of metallurgical grade coke in the Solvay process to the **Energy Sector** means that a methodology for estimating these emissions is not provided in the **Industrial Processes and Product Use Sector**. However, data on soda ash production from the Solvay process should be collected and collated to ensure that all data on soda ash production by process are available for recording, reporting, archiving and reconciliation with national statistics on soda ash use.

#### **QUALITY ASSURANCE/ QUALITY CONTROL**

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6. Additional quality control checks as outlined in Volume 1, and quality assurance procedures may also be applicable. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### **REPORTING AND DOCUMENTATION**

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to data sources, and all the information needed to reproduce the estimate.



## 3.9 PETROCHEMICAL AND CARBON BLACK PRODUCTION

### 3.9.1 Introduction

The petrochemical industry uses fossil fuels (e.g., natural gas) or petroleum refinery products (e.g., naphtha) as feedstocks. This section provides guidance for estimating emissions from the production of methanol, ethylene and propylene<sup>2</sup>, ethylene dichloride, ethylene oxide, and acrylonitrile. These petrochemicals are addressed in detail because their global production volume and associated greenhouse gas emissions are relatively large. However, the chemicals included are not intended to represent the entire petrochemical process industry. There are a number of other petrochemical processes that emit small amounts of greenhouse gases for which specific guidance is not provided (e.g., styrene production).

This section also provides guidance for production of carbon black. Carbon black is not considered to be a petrochemical; however, the carbon black production process uses petrochemical feedstocks. Emissions from carbon black production are smaller than for petrochemical processes but may be significant for certain countries.

Examples of feedstock to product production chains for methanol, ethylene and propylene, ethylene dichloride, ethylene oxide, acrylonitrile, and carbon black are included in the Annex to Section 3.9.

#### Allocation and Reporting

Within the petrochemical industry and carbon black industry, primary fossil fuels (natural gas, petroleum, coal) are used for non-fuel purposes in the production of petrochemicals and carbon black. The use of these primary fossil fuels may involve combustion of part of the hydrocarbon content for heat raising and the production of secondary fuels (e.g., off gases).

Combustion emissions from fuels obtained from the feedstocks should be allocated to the source category in the IPPU Sector. However, where the fuels are not used within the source category but are transferred out of the process for combustion elsewhere (e.g., for district heating purposes) the emissions should be reported in the appropriate Energy Sector source category. The industries are included in the source category Chemical Industry (2B1 – 2B10), see Figure 1.1, Industrial Process and Product Use Source Categories in Chapter 1 of this volume. Further discussion of the non-energy use of fuels is included in Chapters 1 and 5 of this volume.

Note that national energy statistics may include total combustion of fossil fuels (including natural gas, oil, and coal,) and also secondary fuels (such as industrial process off gases) for energy production. It is important to investigate if fuels used in petrochemical industries are included in national energy statistics. If this is the case, emissions from petrochemical processes should be subtracted from the calculated energy sector emissions to avoid double counting. This is particularly relevant for ethylene and methanol, where primary fuel (e.g., natural gas, ethane, propane) feedstock consumption may be reported in national energy statistics.

Should carbon dioxide (CO<sub>2</sub>) capture technology be installed and used at a plant, it is *good practice* to deduct the CO<sub>2</sub> captured in a higher tier emissions calculation. The default assumption is that there is no CO<sub>2</sub> capture and storage (CCS) taking place. Any methodology taking into account CO<sub>2</sub> capture should consider that CO<sub>2</sub> emissions captured in the process may be both combustion and process-related. In cases where combustion and process emissions are to be reported separately, inventory compilers should ensure that the same quantities of CO<sub>2</sub> are not double counted. In these cases the total amount of CO<sub>2</sub> captured should preferably be reported in the corresponding energy combustion and IPPU source categories in proportion to the amounts of CO<sub>2</sub> generated in these source categories. For additional information on CO<sub>2</sub> capture and storage refer to Volume 3, Section 1.2.2 and for more details on capture and storage to Volume 2, Section 2.3.4.

Petrochemical processes may utilise CO<sub>2</sub> captured elsewhere as a feedstock, and CO<sub>2</sub> may also be captured from petrochemical processes. This may create potential double counting issues. For example, some methanol plants may utilise by-product CO<sub>2</sub> captured from other industrial processes as a feedstock for methanol production. To avoid double counting the CO<sub>2</sub> captured should not be reported as CO<sub>2</sub> emissions from the process from which the CO<sub>2</sub> is captured.

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<sup>2</sup> Note that there is no separate inventory methodology for propylene. Propylene is assumed to be a co-product of ethylene production.

## METHANOL

Worldwide almost all methanol is made by way of steam reforming of natural gas. The steam reforming and shift reaction produce 'synthesis gas' comprised of CO<sub>2</sub>, carbon monoxide (CO), and hydrogen (H<sub>2</sub>). The natural gas to methanol production process produces methanol and by-product CO<sub>2</sub>, CO, and H<sub>2</sub> from the synthesis gas. There are several alternative processes for producing methanol from natural gas or other feedstocks. These include conventional reforming process, combined reforming and partial oxidation process. An example of a feedstock to product process flow diagram for methanol production is provided in an Annex to Section 3.9 (Annex 3.9A). Process descriptions for methanol production are included in Box 3.8 below.

| <b>BOX 3.8</b>  |  |  |
|---|--|--|
| <b>METHANOL PROCESS DESCRIPTIONS</b>  |  |  |
| <b><u>Conventional Reforming Process</u></b>  |  |  |
| The Conventional Reforming Process for methanol production involves steam reforming (which may include either a single reformer unit or both a primary reformer unit and a secondary reformer unit) and methanol synthesis. The overall equations for the Conventional Reforming Process are:   |  |  |
| <u>Steam Reforming</u><br>CH <sub>4</sub> + H <sub>2</sub> O → CO + 3 H <sub>2</sub><br>C <sub>n</sub> H <sub>m</sub> + nH <sub>2</sub> O → nCO + (m/2 + n) H <sub>2</sub>  | <u>Shift Reaction</u><br>CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub>  | <u>Methanol Production</u><br>CO + 2 H <sub>2</sub> → CH <sub>3</sub> OH<br>CO <sub>2</sub> + 3 H <sub>2</sub> → CH <sub>3</sub> OH + H <sub>2</sub> O |
| <u>Reforming/Shift Reaction</u><br>2 CH <sub>4</sub> + 3 H <sub>2</sub> O → CO + CO <sub>2</sub> + 7 H <sub>2</sub>   | <u>Methanol Production</u><br>CO + CO <sub>2</sub> + 7 H <sub>2</sub> → 2 CH <sub>3</sub> OH + 2 H <sub>2</sub> + H <sub>2</sub> O |  |
| The surplus hydrogen from this process and methanol process purge gas containing methane (CH <sub>4</sub> ) and non-methane volatile organic compounds (NMVOC) are recovered and burned for energy recovery, generally within the methanol production process, to produce process steam and/or electricity for the process. The Conventional Reforming Process may utilise CO <sub>2</sub> captured from other industrial processes as a supplemental feedstock to the methanol production process. |  |  |
| <b><u>Combined Reforming Process</u></b>  |  |  |
| The Combined Reforming Process combines the Conventional Steam Reforming process with a Catalytic Partial Oxidation process. The Partial Oxidation chemical equations are:  |  |  |
| <u>Methanol Steam Reforming Reaction</u><br>CH <sub>4</sub> + ½ O <sub>2</sub> → CO + 2 H <sub>2</sub> → CH <sub>3</sub> OH   | <u>Feedstock Oxidation Reaction</u><br>CH <sub>4</sub> + O <sub>2</sub> → CO <sub>2</sub> + 2 H <sub>2</sub>                       |  |
| The Combined Reforming Process produces a synthesis gas that contains a more balanced ratio of hydrogen to carbon monoxide (CO) and CO <sub>2</sub> than does the Conventional Reforming Process, and does not produce a hydrogen gas stream for energy recovery. The Combined Reforming Process produces a purge gas containing CH <sub>4</sub> that is burned for energy recovery within the methanol process.  |  |  |
| <b><u>Other Production Processes</u></b>  |  |  |
| Methanol may also be produced from the partial oxidation of oil, coal, or petrochemical feedstocks, or by gasification of coal to synthesis gas, however; these feedstocks and processes currently represent only a small amount of worldwide methanol production.  |  |  |

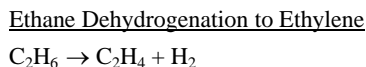
## ETHYLENE

Worldwide almost all ethylene is made by way of steam cracking of petrochemical feedstocks. Ethylene may be produced from steam cracking of petrochemical feedstocks in a petrochemical plant, and may also be produced from cracking and other processes operated at petroleum refineries. Steam cracking for ethylene production also produces secondary products including propylene and butadiene. A process description for steam cracking process for ethylene production is provided in Box 3.9 below.

**BOX 3.9**  
**ETHYLENE PROCESS DESCRIPTION**

**Steam Cracking**

The fundamental chemical equation for ethylene production is as follows:



The types and mix of feedstock used in steam cracking for ethylene production varies by region, and include ethane, propane, butane, naphtha, gas oil, and other petrochemical feedstocks. In the United States, most ethylene is produced from steam cracking of ethane, while in Europe, Korea, and Japan most ethylene is produced from steam cracking of naphtha.

Steam cracking of petrochemical feedstocks to produce ethylene also produces other high value (saleable) petrochemical products, including propylene, butadiene, and aromatic compounds. Most propylene worldwide is produced as a by-product of ethylene production, recovered either from steam crackers or from fluid catalytic cracking units at petroleum refineries. Steam crackers using naphtha feedstock are the largest source of propylene. There are other process technologies that are used to produce propylene including catalytic dehydrogenation of propane. Note that the emissions estimation methods in this section apply only to production of ethylene and propylene in steam crackers and do not apply to other process technologies used to produce ethylene or propylene. The steam cracking process also produces by-product hydrogen and methane and C4+ hydrocarbons that are generally burned for energy recovery within the process.

(Houdek, 2005: Figure 1 on Page 3, Page 4)

**ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER**

Worldwide almost all ethylene dichloride (1, 2 dichloroethane) is made by way of direct chlorination or oxychlorination of ethylene, or by a combination of the two processes (referred to as the ‘balanced process.’) An example of a feedstock to product process flow diagram for ethylene dichloride production is provided in an Annex to Section 3.9 (Annex 3.9A). Process descriptions for ethylene dichloride and vinyl chloride monomer production are provided in Box 3.10 below. Note that the chemical compound ‘ethylene dichloride’ is also referred to as 1,2-dichloroethane. The chemical compound ‘dichloroethylene,’ also referred to as 1, 2-dichloroethene, is a different compound.

**BOX 3.10**  
**ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER PROCESS DESCRIPTIONS**

**Direct Chlorination and Oxychlorination Processes**

The direct chlorination process involves gas-phase reaction of ethylene with chlorine to produce ethylene dichloride. The oxychlorination process involves gas-phase reaction of ethylene with hydrochloric acid and oxygen to produce ethylene dichloride and water. The ethylene dichloride is then cracked to produce vinyl chloride monomer and hydrochloric acid. The oxychlorination process produces a process off gas containing by-product CO<sub>2</sub> produced from the direct oxidation of the ethylene feedstock.

The fundamental chemical equations for the direct chlorination and oxychlorination processes are as follows:

| <u>Direct chlorination</u>             | <u>Oxychlorination reaction</u>   | <u>Ethylene dichloride&gt;vinyl chloride</u>  |
|--|---|---|
| $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ | $C_2H_4 + \frac{1}{2} O_2 + 2 HCl$<br>$\rightarrow C_2H_4Cl_2 + H_2O$<br>[ $C_2H_4 + 3 O_2 \rightarrow 2 CO_2 + 2 H_2O$ ] | $2 C_2H_4Cl_2 \rightarrow 2 CH_2CHCl + 2 HCl$ |

**BOX 3.10 (CONTINUATION)****ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER PROCESS DESCRIPTIONS****Balanced Process**

The combination of the direct chlorination process to produce ethylene dichloride and the ethylene dichloride cracking process to produce vinyl chloride monomer produces a surplus of hydrogen chloride. The oxychlorination process provides a sink for the hydrogen chloride. Therefore, ethylene dichloride/vinyl chloride monomer production facilities may operate a 'balanced process' in which both the direct chlorination process and the oxychlorination process are combined. The 'balanced process' also produces process vent gas containing by-product CO<sub>2</sub> from the direct oxidation of the ethylene feedstock.

The fundamental chemical equations for the 'balanced process' for producing vinyl chloride monomer from ethylene are as follows:

| <u>Ethylene Dichloride-Vinyl Chloride Monomer Reaction</u>  | <u>Feedstock Oxidation Reaction</u>  |
|---|--|
| $2 \text{C}_2\text{H}_4 + \text{Cl}_2 + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{CH}_2\text{CHCl} + \text{H}_2\text{O}$ | $[\text{C}_2\text{H}_4 + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O}]$ |

The direct chlorination process and the oxychlorination process for ethylene dichloride production are not 100 percent efficient in the utilisation of the ethylene feedstock. On the order of three percent of the ethylene feedstock is not converted to ethylene dichloride but is converted either to CO<sub>2</sub> (by direct oxidation in the oxychlorination process) or to other chlorinated hydrocarbons (in either the oxychlorination process or the direct chlorination process.) Process off gas containing other chlorinated hydrocarbons is generally treated prior to discharge to the atmosphere. The chlorinated hydrocarbons are converted to CO<sub>2</sub> in a thermal incineration process or a catalytic incineration process. Most ethylene dichloride/vinyl chloride monomer plants recover energy from the incinerator off gases and process off gases.

**ETHYLENE OXIDE**

Ethylene oxide (C<sub>2</sub>H<sub>4</sub>O) is manufactured by reacting ethylene with oxygen over a catalyst. The by-product CO<sub>2</sub> from the direct oxidation of the ethylene feedstock is removed from the process vent stream using a recycled carbonate solution, and the recovered CO<sub>2</sub> may be vented to the atmosphere or recovered for further utilisation (e.g., food production.) The oxygen may be supplied to the process through either air or through pure oxygen separated from air. An example of a feedstock to product process flow diagram for ethylene oxide production is provided in an Annex to Section 3.9 (Annex 3.9A). A process description for ethylene oxide production is provided in Box 3.11 below.

**BOX 3.11****ETHYLENE OXIDE PROCESS DESCRIPTION**

The fundamental chemical equations for the production of ethylene oxide from ethylene and the production of monoethylene glycol are as follows:

| <u>Ethylene Oxide Reaction</u>   | <u>Feedstock Oxidation Reaction</u>  | <u>Monoethylene Glycol Production</u>  |
|--|--|--|
| $\text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$ | $\text{C}_2\text{H}_4 + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O}$ | $\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O} \rightarrow \text{HO}-\text{C}_2\text{H}_4-\text{OH}$ |

The ratio of the ethylene oxide reaction and the by-product reaction defines the selectivity of the ethylene oxide process, in terms of tonnes of ethylene consumed per tonne of ethylene oxide produced. The combined ethylene oxide reaction and by-product CO<sub>2</sub> reaction is exothermic and generates heat, which is recovered to produce steam for the process. The ethylene oxide process also produces other liquid and off-gas by-products (e.g., ethane) that may be burned for energy recovery within the process. The amount of CO<sub>2</sub> and other by-products produced from the process and the amount of steam produced from the process is dependent upon the selectivity of the process.

Ethylene oxide is used as a feedstock in the manufacture of glycols, glycol ethers, alcohols, and amines. Worldwide approximately 70 percent of ethylene oxide produced is used in the manufacture of glycols, including monoethylene glycol.

## ACRYLONITRILE

Worldwide more than 90 percent of acrylonitrile (vinyl cyanide) is made by way of direct ammoxidation of propylene with ammonia (NH<sub>3</sub>) and oxygen over a catalyst. This process is referred to as the SOHIO process, after the Standard Oil Company of Ohio (SOHIO). Acrylonitrile can also be manufactured by ammoxidation of propane or directly from reaction of propane with hydrogen peroxide. The propane-peroxide direct process has recently been commercialised by British Petroleum (BP) and other manufacturers. (DOE, 2000) However, process data were not readily available for production of acrylonitrile from propane feedstocks. Therefore no emission estimation methodology is provided for this process. An example of a feedstock to product process flow diagram for acrylonitrile production from propylene is provided in an Annex to Section 3.9 (Annex 3.9A). Process descriptions for acrylonitrile production are provided in Box 3.12 below.

**Box 3.12**  
**ACRYLONITRILE PROCESS DESCRIPTION**

### SOHIO Process

The SOHIO process involves a fluidized bed reaction of chemical-grade propylene, ammonia, and oxygen over a catalyst. The catalyst is a mixture of heavy metal oxides (including bismuth and molybdenum). The process produces acrylonitrile as its primary product and acetonitrile (methyl cyanide) and hydrogen cyanide (HCN) as secondary products. The process yield of the primary product acrylonitrile depends in part on the type of catalyst used and the process configuration. The ammoxidation process also produces by-product CO<sub>2</sub>, CO, and water from the direct oxidation of the propylene feedstock, and produces other hydrocarbons from side reactions in the ammoxidation process.

The acetonitrile and hydrogen cyanide are separated from the acrylonitrile by absorption, and the hydrogen cyanide may be used in manufacturing other products on site or sold as product. Hydrogen cyanide that is not used or sold may be burned for energy recovery or flared. The acetonitrile may be also recovered for sale as a product, but more often the acetonitrile is burned for energy recovery or flared. The off gas from the main absorber vent containing CO<sub>2</sub>, CO, nitrogen, water, unreacted propylene, and other hydrocarbons, may be flared or treated in a thermal or catalytic oxidation unit, with or without energy recovery.

Heavy bottoms liquids from the acetonitrile – hydrogen cyanide - acrylonitrile absorption separations process may also be burned for energy recovery or recycled. Acrylonitrile and other non-methane hydrocarbons are also released from miscellaneous process vents, including storage tanks. These miscellaneous process vents may be flared or captured and burned for energy recovery.

The fundamental chemical equations for the production of acrylonitrile by ammoxidation are as follows:

|  |   |
|--|---|
| <u>Acrylonitrile Reaction</u><br>$\text{CH}_2=\text{CHCH}_3 + 1.5 \text{ O}_2 + \text{NH}_3 \rightarrow \text{CH}_2=\text{CHCN} + 3 \text{ H}_2\text{O}$       | <u>Hydrogen Cyanide Reaction</u><br>$\text{CH}_2=\text{CHCH}_3 + 3 \text{ O}_2 + 3 \text{ NH}_3 \rightarrow 3 \text{ HCN} + 6 \text{ H}_2\text{O}$  |
| <u>Acetonitrile Reaction</u><br>$\text{CH}_2=\text{CHCH}_3 + 1.5 \text{ O}_2 + 1.5 \text{ NH}_3 \rightarrow 1.5 \text{ CH}_3\text{CN} + 3 \text{ H}_2\text{O}$ | <u>Feedstock Oxidation</u><br>$\text{C}_3\text{H}_6 + 4.5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 3 \text{ H}_2\text{O}$ $\text{C}_3\text{H}_6 + 3 \text{ O}_2 \rightarrow 3 \text{ CO} + 3 \text{ H}_2\text{O}$ |

The ammoxidation of propylene to acrylonitrile is not 100 percent efficient in utilisation of the propylene feedstock. On the order of 70 percent of the propylene feedstock is converted to acrylonitrile. On the order of 85 percent of the propylene feedstock is converted to either the primary product acrylonitrile or secondary products acetonitrile or hydrogen cyanide. The remainder of the propylene feedstock is either converted directly to CO<sub>2</sub> by direct oxidation of the feedstock in the ammoxidation process or converted to other hydrocarbons through side reactions in the ammoxidation process.

## CARBON BLACK

Worldwide almost all carbon black is produced from petroleum-based or coal-based feedstocks using the 'furnace black' process. Process descriptions for carbon black production are provided in Box 3.13 below.

The furnace black process is a partial combustion process where a portion of the carbon black feedstock is combusted to provide energy to the process. Carbon black may also be produced using other petroleum-feedstock or coal-based feedstock partial oxidation processes, including the ‘channel black’ process and ‘lamp black’ process, or may be produced directly by the partial oxidation of natural gas or aromatic oils (‘channel black process’). Carbon black may also be produced by the thermal cracking of acetylene-containing feedstocks (‘acetylene black process’) or by the thermal cracking of other hydrocarbons (‘thermal black process’). Approximately 95 percent of worldwide carbon black production is by way of the furnace black process; the remaining 5 percent being produced by way of other processes.

Approximately 90 percent of carbon black produced worldwide is used in the tire and rubber industry (referred to as ‘rubber black.’) and the remainder is used in pigment applications (e.g., inks) and other applications (e.g., carbon dry cell batteries.) Carbon black may be produced using a furnace black process, thermal black process, acetylene carbon black process, channel black process and lamp black process. These processes are further described in Box 3.13 below. An example of a feedstock to product process flow diagram for carbon black production using the furnace black process is provided in an Annex to Section 3.9 (Annex 3.9A).

### BOX 3.13

#### CARBON BLACK PRODUCTION PROCESS DESCRIPTIONS

##### **Furnace Black Process**

The furnace black process produces carbon black from ‘carbon black feedstock’ (also referred to as ‘carbon black oil’) which is a heavy aromatic oil that may be derived either as a by-product of the petroleum refining process or the metallurgical (coal) coke production process. For either petroleum-derived or coal-derived feedstock, the carbon black feedstock, the ‘primary feedstock,’ is injected into a furnace heated by a ‘secondary feedstock’ (generally natural gas or oil). Both the natural gas secondary feedstock and a portion of the carbon black feedstock are oxidized to provide heat to the production process that pyrolyzes the remaining carbon black feedstock to carbon black. The vent gas from the furnace black process contains CO<sub>2</sub>, CO, sulphur compounds, CH<sub>4</sub>, and NMVOCs. A portion of the tail gas is generally burned for energy recovery to heat the downstream carbon black product dryers. The remaining tail gas may also be burned for energy recovery, flared, or vented uncontrolled to the atmosphere.

##### **Thermal Black Process**

Carbon black is produced in the thermal black process by thermal decomposition of gaseous hydrocarbons or atomized petroleum oils in the absence of air in a pair of production furnaces. The carbon black feedstock is introduced into a preheated furnace that is heated by a secondary feedstock, usually natural gas, and by the off gas from the carbon black production process. One of the pair of furnaces is being preheated by the secondary feedstock while the other furnace is receiving carbon black feedstock. Yield from this process is approximately 45 percent of total carbon input to the process (or 40 percent with respect to the total carbon black feedstock used) and energy utilisation is approximately 280 MJ/kg carbon black produced.

##### **Acetylene Black Process**

Carbon black produced from acetylene or acetylene-containing light hydrocarbons by feeding the feedstock to a preheated reactor where the acetylene decomposes to carbon black in an exothermic process. Total worldwide production of acetylene black is only approximately 40 000 metric tons per year. The carbon black yield from this process is approximately 95-99 percent of theoretical yield. Acetylene black is approximately 99.7 percent carbon.

##### **Other Production Processes**

The channel black process involves partial oxidation of vaporised carbon black feedstock that is burned in a furnace with a carrier gas (which may be coke oven gas, hydrogen, or methane). The carbon black yield for this process may be 60 percent of total carbon input for production of rubber-grade carbon black or 10-30 percent of total carbon input for pigment-grade carbon black.

The lamp black process involves open burning of carbon black feedstock in shallow pans. Data are not readily available concerning feedstock yield and energy consumption for the lamp black process. This process represents an insignificant percentage of worldwide carbon black production.

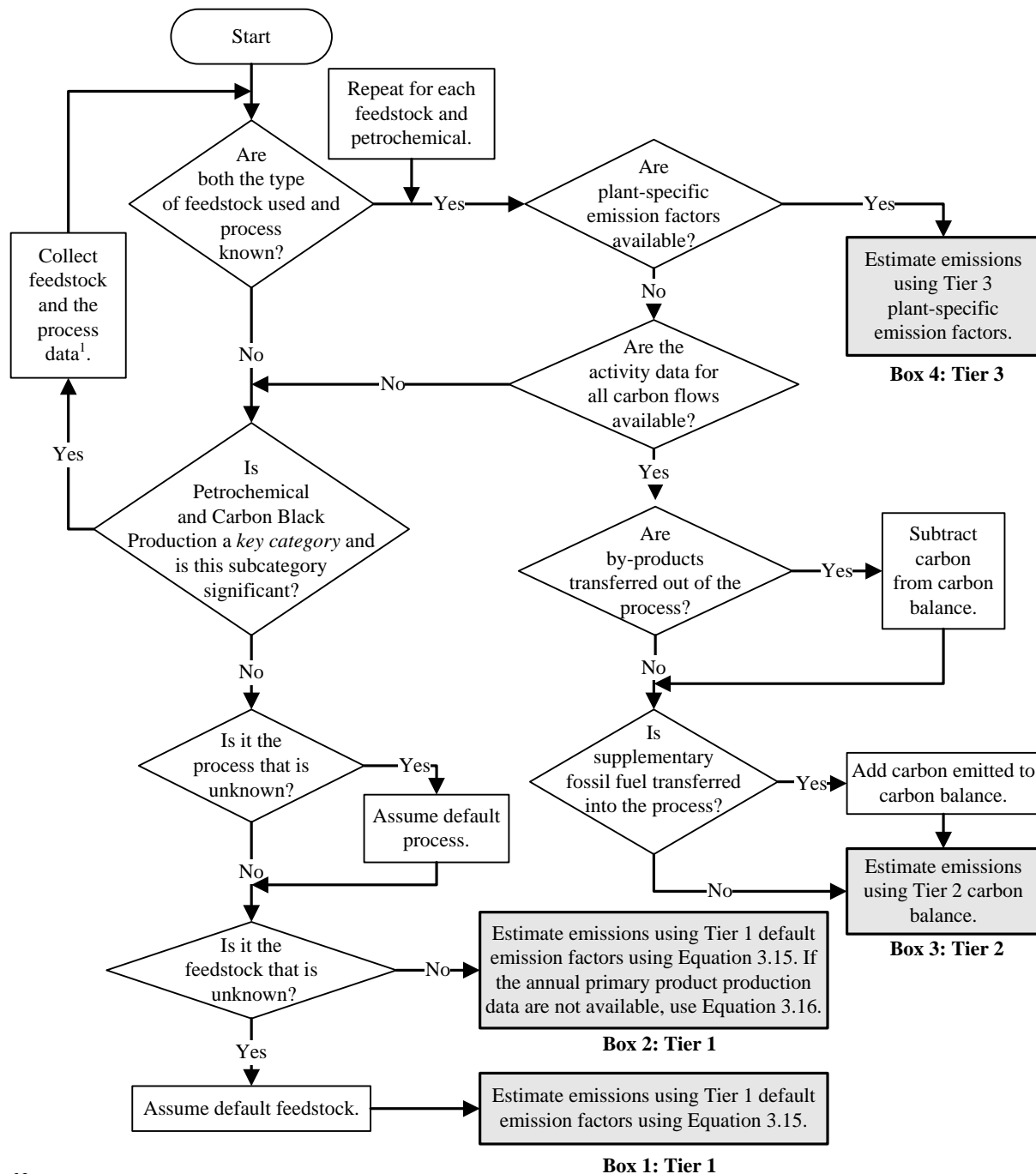
(Kirk Othmer, 1992)

## 3.9.2 Methodological issues

### 3.9.2.1 CHOICE OF METHOD

The emissions from petrochemical and carbon black production vary both with the process used and the feedstock used. The choice of method should thus be repeated for each product, process and feedstock used. Three methodological tiers are provided depending on the availability of data. The choice of method depends on national circumstances and is given by the decision trees in Figure 3.8 and Figure 3.9.

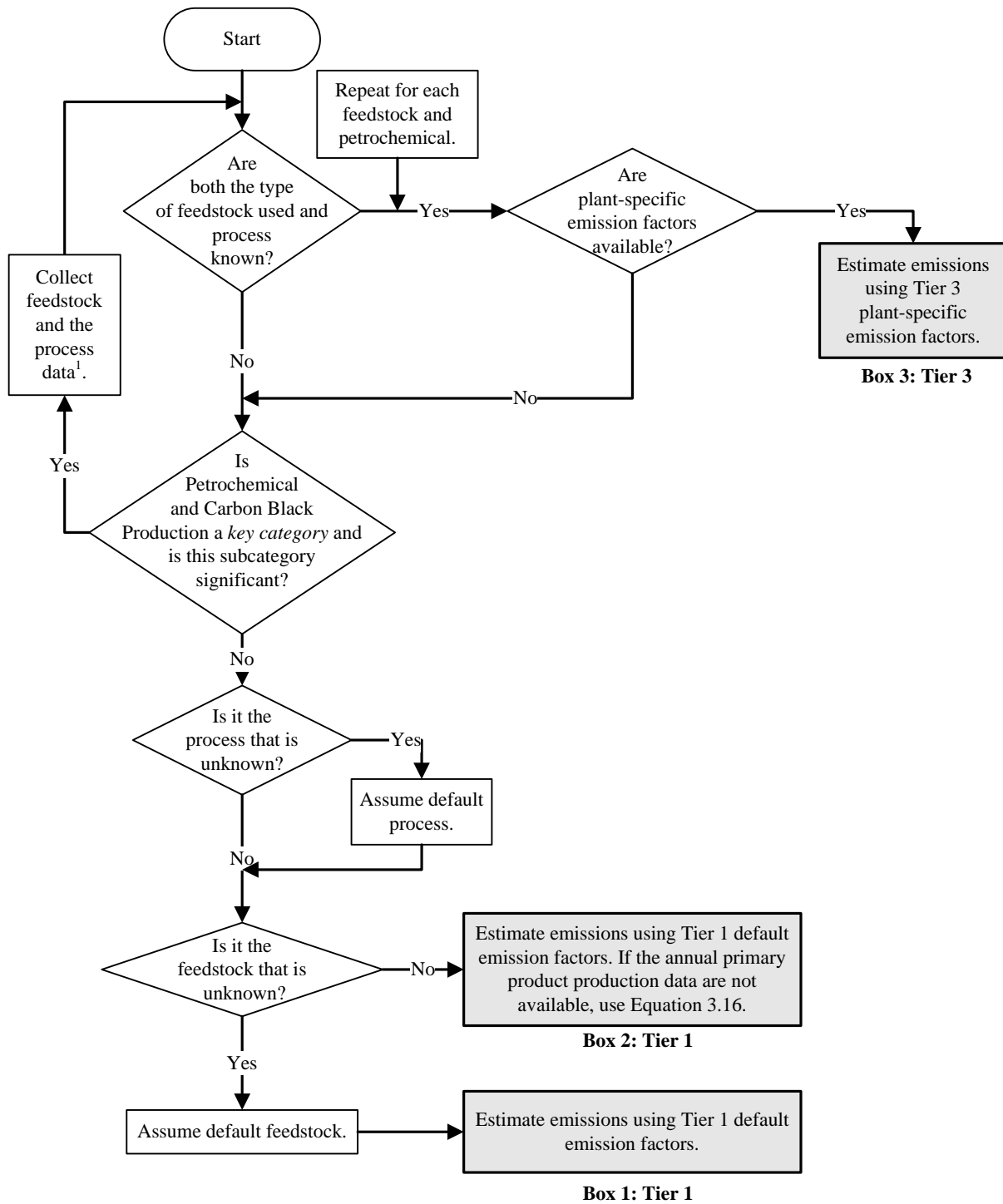
**Figure 3.8** Decision tree for estimation of CO<sub>2</sub> emissions from petrochemical industry and carbon black industry



Note:

1. See Volume 1 Chapter 4, "Methodological Choice and Identification of Key Categories" (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

**Figure 3.9 Decision tree for estimation of CH<sub>4</sub> emissions from petrochemical industry and carbon black industry**



Note:

1. See Volume 1 Chapter 4, "Methodological Choice and Identification of Key Categories" (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.
2. Note that there is no Tier 2 method for estimating CH<sub>4</sub> emissions. The Tier 2 method is a total feedstock carbon mass balance method that is applicable to estimating total carbon (CO<sub>2</sub>) emissions but not applicable to estimating CH<sub>4</sub> emissions.

The Tier 3 methodology can be used to estimate plant-level CO<sub>2</sub> emissions and CH<sub>4</sub> emissions. The Tier 3 method depends upon the availability of plant-specific data for the petrochemical process. The Tier 2 methodology is a mass balance approach that is applicable to estimating CO<sub>2</sub> emissions but is not applicable to estimating CH<sub>4</sub> emissions. When using the Tier 2 methodology, both carbon flows of primary and secondary feedstocks to the process are included in the mass balance calculation. Carbon flows of primary fuels to the



process may involve combustion of part of the hydrocarbon content for heat raising and the production of secondary fuels (e.g., off gases). In order to apply the Tier 2 methodology the flows of primary and secondary feedstocks to the process and the flows of primary and secondary products must be characterised, and the flows of by-products burned for energy recovery within the process and flows of by-products transferred out of the process must be characterised.

## CARBON DIOXIDE

The decision tree for choice of method for CO<sub>2</sub> emissions is shown in Figure 3.8. The Tier 1, Tier 2, and Tier 3 methods are described in this section.

### Tier 1 product-based emission factor method

The Tier 1 emission factor methodology is applied to estimate CO<sub>2</sub> emissions from the petrochemical process in cases where neither plant specific data nor activity data for carbon flows are available for the petrochemical process. The Tier 1 emission factor method does not require activity data for the consumption of each carbon-containing feedstock to the petrochemical production process. It requires only activity data for the amount of product produced. The Tier 1 methodology does not consider the carbon content of emissions of carbon monoxide or NMVOC that may be generated by the petrochemical processes. The equations in this section for petrochemical production processes also apply to carbon black production.

The Tier 1 method calculates emissions from petrochemical processes on the basis of activity data for production of each petrochemical and the process-specific emission factor for each petrochemical, as shown in the Equation 3.15 for production of each primary petrochemical product (e.g., methanol, ethylene, ethylene dichloride, ethylene oxide, acrylonitrile) and carbon black.

**EQUATION 3.15**  
**TIER 1 CO<sub>2</sub> EMISSION CALCULATION**  

$$ECO_{2i} = PP_i \cdot EF_i \cdot GAF / 100$$

Where:

ECO<sub>2i</sub> = CO<sub>2</sub> emissions from production of petrochemical *i*, tonnes

PP<sub>i</sub> = annual production of petrochemical *i*, tonnes

EF<sub>i</sub> = CO<sub>2</sub> emission factor for petrochemical *i*, tonnes CO<sub>2</sub>/tonne product produced

GAF = Geographic Adjustment Factor (for Tier 1 CO<sub>2</sub> emission factors for ethylene production, See Table 3.15), percent

Tier 1 CO<sub>2</sub> emission factors for ethylene production (discussed in Section 3.9.2.2) have been developed based on data for ethylene steam crackers operating in Western Europe. Geographic Adjustment Factors are applied to the Tier 1 emission factor to account for regional variability in steam cracker operating efficiency. Geographic Adjustment Factors are only applicable to ethylene production.

If activity data for annual primary product production are not available, primary product production may be estimated from feedstock consumption, as shown in the Equation 3.16:

**EQUATION 3.16**  
**PRIMARY PRODUCT PRODUCTION ESTIMATE CALCULATION**  

$$PP_i = \sum_k (FA_{i,k} \cdot SPP_{i,k})$$

Where:

PP<sub>i</sub> = annual production of petrochemical *i*, tonnes

FA<sub>i,k</sub> = annual consumption of feedstock *k* consumed for production of petrochemical (*i*), tonnes

SPP<sub>i,k</sub> = specific primary product production factor for petrochemical *i* and feedstock *k*, tonnes primary product/tonne feedstock consumed

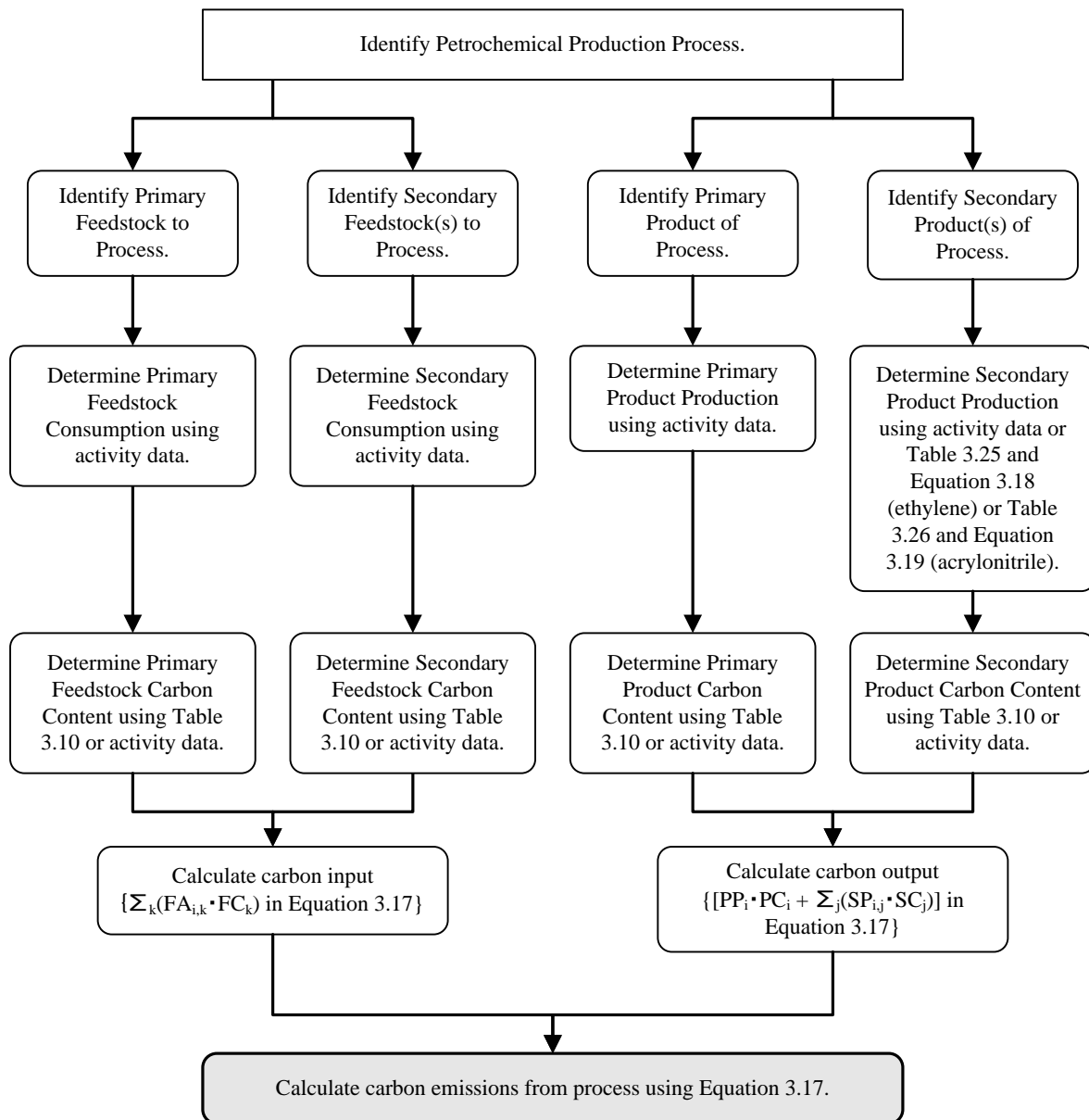
Either Equation 3.15 or both Equation 3.15 and Equation 3.16 would be applied separately to each of the known feedstocks for each petrochemical process. The Tier 1 emissions estimate shown in Box 1 of Figure 3.8 would utilise Equation 3.15, while the Tier 1 emissions estimate shown in Box 2 of Figure 3.8 would use either

Equation 3.15 or both Equation 3.16 and Equation 3.15. Equation 3.15 would be utilised alone in cases where annual primary product production data are available for the petrochemical process. In cases where annual primary product production data are not available but feedstock consumption data are available for the petrochemical process, Equation 3.16 would be utilised to estimate the annual production of primary products, and the annual primary product production estimated using Equation 3.16 would then be applied in Equation 3.15 to estimate the emissions.

### Tier 2 total feedstock carbon balance method

The Tier 2 method is a feedstock-specific and process-specific carbon balance approach. This approach is applicable in cases where activity data are available for both feedstock consumption and primary and secondary product production and disposition. Activity data for all carbon flows are required to implement the Tier 2 methodology. Examples of process flow diagrams that illustrate feedstock and product flows for the methanol, ethylene dichloride, ethylene oxide, acrylonitrile, and carbon black production processes are included in an Annex to Section 3.9. The number of potential feedstocks and products for ethylene production from the steam cracking process is such that the process is better illustrated by a feedstock-product matrix rather than by a process flow diagram. The feedstock-product matrix for ethylene production is included in Table 3.25 in Section 3.9.2.3. A flow diagram of the Tier 2 method is shown in Figure 3.10.

**Figure 3.10 Tier 2 carbon mass balance flow diagram**



The Tier 2 method calculates the difference between the total amount of carbon entering into the production process as primary and secondary feedstock and the amount of carbon leaving the production process as petrochemical products. The difference in carbon content of the primary and secondary feedstocks and the carbon content of the primary and secondary products produced by and recovered from the process is calculated as CO<sub>2</sub>. The Tier 2 mass balance methodology is based on the assumption that all of the carbon input to the process is converted either into primary and secondary products or into CO<sub>2</sub>. This means that any of the carbon input to the process that is converted into CO, CH<sub>4</sub>, or NMVOC are assumed to be CO<sub>2</sub> emissions for the purposes of the mass balance calculation.

The overall mass balance equation for the Tier 2 methodology is Equation 3.17.

$$\text{EQUATION 3.17}$$

$$\text{OVERALL TIER 2 MASS BALANCE EQUATION}$$

$$ECO2_i = \left\{ \sum_k (FA_{i,k} \cdot FC_k) - \left[ PP_i \cdot PC_i + \sum_j (SP_{i,j} \cdot SC_j) \right] \right\} \cdot 44/12$$

Where:

$ECO2_i$  = CO<sub>2</sub> emissions from production of petrochemical  $i$ , tonnes

$FA_{i,k}$  = annual consumption of feedstock  $k$  for production of petrochemical  $i$ , tonnes

$FC_k$  = carbon content of feedstock  $k$ , tonnes C/tonne feedstock

$PP_i$  = annual production of primary petrochemical product  $i$ , tonnes

$PC_i$  = carbon content of primary petrochemical product  $i$ , tonnes C/tonne product

$SP_{i,j}$  = annual amount of secondary product  $j$  produced from production process for petrochemical  $i$ , tonnes

[The value of  $SP_{i,j}$  is zero for the methanol, ethylene dichloride, ethylene oxide, and carbon black processes because there are no secondary products produced from these processes. For ethylene production and acrylonitrile production, see secondary product production Equations 3.18 and 3.19 below to calculate values for  $SP_{i,j}$ .]

$SC_j$  = carbon content of secondary product  $j$ , tonnes C/tonne product

For ethylene production and acrylonitrile production there are both primary and secondary products produced by the process. If activity data are not available for the amount of secondary products produced by these processes, the amount of secondary products produced may be estimated by applying default values to the primary feedstock consumption, as shown in Equations 3.18 and 3.19:

$$\text{EQUATION 3.18}$$

$$\text{ESTIMATE SECONDARY PRODUCT PRODUCTION FROM PRIMARY PRODUCT [ETHYLENE]}$$

$$\text{PRODUCTION}$$

$$SP_{Ethylene,j} = \sum_k (FA_{Ethylene,k} \cdot SSP_{j,k})$$

Where:

$SP_{Ethylene,j}$  = annual production of secondary product  $j$  from ethylene production, tonnes

$FA_{Ethylene,k}$  = annual consumption of feedstock  $k$  consumed for ethylene production, tonnes

$SSP_{j,k}$  = specific secondary product production factor for secondary product  $j$  and feedstock  $k$ , tonnes secondary product/tonne feedstock consumed

$$\text{EQUATION 3.19}$$

$$\text{ESTIMATE SECONDARY PRODUCT PRODUCTION FROM PRIMARY PRODUCT [ACRYLONITRILE]}$$

$$\text{PRODUCTION}$$

$$SP_{Acrylonitrile,j} = \sum_k (FP_{Acrylonitrile,k} \cdot SSP_{j,k})$$

Where:

$SP_{Acrylonitrile,j}$  = annual production of secondary product  $j$  from acrylonitrile production, tonnes

$FP_{Acrylonitrile,k}$  = annual production of acrylonitrile from feedstock  $k$ , tonnes

$SSP_{j,k}$  = specific secondary product production factor for secondary product  $j$  and feedstock  $k$ , tonnes secondary product/tonne acrylonitrile produced

Note: It is anticipated that in most cases only a single feedstock (propylene) would be used for acrylonitrile production.

### **Feedstock and product carbon contents**

Carbon contents of feedstocks and products of petrochemical production processes are listed in Table 3.10, in units of tonnes of carbon per tonne of feedstock or product. Carbon contents of pure substances (e.g., methanol) are calculated from the chemical formula. Carbon contents of other feedstocks and products (e.g., carbon black feedstock, carbon black) are estimated from literature sources. Representative carbon contents of fossil fuels (e.g., natural gas, naphtha) can be found in Table 1.3 in Chapter 1 of Volume 2: Energy; however, carbon contents for fossil fuels will vary by country and region and are best obtained from national energy statistics or fossil fuel product specifications or national standards.

### **Tier 3 direct estimate of plant-specific emissions**

The most rigorous *good practice* method is to use plant specific data to calculate CO<sub>2</sub> emissions from the petrochemical production process. In order to apply the Tier 3 method, plant-specific data and/or plant-specific measurements are required. The emissions from the petrochemical production process include CO<sub>2</sub> emitted from fuel or process by-products combusted to provide heat or thermal energy to the production process, CO<sub>2</sub> emitted from process vents, and CO<sub>2</sub> emitted from flared waste gases. These emissions are calculated using Equations 3.20 through 3.22.

Overall CO<sub>2</sub> emissions from the petrochemical production process are calculated using Equation 3.20

**EQUATION 3.20**  
**TIER 3 CO<sub>2</sub> EMISSIONS CALCULATION EQUATION**

$$ECO2_i = E_{Combustion,i} + E_{Process Vent,i} + E_{Flare,i}$$

Where:

$ECO2_i$  = CO<sub>2</sub> emissions from production of petrochemical  $i$ , tonnes

$E_{Combustion,i}$  = CO<sub>2</sub> emitted from fuel or process by-products combusted to provide heat or thermal energy to the production process for petrochemical  $i$ , tonnes

$E_{Process Vent,i}$  = CO<sub>2</sub> emitted from process vents during production of petrochemical  $i$ , tonnes

$E_{Flare,i}$  = CO<sub>2</sub> emitted from flared waste gases during production of petrochemical  $i$ , tonnes

$E_{combustion}$  and  $E_{flare}$  are given by Equations 3.21 and 3.22 where plant specific or national net calorific value data should be used. The emission factor is given by the carbon content of the fuel, the combustion oxidation factor and a constant (44/12) converting the result from carbon to CO<sub>2</sub>. If the emission factor is not known a default value may be found in Table 1.4 in Chapter 1 of Volume 2: Energy. Net calorific values are included in Table 1.2 in Chapter 1 of Volume 2: Energy. Carbon contents are included in Table 1.3 in Chapter 1 of Volume 2: Energy. For the process vents, inventory compilers should measure/estimate emissions of CO<sub>2</sub> directly and thus no further equation is provided.

**EQUATION 3.21**  
**FUEL COMBUSTION TIER 3 CO<sub>2</sub> EMISSIONS CALCULATION**

$$E_{Combustion,i} = \sum_k (FA_{i,k} \cdot NCV_k \cdot EF_k)$$

Where:

$FA_{i,k}$  = amount of fuel  $k$  consumed for production of petrochemical  $i$ , tonnes

$NCV_k$  = net calorific value of fuel  $k$ , TJ/tonne

(Note: In Table 1.2 in Chapter 1 of Volume 2, net calorific values are expressed in TJ/kg)

$EF_k$  = CO<sub>2</sub> emission factor of fuel  $k$ , tonnes CO<sub>2</sub>/TJ  
 (Note: In Table 1.4 in Chapter 1 of Volume 2, CO<sub>2</sub> emission factors are expressed in kg/TJ)

**EQUATION 3.22**  
**FLARE GAS TIER 3 CO<sub>2</sub> EMISSIONS CALCULATION**

$$E_{Flare,i} = \sum_k (FG_{i,k} \cdot NCV_k \cdot EF_k)$$

Where:

$FG_{i,k}$  = amount of gas  $k$  flared during production of petrochemical  $i$ , tonnes

$NCV_k$  = net calorific value of flared gas  $k$ , TJ/tonne  
 (Note: In Table 1.2 in Chapter 1 of Volume 2, net calorific values are expressed in TJ/kg)

$EF_k$  = CO<sub>2</sub> emission factor of flared gas  $k$ , tonnes CO<sub>2</sub>/TJ  
 (Note: In Table 1.4 in Chapter 1 of Volume 2, CO<sub>2</sub> emission factors are expressed in kg/TJ)

| Substance              | Carbon (tonne carbon per tonne feedstock or product) |
|------------------------|--|
| Acetonitrile           | 0.5852   |
| Acrylonitrile          | 0.6664   |
| Butadiene              | 0.888  |
| Carbon black           | 0.970  |
| Carbon Black Feedstock | 0.900  |
| Ethane                 | 0.856  |
| Ethylene               | 0.856  |
| Ethylene dichloride    | 0.245  |
| Ethylene glycol        | 0.387  |
| Ethylene oxide         | 0.545  |
| Hydrogen Cyanide       | 0.4444   |
| Methanol               | 0.375  |
| Methane                | 0.749  |
| Propane                | 0.817  |
| Propylene              | 0.8563   |
| Vinyl Chloride Monomer | 0.384  |

Note: Carbon content values for natural gas and naphtha vary by country and region. Net calorific values (NCV) for natural gas, naphtha, and other primary fuels that may be used as petrochemical feedstocks are included in Table 1.2 in Chapter 1 of Volume 2: Energy. Feedstock carbon contents are included in Table 1.3 in Chapter 1 of Volume 2: Energy.

## METHANE

The decision tree for choice of method for CH<sub>4</sub> emissions is shown in Figure 3.9. The Tier 1 and Tier 3 methods for CH<sub>4</sub> are described in this section. There is no Tier 2 method applicable to CH<sub>4</sub> emissions.

### Tier 1 product-based emission factor method

CH<sub>4</sub> emissions from petrochemical processes may be fugitive emissions and/or process vent emissions. Fugitive emissions are emitted from flanges, valves, and other process equipment. Emissions from process vent sources include incomplete combustion of waste gas in flare and energy recovery systems. CH<sub>4</sub> emissions using the Tier 1 method may be calculated using Equation 3.23 for fugitive CH<sub>4</sub> emissions and Equation 3.24 for process vent

emissions and Equation 3.25 for total CH<sub>4</sub> emissions. If annual primary product production data are not available but feedstock consumption data are available for the petrochemical process, Equation 3.16 would be utilised to estimate the annual production of primary products, and the annual primary product production estimated using Equation 3.16 would then be applied in Equations 3.23 and 3.24 to estimate the emissions.

**EQUATION 3.23**

**TIER 1 CH<sub>4</sub> FUGITIVE EMISSION CALCULATION**

$$ECH4_{Fugitive,i} = PP_i \bullet EFf_i$$

**EQUATION 3.24**

**TIER 1 CH<sub>4</sub> PROCESS VENT EMISSION CALCULATION**

$$ECH4_{Process Vent,i} = PP_i \bullet EFP_i$$

**EQUATION 3.25**

**TIER 1 CH<sub>4</sub> TOTAL EMISSIONS CALCULATION**

$$ECH4_{Total,i} = ECH4_{Fugitive,i} + ECH4_{Process Vent,i}$$

Where:

$ECH4_{Total,i}$  = total emissions of CH<sub>4</sub> from production of petrochemical *i*, kg

$ECH4_{Fugitive,i}$  = fugitive emissions of CH<sub>4</sub> from production of petrochemical *i*, kg

$ECH4_{Process Vent,i}$  = process vent emissions of CH<sub>4</sub> from production of petrochemical *i*, kg

$PP_i$  = annual production of petrochemical *i*, tonnes

$EFf_i$  = CH<sub>4</sub> fugitive emission factor for petrochemical *i*, kg CH<sub>4</sub>/tonne product

$EFP_i$  = CH<sub>4</sub> process vent emission factor for petrochemical *i*, kg CH<sub>4</sub>/tonne product

### **Tier 2 total feedstock carbon balance method**

The total feedstock carbon mass balance method is not applicable to estimation of CH<sub>4</sub> emissions. The total carbon mass balance method estimates the total carbon emissions from the process but does not directly provide an estimate of the amount of the total carbon emissions that is emitted as CO<sub>2</sub>, CH<sub>4</sub>, CO, or NMVOC.

### **Tier 3 direct estimate of plant-specific emissions**

The Tier 3 method is based on continuous or periodic plant-specific measurements. The emissions from the petrochemical production process include CH<sub>4</sub> emitted from fuel or process by-products combusted to provide heat or thermal energy to the production process, CH<sub>4</sub> emitted from process vents, and CH<sub>4</sub> emitted from flared waste gases. If methane is vented directly to the atmosphere this will dominate the emissions. CH<sub>4</sub> emissions from process vents may also be combusted in a flare or energy recovery device. Measurement of atmospheric concentration of VOCs directly above the plants or in the plume is the preferred activity data for estimating fugitive CH<sub>4</sub> emissions; however, such data may not be available. The atmospheric measurements are generally expensive and will most often not be continuous measurements but rather a discrete and periodic measurement program to obtain data to be used as basis for the development of plant specific emission factors. The results of such measurement programs would then be related to other plant process parameters to enable estimation of emissions between measurement periods.

Direct measurement of VOC and CH<sub>4</sub> concentrations in plant exhaust gas streams and direct measurement of fugitive VOC and CH<sub>4</sub> emissions from plant valves, fittings, and related equipment using a comprehensive leak detection programme can also be used to obtain plant-specific activity data for developing Tier 3 estimates of CH<sub>4</sub> emissions. However the plant-specific leak detection programme should provide fugitive CH<sub>4</sub> emissions data for all of the relevant CH<sub>4</sub>-emitting plant equipment. Similarly, the plant-specific measurement data for stacks and vents would need to cover the major portion of stack and vent CH<sub>4</sub> emissions sources at the plant in order to provide a basis for a Tier 3 emission calculation.

Emissions of CH<sub>4</sub> from process stacks and vents may be estimated by direct measurement of the CH<sub>4</sub> concentration of the exhaust gas or estimated as a component of the total VOC concentration measured in the exhaust gas. Fugitive emissions of CH<sub>4</sub> from plant equipment (e.g., valves, fittings) may be estimated through application of plant-specific leak detection data and plant equipment inventories, provided that the plant-specific leak detection program and equipment inventory are comprehensive, such that the program provides fugitive CH<sub>4</sub> emissions data for all of the relevant CH<sub>4</sub>-emitting plant equipment. Similarly, the plant-specific measurement data for stacks and vents would need to cover the major portion of stack and vent CH<sub>4</sub> emissions sources at the plant in order to provide a basis for a Tier 3 emission calculation.

Measurement of fugitive emissions may also be based on the CH<sub>4</sub> concentration in the atmosphere immediately above the plant or in a plume downwind. Such atmospheric measurement data would generally measure emissions from the entire plant, and does not separate between the different sources. In addition to CH<sub>4</sub> concentration the area of the plume and the wind speed must be measured. The emissions are given by Equation 3.26.

**EQUATION 3.26**  
**TIER 3 CH<sub>4</sub> EMISSION CALCULATION BASED ON ATMOSPHERIC MEASUREMENT DATA**

$$CH_4_{Emissions} = \int_t [(C_{total\ VOCs} \bullet CH_4\ fraction - CH_4\ background\ level) \bullet WS \bullet PA]$$

Where:

CH<sub>4</sub><sub>Emissions</sub> = total plant CH<sub>4</sub> emissions, µg/s

C<sub>total VOCs</sub> = VOC concentration at the plant, µg/m<sup>3</sup>

CH<sub>4</sub> fraction = fraction of total VOC concentration that is CH<sub>4</sub>, fraction

CH<sub>4</sub> background level = ambient CH<sub>4</sub> concentration at background location, µg/m<sup>3</sup>

WS = wind speed at the plant, m/s

PA = plume area, m<sup>2</sup>

Note:  $\int_t$  means the quantity should be summed over time.

Note that the Tier 3 methodology does not direct inventory compilers to conduct atmospheric measurements or other specific types of direct measurements to estimate site-specific CH<sub>4</sub> emissions. It is anticipated that plant-specific leak detection data and plant-specific stack and vent emission data will be more readily available than atmospheric measurement data. However, if atmospheric measurement data are available the data may be used to develop Tier 3 estimates of CH<sub>4</sub> emissions, or to verify other estimates. Atmospheric measurement data may provide a more accurate estimate of process CH<sub>4</sub> emissions than leak detection data and stack and vent emission data. A plant would use either i) Equation 3.26 or ii) Equations 3.27, 3.28, and 3.29 to estimate CH<sub>4</sub> emissions. Process vent emissions are assumed to be monitored either discretely or continuously. The method of calculation will vary depending upon the type of data, and therefore no separate equation is provided for process vent emissions calculation.

Overall emissions of CH<sub>4</sub> from the petrochemical production process based on plant-specific leak detection data and plant-specific stack and vent emissions data are calculated using Equation 3.27

**EQUATION 3.27**  
**TIER 3 CH<sub>4</sub> EMISSIONS CALCULATION EQUATION**

$$ECH_4_i = E_{Combustion,i} + E_{Process\ Vent,i} + E_{Flare,i}$$

Where:

ECH<sub>4</sub><sub>i</sub> = total emissions of CH<sub>4</sub> from production of petrochemical *i*, kg

E<sub>Combustion,i</sub> = emissions of CH<sub>4</sub> from fuel or process by-products combusted to provide heat or thermal energy to the production process for petrochemical *i*, kg

E<sub>Process Vent,i</sub> = emissions of CH<sub>4</sub> from process vents during production of petrochemical *i*, kg

E<sub>Flare,i</sub> = emissions of CH<sub>4</sub> from flared waste gases during production of petrochemical *i*, kg

E<sub>combustion</sub> and E<sub>flare</sub> are given by Equations 3.28 and 3.29 where plant specific or national net calorific value data should be used.

**EQUATION 3.28**  
**FUEL COMBUSTION TIER 3 CH<sub>4</sub> EMISSIONS CALCULATION**

$$E_{Combustion,i} = \sum_k (FA_{i,k} \cdot NCV_k \cdot EF_k)$$

Where:

$FA_{i,k}$  = amount of fuel  $k$  consumed for production of petrochemical  $i$ , tonnes

$NCV_k$  = net calorific value of fuel  $k$ , TJ/tonne

(Note: In Table 1.2 in Chapter 1 of Volume 2, net calorific values are expressed in TJ/kg)

$EF_k$  = CH<sub>4</sub> emission factor of fuel  $k$ , kg/TJ

**EQUATION 3.29**  
**FLARE GAS TIER 3 CH<sub>4</sub> EMISSIONS CALCULATION**

$$E_{Flare,i} = \sum_k (FG_{i,k} \cdot NCV_k \cdot EF_k)$$

Where:

$FG_{i,k}$  = amount of gas  $k$  flared during production of petrochemical  $i$ , tonnes

$NCV_k$  = net calorific value of flared gas  $k$ , TJ/tonne

(Note: In Table 1.2 in Chapter 1 of Volume 2, net calorific values are expressed in TJ/kg)

$EF_k$  = CH<sub>4</sub> emission factor of flared gas  $k$ , kg/TJ

### 3.9.2.2 CHOICE OF EMISSION FACTORS

This section includes a discussion of the choice of emission factors for the Tier 1 method. The Tier 2 method is based on mass balance principles and the Tier 3 method is based on plant-specific data; therefore there are no default emission factors applicable to the Tier 2 and Tier 3 methods.

| <b>Petrochemical Process</b>                 | <b>Default Feedstock</b>   | <b>Default Process</b>   |
|--|--|--|
| Methanol                                     | Natural Gas  | Conventional steam reforming without primary reformer                            |
| Ethylene                                     | North America, South America, Australia - Ethane<br>Other Continents - Naphtha | Steam cracking<br>Steam cracking   |
| Ethylene Dichloride / Vinyl Chloride Monomer | Ethylene   | Balanced Process for EDC production with integrated VCM production plant         |
| Ethylene Oxide                               | Ethylene   | Catalytic Oxidation, Air Process, with thermal treatment                         |
| Acrylonitrile                                | Propylene  | Direct Ammoxidation with secondary products burned for energy recovery or flared |
| Carbon Black                                 | Carbon black feedstock and natural gas   | Furnace black process with thermal treatment                                     |

#### TIER 1

Tier 1 emission factors for CO<sub>2</sub> emissions and CH<sub>4</sub> emissions for petrochemical products are provided below. Tier 1 emission factors for CO<sub>2</sub> emissions do not include carbon emitted as CO, CH<sub>4</sub>, or NMVOC. Separate Tier 1 emission factors are provided for CH<sub>4</sub> emissions from petrochemical processes. Tier 1 emission factors are not provided for carbon monoxide and NMVOC emissions.

The Tier 1 method allows for the selection of a 'default' feedstock and 'default' process in instances where activity data are not available to identify the feedstock or the process utilised to produce the petrochemical. Table 3.11 provides the default feedstocks and default processes for each petrochemical production process. In



the event that no activity data are available concerning the specific processes and feedstocks used within a country to produce the petrochemical, the default process and default feedstock identified in Table 3.11 and the associated Tier 1 emission factors identified in the subsequent tables in this section are used to estimate the CO<sub>2</sub> emissions from the petrochemical production process. Country-specific emission factors may be used instead of the default emission factors if country-specific factors are available.

## Methanol

### *Carbon dioxide emissions*

Emissions of CO<sub>2</sub> from methanol production from the steam reforming and partial oxidation processes may be estimated by applying the default process feedstock emission factors, or the feedstock-specific and process-specific emission factors in Table 3.12, to activity data for methanol production, process configuration and process feedstock. The default emission factors are based on the average of plant-specific CO<sub>2</sub> emissions data reported for four methanol plants using the conventional steam reforming process without primary reformer and using natural gas feedstock. Emissions data used in developing the default CO<sub>2</sub> emission factor were reported for conventional process methanol plants in New Zealand, Chile, and Canada and in the Netherlands. Emission factors in the table include both the CO<sub>2</sub> emissions arising from the process feedstock and the CO<sub>2</sub> emissions arising from feedstock combusted within the steam reforming process. Table 3.13 summarises the total feedstock consumption, in units of GJ/tonne methanol produced, for the various methanol production process configurations and feedstocks shown in Table 3.12.

The conventional reforming process can include a single reformer unit or both a primary reformer unit and a secondary reformer. The emission factors differ depending upon the number of reformer units. Lurgi is a provider of methanol process technology and has published emission factors for several conventional reforming process technologies, see Table 3.12. The production capacity of Mega Methanol plants is generally greater than 5 000 tonnes per day of methanol. The emission factors for the Lurgi Conventional process technologies should be applied only if the specific process technology is known. Otherwise the emission factor for conventional steam reforming without primary reformer, or the emission factor for conventional steam reforming with primary reformer, should be applied.

The conventional steam reforming process for methanol production can be integrated with an ammonia production process. The emission factor for integrated methanol and ammonia production should be used only if the specific process technology is known.

| TABLE 3.12<br>METHANOL PRODUCTION CO <sub>2</sub> EMISSION FACTORS  |           |  |                            |       |       |         |
|---|-----------|--|----------------------------|-------|-------|---------|
| Process Configuration   | Feedstock | tonne CO <sub>2</sub> /tonne methanol produced |                            |       |       |         |
|   |           | Nat. gas                                       | Nat. gas + CO <sub>2</sub> | Oil   | Coal  | Lignite |
| Conventional Steam Reforming, without primary reformer (a)<br>(Default Process and Natural Gas Default Feedstock)   |           | 0.67   |                            |       |       |         |
| Conventional Steam Reforming, with primary reformer (b)   |           | 0.497  |                            |       |       |         |
| Conventional Steam Reforming, Lurgi Conventional process (c1)   |           | 0.385  | 0.267                      |       |       |         |
| Conventional Steam Reforming, Lurgi Low Pressure Process (c2)   |           | 0.267  |                            |       |       |         |
| Combined Steam Reforming, Lurgi Combined Process (c3)   |           | 0.396  |                            |       |       |         |
| Conventional Steam Reforming, Lurgi Mega Methanol Process (c4)  |           | 0.310  |                            |       |       |         |
| Partial oxidation process (d)   |           |  |                            | 1.376 | 5.285 | 5.020   |
| Conventional Steam Reforming with integrated ammonia production   |           | 1.02   |                            |       |       |         |
| Nat. gas + CO <sub>2</sub> feedstock process based on 0.2-0.3 tonne CO <sub>2</sub> feedstock per tonne methanol<br>Emission factors in this table are calculated from the feedstock consumption values in Table 3.13 based on the following feedstock carbon contents and heating values:<br>Natural Gas: 56 kg CO <sub>2</sub> /GJ      48.0 GJ/tonne<br>Oil: 74 kg CO <sub>2</sub> /GJ      42.7 GJ/tonne<br>Coal: 93 kg CO <sub>2</sub> /GJ      27.3 GJ/tonne<br>Lignite: 111 kg CO <sub>2</sub> /GJ<br>Uncertainty values for this table are included in Table 3.27 |           |  |                            |       |       |         |
| Sources: (a) Strucker, A, and Blok, K, 1995; Methanex, 2003; (b) Hinderink, 1996; (c1 – c4) Lurgi, 2004a; Lurgi, 2004b; Lurgi, 2004c; (d) FgH-ISI, 1999   |           |  |                            |       |       |         |

**TABLE 3.13**  
**METHANOL PRODUCTION FEEDSTOCK CONSUMPTION FACTORS**

| Process Configuration   | Feedstock | GJ feedstock input /tonne methanol produced |                            |       |      |         |
|---|-----------|---|----------------------------|-------|------|---------|
|   |           | Nat. gas                                    | Nat. gas + CO <sub>2</sub> | Oil   | Coal | Lignite |
| Conventional Steam Reforming, without primary reformer (a)<br>(Default Process and Natural Gas Default Feedstock)                                       |           | 36.5  |                            |       |      |         |
| Conventional Steam Reforming, with primary reformer (b)   |           | 33.4  | 29.3                       |       |      |         |
| Conventional Steam Reforming, Lurgi Conventional process (c1)   |           | 31.4  |                            |       |      |         |
| Conventional Steam Reforming, Lurgi Low Pressure Process (c2)   |           | 29.3  |                            |       |      |         |
| Combined Steam Reforming, Lurgi Combined Process (c3)   |           | 31.6  |                            |       |      |         |
| Conventional Steam Reforming, Lurgi Mega Methanol Process (c4)  |           | 30.1  |                            |       |      |         |
| Partial oxidation process (d)   |           |   |                            | 37.15 | 71.6 | 57.6    |
| Nat. gas + CO <sub>2</sub> feedstock process based on 0.2-0.3 tonne CO <sub>2</sub> feedstock per tonne methanol  |           |   |                            |       |      |         |
| Sources: (a) Straker, A, and Blok, K, 1995; Methanex, 2003; (b) Hinderink, 1996; (c1 – c4) Lurgi, 2004a; Lurgi, 2004b; Lurgi, 2004c ; (d) FgH-ISI, 1999 |           |   |                            |       |      |         |
| Uncertainty values for this table are included in Table 3.27  |           |   |                            |       |      |         |

### ***Methane emissions***

Methanex reported CH<sub>4</sub> emissions from two Canadian methanol production plants in their 1996 Climate Change Action Plan (Methanex, 1996). Methanex reported that CH<sub>4</sub> emissions from methanol production may arise from reformers, package boilers, methanol distillation units, and crude methanol storage tanks. CH<sub>4</sub> emissions from the plants accounted for approximately 0.5 percent to 1.0 percent of the total greenhouse gas emissions from the plants, but were reported to vary depending upon the level of maintenance and operational control of the plant equipment. The average emission factor reported for two reporting years is 2.3 kg CH<sub>4</sub> emissions per tonne of methanol produced. CH<sub>4</sub> emissions from a second Methanex methanol production plant were reported to be 0.15 kg CH<sub>4</sub> per tonne of methanol produced. The higher of the two reported values, 2.3 kg CH<sub>4</sub> per tonne of methanol produced, should be applied as the default CH<sub>4</sub> emission factor for methanol production. CH<sub>4</sub> emissions as low as 0.1 kg/tonne have been estimated for the methanol plant Tjeldbergodden, Norway (SFT, 2003a).

## **Ethylene**

### ***Carbon dioxide emissions***

Emissions of CO<sub>2</sub> from steam cracking for ethylene production may be estimated using the feedstock-specific emission factors in Table 3.14 and activity data for the amount of ethylene produced from the steam cracking processes. Separate emission factors are provided in Table 3.14 for the CO<sub>2</sub> emissions from feedstock consumption and from supplemental energy consumption in the steam cracking process. However, the CO<sub>2</sub> emissions from both feedstock consumption and supplemental energy consumption are to be reported as Industrial Process emissions under the reporting convention discussed above. The default emission factors are derived from plant-specific data for steam crackers operating in Western Europe. The emission factors may be adjusted by applying the default geographic adjustment factors in Table 3.15 to account for differences in the energy efficiency of steam cracking units among various countries and regions. Note that as indicated in Table 3.11, the default feedstock for steam crackers operating in North and South America and Australia is ethane, and the default feedstock for steam crackers operating on other continents is naphtha.

These default emission factors do not include CO<sub>2</sub> emissions from flaring. Emissions from flaring amount to about 7 percent of total emissions in a well-maintained plant in Norway. Steam cracking processes that utilise naphtha, propane, and butane feedstocks are assumed to be energy neutral, requiring no use of supplemental fuel, therefore there are assumed to be no CO<sub>2</sub> emissions associated with supplemental fuel consumption for these feedstocks.

**TABLE 3.14**  
**STEAM CRACKING ETHYLENE PRODUCTION TIER 1 CO<sub>2</sub> EMISSION FACTORS**

| Feedstock   | tonnes CO <sub>2</sub> /tonne ethylene produced |         |        |         |        |       |
|---|---|---------|--------|---------|--------|-------|
|   | Naphtha   | Gas Oil | Ethane | Propane | Butane | Other |
| Ethylene (Total Process and Energy Feedstock Use) | 1.73  | 2.29    | 0.95   | 1.04    | 1.07   | 1.73  |
| - Process Feedstock Use                           | 1.73  | 2.17    | 0.76   | 1.04    | 1.07   | 1.73  |
| - Supplemental Fuel (Energy Feedstock) Use        | 0   | 0.12    | 0.19   | 0       | 0      | 0     |

Source: Neelis, M., Patel, M., and de Feber, M., 2003, Table 2.3, Page 26.  
Default feedstocks for ethylene production are identified in Table 3.11. The emission factors do not include supplemental fuel use in flares. Other feedstocks are assumed to have the same product yields as naphtha feedstock.  
Uncertainty values for this table are included in Table 3.27.

The emission factors in Table 3.14 may be used in the event that activity data are available only for the amount of ethylene produced by the steam cracking process. Steam cracking is a multi-product process that leads to ethylene, propylene, butadiene, aromatics, and several other high-value chemicals. There is an inherent assumption of a specific product mix in the default emission factors in Table 3.14. The default product mix for each emission factor in Table 3.14 is identified in the ethylene steam cracking feedstock-product matrix in Section 3.9.2.3. The feedstock/product matrix identifies the default values for production of ethylene, propylene, and other hydrocarbon products from the steam cracking process in units of kilograms of each product produced per tonne of feedstock. In order to develop the emission factors for steam cracking shown in Table 3.14 the total CO<sub>2</sub> process emissions of a steam cracker have been divided by the output of ethylene only. In other words ethylene has been chosen as the reference for estimating the total CO<sub>2</sub> emissions from the steam cracking process as a whole. Multiplication of the emission factors in Table 3.14 by the ethylene production therefore leads to the total CO<sub>2</sub> emissions resulting not only from the production of ethylene but also from the production of propylene, butadiene, aromatics, and all other chemicals produced by the steam cracking process. The default emission factors in Table 3.14 provide the total CO<sub>2</sub> emissions from the steam cracking process, not only the CO<sub>2</sub> emissions associated with the production of the ethylene from the steam cracking process.

**TABLE 3.15**  
**DEFAULT GEOGRAPHIC ADJUSTMENT FACTORS FOR TIER 1 CO<sub>2</sub> EMISSION FACTORS FOR STEAM CRACKING ETHYLENE PRODUCTION**

| Geographic Region                             | Adjustment Factor | Notes   |
|---|-------------------|---|
| Western Europe                                | 100%              | Values in Table 3.14 are based on data from Western European steam crackers |
| Eastern Europe                                | 110%              | Not including Russia  |
| Japan and Korea                               | 90%               |   |
| Asia, Africa, Russia                          | 130%              | Including Asia other than Japan and Korea                                   |
| North America and South America and Australia | 110%              |   |

Source: Adjustment factors are based on data provided by Mr. Roger Matthews in personal communication to Mr. Martin Patel, May 2002.  
Uncertainty values for this table are included in Table 3.27.

### ***Methane emissions***

Default fugitive CH<sub>4</sub> emission factors for steam cracking of ethane and naphtha for ethylene production are estimated from total VOC emissions factors and VOC species profile data from EMEP/CORINAIR Emission Inventory Guidebook (EEA, 2005). Overall volatile organic compound emissions from steam cracking are estimated to be 5 kg/tonne ethylene produced based on a European publication, for which the feedstock is assumed to be naphtha, and estimated to be 10 kg VOC/tonne ethylene produced based on a U.S. publication, for which the feedstock is assumed to be ethane. From the total VOC emission factors the overall CH<sub>4</sub> emissions from steam cracking of naphtha are estimated from the VOC species profile to be 3 kg/tonne ethylene produced, primarily from leakage losses, and the overall CH<sub>4</sub> emissions from cracking of ethane are estimated from the species profile to be twice those from cracking of naphtha (6 kg/tonne ethylene produced); however these factors are subject to uncertainty as the overall VOC emission factors of 5 kg VOC/tonne ethylene for naphtha feedstock and 10 kg VOC/tonne ethylene for ethane feedstock are each based on a single publication. Emissions of CH<sub>4</sub>

from steam cracking of feedstocks other than ethane and naphtha have been assumed to be the same as that estimated from the EMEP/CORINAIR data for steam cracking of naphtha.

Published data show a large variability in reported CH<sub>4</sub> emission factors for ethylene production. The European Association of Plastics Manufacturers (APME) Eco-Profiles of the European Plastics Industry reports a CH<sub>4</sub> emission factor for ethylene production of 2.9 kg CH<sub>4</sub>/tonne ethylene produced, as referenced in the APME Eco-Profiles for Olefins Production (Boustead, 2003a). The CH<sub>4</sub> emission factor for ethylene steam cracker process operations is based on life-cycle analysis data for 15 European steam crackers. Emissions as low as 0.14 kg CH<sub>4</sub>/tonne ethylene are estimated on the basis of direct measurement at a Norwegian ethylene plant (SFT 2003b) and as low as 0.03 kg CH<sub>4</sub>/tonne ethylene based on company data reported in the Australian Methodology for the Estimation of Greenhouse Gas Emissions and Sinks, 2003 (AGO, 2005). Other European and Australian steam cracker operators reported plant-specific CH<sub>4</sub> emissions on the order of 10 percent of the values reported in Table 3.16 (DSM, 2002; Qenos, 2003; Qenos, 2005). Therefore, the emission factors in Table 3.16 should not be used to estimate CH<sub>4</sub> emissions from steam cracker ethylene plants for which plant-specific data are available. In this case the plant-specific data and the Tier 3 method should be used. Default CH<sub>4</sub> emission factors for various process feedstocks are shown in Table 3.16. Note that the default feedstocks for ethylene production are identified in Table 3.11.

| <b>Feedstock</b>   | <b>kg CH<sub>4</sub>/ tonne ethylene produced</b> |
|--|---|
| Ethane   | 6   |
| Naphtha  | 3   |
| All Other Feedstocks   | 3   |
| Source: EEA, 2005 (EMEP/CORINAIR Emission Inventory Guidebook) |   |
| Uncertainty values for this table are included in Table 3.27.  |   |

## **Ethylene dichloride and vinyl chloride monomer**

### ***Carbon dioxide emissions***

Emission factors are provided in Table 3.17 for the ethylene dichloride and vinyl chloride monomer production processes, including the direct chlorination process, oxychlorination process, and balanced process. The CO<sub>2</sub> emission factors are derived by averaging plant-specific CO<sub>2</sub> emissions data for European plants reported in the Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry (European IPPC Bureau, February 2003; referred to in this section as the IPPC LVOC BAT Document). Note that as indicated in Table 3.11, the default process is the balanced process for EDC production with an integrated VCM production plant. The total CO<sub>2</sub> emission factor for each process includes noncombustion CO<sub>2</sub> emissions from the ethylene dichloride process vent and combustion CO<sub>2</sub> emissions from ethylene dichloride plant combustion sources. Plant combustion source emission factors include combustion of both process waste gas and auxiliary fuel in the process waste gas thermal incinerator. The combustion-related emission factor does not include emissions from flares. Combustion-related emission factors in Table 3.17 are based on data from oxychlorination process plants but the emission factors are assumed also to apply to direct chlorination and balanced process plants. Feedstock consumption factors for ethylene dichloride and vinyl chloride monomer production processes are provided in Table 3.18. The PlasticsEurope EcoProfiles (Boustead, 2005) for EDC production indicates ethylene utilisation of 0.306 tonnes ethylene per tonne EDC produced, based on eight European plants.

It should be noted that the CO<sub>2</sub> emission factors in Table 3.17 in units of tonnes CO<sub>2</sub> per tonne EDC produced and in units of tonnes CO<sub>2</sub> per tonne VCM produced are not additive. The two CO<sub>2</sub> emission factors both apply to the integrated EDC/VCM production process, however the tonnes CO<sub>2</sub> per tonne EDC factor is based on EDC production activity data while the tonnes CO<sub>2</sub> per tonne VCM factor is based on VCM production activity data. The CO<sub>2</sub> emission factor that will be applied will depend upon whether activity data for EDC production or activity data for VCM production are available. Similarly, the feedstock consumption factors in Table 3.18 in units of tonnes ethylene consumed per tonne EDC produced and in units of tonnes ethylene consumed per tonne VCM produced are not additive. The feedstock consumption factor that will be applied will depend upon whether activity data are available for EDC production or for VCM production.

| <b>Process Configuration</b>  | <b>tonne CO<sub>2</sub>/tonne EDC produced</b> | <b>tonne CO<sub>2</sub>/tonne VCM produced</b> |
|---|--|--|
| <b>Direct Chlorination Process</b>  |  |  |
| Noncombustion Process Vent  | negligible emissions                           | negligible emissions                           |
| Combustion Emissions  | 0.191  | 0.286  |
| <b>Total CO<sub>2</sub> Emission Factor</b>   | <b>0.191</b>                                   | <b>0.286</b>                                   |
| <b>Oxychlorination Process</b>  |  |  |
| Noncombustion Process Vent  | 0.0113   | 0.0166   |
| Combustion Emissions  | 0.191  | 0.286  |
| <b>Total CO<sub>2</sub> Emission Factor</b>   | <b>0.202</b>                                   | <b>0.302</b>                                   |
| <b>Balanced Process [default process]</b>   |  |  |
| Noncombustion Process Vent  | 0.0057   | 0.0083   |
| Combustion Emissions  | 0.191  | 0.286  |
| <b>Total CO<sub>2</sub> Emission Factor</b>   | <b>0.196</b>                                   | <b>0.294</b>                                   |
| Values for CO <sub>2</sub> emissions from EDC and VCM production for several European production plants were provided in Tables 12.6 and 12.7 of the IPPC LVOC BAT Document (European IPPC Bureau, 2003). These values were averaged to calculate CO <sub>2</sub> emission factors for EDC and VCM production. One EDC plant that is equipped with a CO <sub>2</sub> control device and that reported zero CO <sub>2</sub> emissions from the process is not included in the average emission factor. |  |  |
| Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Tables 12.6 and 12.7 data).   |  |  |
| Uncertainty values for this table are included in Table 3.27.   |  |  |

| <b>Process Configuration</b>  | <b>tonne ethylene/tonne EDC produced</b> | <b>tonne ethylene/tonne VCM produced</b> |
|---|--|--|
| Direct Chlorination Process   | 0.290                                    | --                                       |
| Oxychlorination Process   | 0.302                                    | --                                       |
| Balanced Process  | 0.296                                    | 0.47                                     |
| Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 12.3.1, Page 299-300, Section 12.1 Table 12.3, Page 293). |  |  |
| Uncertainty values for this table are included in Table 3.27.   |  |  |

### ***Methane emissions***

The EMEP/CORINAIR 'species profile' for the ethylene dichloride/vinyl chloride monomer balanced process indicates that there are no CH<sub>4</sub> emissions from the process other than CH<sub>4</sub> emissions from combustion sources. The EMEP/CORINAIR species profile reports that VOC emissions from leakage losses and storage and handling do not contain CH<sub>4</sub>. The EMEP/CORINAIR also reports that 2 percent of the total VOC emissions from the balanced process are from combustion sources and that CH<sub>4</sub> constitutes 1.2 percent of overall VOC emissions. Therefore it may be assumed that non-combustion CH<sub>4</sub> emissions from ethylene dichloride/vinyl chloride monomer production are negligible.

CH<sub>4</sub> emissions from combustion of natural gas supplemental fuel in the ethylene dichloride/vinyl chloride monomer production process may be estimated from activity data for natural gas supplemental fuel consumption and CH<sub>4</sub> emission factor for natural gas combustion. Natural gas consumption for integrated ethylene dichloride/vinyl chloride monomer production is estimated to be 110.1 Nm<sup>3</sup> natural gas/tonne VCM produced for an integrated ethylene dichloride/vinyl chloride monomer production plant in the Netherlands and 126.4 Nm<sup>3</sup> natural gas/tonne VCM produced for an integrated ethylene dichloride/vinyl chloride monomer production plant in Germany. The average of these two values is 118.3 Nm<sup>3</sup> natural gas/tonne VCM. The CH<sub>4</sub> emission factor for the integrated EDC/VCM production process is based on a CH<sub>4</sub> emission factor of 5 g CH<sub>4</sub>/GJ natural gas combusted and the average natural gas consumption of the two European plants. The default CH<sub>4</sub> emission factor for the integrated ethylene dichloride/vinyl chloride monomer production process is provided in Table 3.19. The

default emission factor is not applicable to stand-alone EDC production plants. If natural gas consumption activity data are available, the CH<sub>4</sub> emission factor of 5 g CH<sub>4</sub>/GJ may be applied directly to the activity data, rather than using the default emission factor.

| Process Configuration               | kg CH <sub>4</sub> /tonne VCM product produced |
|-------------------------------------|--|
| Integrated EDC/VCM Production Plant | 0.0226   |

Sources: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 12.3.1, Table 12.4, Page 300); EEA, 2005 (EMEP/CORINAIR Emission Inventory Guidebook, Processes in Organic Chemical Industries (Bulk Production) 1, 2-Dichloroethane and Vinyl Chloride (Balanced Process), Activity 040505, February 15, 1996, Section 3.4, Page B455-3, and Table 9.2, B455-5).

## Ethylene oxide

### *Carbon dioxide emissions*

Emissions of CO<sub>2</sub> from ethylene oxide production may be estimated using emission factors based on activity data for ethylene oxide production, and activity data for process configuration and catalyst selectivity. Separate CO<sub>2</sub> emission factors are provided in Table 3.20 for the CO<sub>2</sub> emissions from the air process and for the CO<sub>2</sub> emissions from the oxygen process for a range of catalyst selectivity. The default emission factors for the air process and for the oxygen process are estimated from process-specific catalyst selectivity data provided in the IPPC LVOC BAT document. Specific data concerning the type of process and the selectivity of the process catalyst are needed in order to select emission factors from Table 3.20. The emission factors are derived from the catalyst selectivity using stoichiometric principles and are based on the assumption that emissions of CH<sub>4</sub> and NMVOC from the process are negligible and that all of the carbon contained in the ethylene feedstock is converted either into ethylene oxide product or to CO<sub>2</sub> emissions. The emission factors in Table 3.20 do not include emissions from flares.

As shown in Table 3.20, the default emission factor for the air process is based on a default process catalyst selectivity of 70 percent and the default emission factor for the oxygen process is based on a default catalyst selectivity of 75 percent. If activity data are not available for the process configuration or the catalyst selectivity, the default process configuration is the air process and the default catalyst selectivity is 70 percent. If activity data are available that identify the process used as the oxygen process, but activity data are not for the catalyst selectivity for the oxygen process, the emission factor for the default catalyst selectivity of 75 percent for the oxygen process in Table 3.20 should be used.

| Process Configuration         | Catalyst Selectivity | Feedstock Consumption<br>(tonne ethylene/<br>tonne ethylene oxide) | Emission Factor<br>(tonne CO <sub>2</sub> /<br>tonne ethylene oxide) |
|-------------------------------|----------------------|--|--|
| Air Process [default process] | Default (70)         | 0.90   | 0.863  |
|                               | 75                   | 0.85   | 0.663  |
|                               | 80                   | 0.80   | 0.5  |
| Oxygen Process                | Default (75)         | 0.85   | 0.663  |
|                               | 80                   | 0.80   | 0.5  |
|                               | 85                   | 0.75   | 0.35   |

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 9.2.1, Page 224, Section 9.3.1.1, Page 231, Figure 9.6)

### *Methane emissions*

The IPPC LVOC BAT document for ethylene oxide production reported CH<sub>4</sub> emissions factors (in units of kilograms methane per tonne ethylene oxide produced) for the ethylene oxide process vent, ethylene oxide purification process exhaust gas steam, and fugitive emissions sources. CH<sub>4</sub> emission factors were reported in the IPPC LVOC BAT document for European ethylene oxide plant carbon dioxide removal vents before and after treatment. CH<sub>4</sub> emissions were also reported for two ethylene oxide plants in the Netherlands. CH<sub>4</sub> emission factors for ethylene oxide production were developed by averaging these data. Emissions of CH<sub>4</sub> may be estimated by applying the emissions factors included in Table 3.21 to activity data for ethylene oxide production. The default CH<sub>4</sub> emission factor for ethylene oxide production assumes no thermal treatment process.

| Process Configuration                 | kg CH <sub>4</sub> /tonne ethylene oxide produced |
|---------------------------------------|---|
| No Thermal Treatment [default factor] | 1.79  |
| Thermal Treatment                     | 0.79  |

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Table 9.6, Page 233; Table 9.8, Page 236; Table 9.9, Page 236).

## Acrylonitrile

### *Carbon dioxide emissions*

Process vent CO<sub>2</sub> emissions from the acrylonitrile production process by the direct ammoxidation of propylene may be calculated from acrylonitrile production activity data using the emission factors provided in Table 3.22:

| Process Configuration  | tonnes CO <sub>2</sub> /tonne acrylonitrile produced |
|--|--|
| <b>Direct Ammoxidation of Propylene</b>                        |  |
| Secondary Products Burned for Energy Recovery/Flared (default) | 1.00   |
| Acetonitrile Burned for Energy Recovery/Flared                 | 0.83   |
| Acetonitrile and Hydrogen Cyanide Recovered as Product         | 0.79   |

Source: European IPPC Bureau, 2003 (IPPC LVOC BAT Document, Section 11.3.1.1, Table 11.2, Page 274 and Section 11.3.1.2, Page 275)

The emission factors in Table 3.22 are based on an average (default) propylene feedstock consumption factor of 1.09 tonnes propylene feedstock per tonne acrylonitrile produced, corresponding to a primary product yield factor of approximately 70 percent. The default CO<sub>2</sub> emission factor is based on conversion of propylene feedstock to secondary product acetonitrile at 18.5 kilograms per tonne acrylonitrile produced, and conversion of propylene to secondary product hydrogen cyanide at 105 kilograms per tonne acrylonitrile produced, and is based on process-specific acrylonitrile yield data and process-specific feedstock consumption data reported in the IPPC LVOC BAT document (European IPPC Bureau, 2003). Note however that the acrylonitrile production process may be configured and operated to produce a greater or lesser amount of secondary products. The default CO<sub>2</sub> emission factor is based on the assumption that the secondary products (acetonitrile and hydrogen cyanide) of the acrylonitrile production process and hydrocarbon by products in the main absorber vent gas are either burned for energy recovery or flared to CO<sub>2</sub> and are not recovered as products or emitted to the atmosphere without combustion treatment. The CO<sub>2</sub> emission factors do not include CO<sub>2</sub> emissions from any combustion of auxiliary fuel (e.g., natural gas) for the process waste gas energy recovery or flare systems.

If activity data are not available concerning whether secondary products are recovered for sale, the default assumption is that the secondary products are either burned for energy recovery or flared to CO<sub>2</sub> and the default primary product process yield factor is 70 percent.

For the process configuration where secondary products (acetonitrile and hydrogen cyanide) are recovered for sale and are not either flared to CO<sub>2</sub> or burned for energy recovery, the overall process yield factor of primary and secondary products is 85 percent.

If activity data for propylene feedstock consumption are not available, the propylene feedstock consumption may be estimated from the acrylonitrile production activity data by applying a default feedstock consumption factor of 1.09 tonnes propylene feedstock consumed per tonne acrylonitrile produced.

### *Methane emissions*

The Life-Cycle Analysis Data Summary for Acrylonitrile reports a CH<sub>4</sub> emission factor for acrylonitrile production of 0.18 kg CH<sub>4</sub>/tonne acrylonitrile produced, as referenced in the European Association of Plastics Manufacturers (APME) Life-Cycle Analysis Report (Boustead, 1999). The CH<sub>4</sub> emission factor for acrylonitrile process operations is based on life-cycle analysis data for European acrylonitrile plants in Germany, Italy, and the United Kingdom collected between 1990 and 1996. CH<sub>4</sub> emissions from acrylonitrile production may be estimated by applying this default emission factor to the acrylonitrile production data.

## Carbon black

### *Carbon dioxide emissions*

Emissions of CO<sub>2</sub> from carbon black production may be estimated by applying the process and feedstock-specific emission factors to the carbon black production activity data. Separate emission factors are provided in Table 3.23 for the furnace black process, thermal black process, and acetylene black process and their associated feedstocks, and separate emission factors are provided for primary feedstock and secondary feedstock. The emission factors are based on the assumption that process emissions are subjected to a thermal treatment process.

A range of values for primary and secondary carbon black feedstock is included in Table 4.11 of the draft Integrated Pollution Prevention and Control (IPPC) Reference Document for Best Available Techniques in the Large Volume Inorganic Chemicals (LVIC) Solid and Others Industry (European IPPC Bureau, June 2005; referred to in this chapter as the Draft IPPC LVIC BAT Document.) The CO<sub>2</sub> emission factors in Table 3.23 are based on the average of the range of values. Primary and secondary feedstock consumption is converted to carbon consumption using average values for carbon black feedstock carbon content. The CO<sub>2</sub> emission factors are calculated from the carbon input to the process (primary and secondary feedstocks) and carbon output (carbon black) from the process, using an average value for carbon black carbon content.

| Process Configuration                   | tonnes CO <sub>2</sub> /tonne carbon black produced |                     |                 |
|---|---|---------------------|-----------------|
|   | Primary Feedstock                                   | Secondary Feedstock | Total Feedstock |
| Furnace Black Process (default process) | 1.96  | 0.66                | 2.62            |
| Thermal Black Process                   | 4.59  | 0.66                | 5.25            |
| Acetylene Black Process                 | 0.12  | 0.66                | 0.78            |

Source: European IPPC Bureau, 2005 (Draft IPPC LVIC BAT Document, Table 4.11 data)

### *Methane emissions*

CH<sub>4</sub> emissions for the carbon black production process are provided in Table 3.24. The draft IPPC LVIC BAT document for carbon black reported the CH<sub>4</sub> content of uncombusted tail gas from the carbon black production process and the estimated rate of generation of tail gas from the carbon black production process. Based on 10,000 Nm<sup>3</sup> tail gas per tonne carbon black produced and an average reported CH<sub>4</sub> concentration of 0.425 percent by volume, the uncontrolled CH<sub>4</sub> emission factors is 28.7 kg CH<sub>4</sub>/tonne carbon black produced. Combustion flare efficiency for carbon black process flare systems was reported in the Draft IPPC LVIC BAT Document as 99.8 percent for carbon monoxide, and the same efficiency is assumed to apply to CH<sub>4</sub>. The CH<sub>4</sub> emission factor for carbon black production after application of combustion control is 0.06 kg CH<sub>4</sub>/tonne carbon black produced. An overall CH<sub>4</sub> emission factor of 0.11 kg CH<sub>4</sub>/tonne carbon black, based on company data, was reported in the Australian Methodology for the Estimation of Greenhouse Gas Emissions and Sinks, 2003 (AGO, 2005.) Three carbon black production plants in Germany reported a common CH<sub>4</sub> emission factor of 0.03 kg CH<sub>4</sub>/tonne carbon black produced, based on measurement data after waste gas combustion using BAT (Thermische Nachverbrennung als Stand der Technik.)

| Process Configuration               | kilogram CH <sub>4</sub> /tonne carbon black produced<br>(Carbon Black Process Tail Gas) |
|-------------------------------------|--|
| No Thermal Treatment                | 28.7   |
| Thermal Treatment (default process) | 0.06   |

Source: European IPPC Bureau, 2005 (Draft IPPC LVIC BAT Document, Table 4.8, Page 209; Table 4.10, Page 213, Section 4.3.2.3, Page 210).

## TIER 2

The Tier 2 methodology is based on mass balance calculations and therefore there are no emission factors associated with the methodology.



### TIER 3

For the Tier 3 method plant specific emissions may be estimated using Equations 3.20 through 3.22 for CO<sub>2</sub>, and using either Equation 3.26 or Equations 3.27 through 3.29 for CH<sub>4</sub>. The emission factors may be related to annual production for estimation of emissions between measurements when these are not continuous.

#### 3.9.2.3 CHOICE OF ACTIVITY DATA

General aspects of data collection for obtaining activity data are discussed in Chapter 2 of Volume 1. When using the Tier 3 method plant-specific activity data should be obtained from the production plants. Direct measurements of the total flow to the steam cracker and flare system together with an analysis of the gas carbon content will provide the most accurate basis for an emissions estimate.

Plant specific energy balance and/or carbon balance may also be used to derive plant specific emission factors. The variety of energy and carbon flows across the plant boundary makes this a data intensive but still much less resource intensive approach. While feedstock consumption data may be hard to obtain sales data and national statistics may provide approximate production volumes of the chemicals.

#### METHANOL

Emissions of CO<sub>2</sub> from methanol production may be calculated from specific feedstock (e.g., natural gas) consumption and product (methanol) production activity data and carbon mass balance calculations.

#### ETHYLENE

Emissions of CO<sub>2</sub> from ethylene production may be calculated from specific feedstock consumption and product production activity data and carbon mass balance calculations. In order to create a complete mass balance for the ethylene production process and implement the Tier 2 methodology for ethylene production, all feedstocks and the production and disposition of all primary and secondary products of the process should be identified using activity data. In cases where activity data are available for ethylene production but not available for production of secondary products from the steam cracking process, the production of secondary products may be estimated using the default factors in Table 3.25 and Equation 3.18. However, use of these default factors is a less accurate method than use of specific activity data for all primary and secondary products, and will increase the uncertainty of the estimate, as performance of steam crackers may vary depending on site-specific conditions. For example, site-specific data reported for steam crackers operating in Germany indicate that hydrocarbon losses under normal operating conditions are on the order of 8.5 kg per tonne of hydrocarbon feedstock (BASF, 2006) whereas the default value for hydrocarbon losses shown in Table 3.25 is 5 kg per tonne of hydrocarbon feedstock. In the event that activity data are not available for all secondary products, the Tier 1 method can be applied instead of the Tier 2 method.

Secondary products produced by the steam cracking process may be recovered and transferred to a petrochemical plant or petroleum refinery for material reuse, recycled within the steam cracking process as feedstock, or burned for energy recovery. Typically C<sub>4</sub>+ secondary products are recycled as feedstock or recovered for material reuse (BASF, 2006). Allocation of CO<sub>2</sub> emissions from combustion of secondary products for energy recovery is described in Box 1.1 in Chapter 1 of this volume. If activity data are not available for the disposition of C<sub>4</sub>+ secondary products the default assumption is that the C<sub>4</sub>+ secondary products are recovered and transferred to another process for material reuse. If data are not available for the disposition of CH<sub>4</sub> produced by the steam cracking process, the default assumption is that the CH<sub>4</sub> is burned for energy recovery within the steam cracking process and results in CO<sub>2</sub> emissions from the process.

Steam crackers operated within the petrochemical industry may obtain the petrochemical feedstock for the ethylene production process directly from an adjacent petroleum refinery. Depending upon the feedstock and process operating conditions, steam crackers may also generate 'backflows' of hydrocarbon by-products that are returned to the adjacent refinery for further processing. Any CO<sub>2</sub> emissions from processing backflows at petroleum refineries are not included in the process CO<sub>2</sub> emission factors for the steam cracker ethylene production process, but are considered in the feedstock and carbon flow analysis for the process.

| Product                           | Feedstock | kg product/tonne feedstock |              |              |              |              |              |
|-----------------------------------|-----------|----------------------------|--------------|--------------|--------------|--------------|--------------|
|                                   |           | Naphtha                    | Gas oil      | Ethane       | Propane      | Butane       | Others       |
| High Value Chemicals              |           | <b>645</b>                 | <b>569</b>   | <b>842</b>   | <b>638</b>   | <b>635</b>   | <b>645</b>   |
| Ethylene                          |           | 324                        | 250          | 803          | 465          | 441          | 324          |
| Propylene                         |           | 168                        | 144          | 16           | 125          | 151          | 168          |
| Butadiene                         |           | 50                         | 50           | 23           | 48           | 44           | 50           |
| Aromatics                         |           | 104                        | 124          | 0            | 0            | 0            | 104          |
| Fuel grade products and backflows |           | <b>355</b>                 | <b>431</b>   | <b>157</b>   | <b>362</b>   | <b>365</b>   | <b>355</b>   |
| Hydrogen                          |           | 11                         | 8            | 60           | 15           | 14           | 11           |
| Methane                           |           | 139                        | 114          | 61           | 267          | 204          | 139          |
| Ethane and propane after recycle  |           | 0                          | 0            | 0            | 0            | 0            | 0            |
| Other C4                          |           | 62                         | 40           | 6            | 12           | 33           | 62           |
| C5/C6                             |           | 40                         | 21           | 26           | 63           | 108          | 40           |
| C7+ non-aromatics                 |           | 12                         | 21           | 0            | 0            | 0            | 12           |
| <430C                             |           | 52                         | 26           | 0            | 0            | 0            | 52           |
| >430C                             |           | 34                         | 196          | 0            | 0            | 0            | 34           |
| Losses                            |           | 5                          | 5            | 5            | 5            | 5            | 5            |
| <b>Total</b>                      |           | <b>1 000</b>               | <b>1 000</b> | <b>1 000</b> | <b>1 000</b> | <b>1 000</b> | <b>1 000</b> |

Source: Neelis, M; Patel, M; de Feber, M; Copernicus Institute, April 2003, Table 2.2, Page 24

## ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER

Emissions of CO<sub>2</sub> from ethylene dichloride and vinyl chloride monomer production may be calculated from specific feedstock (ethylene) consumption and product (ethylene dichloride) production activity data and carbon mass balance calculations.

## ETHYLENE OXIDE

Emissions of CO<sub>2</sub> from ethylene oxide production may be calculated from specific feedstock (ethylene) consumption and product (ethylene oxide) production activity data and carbon mass balance calculations.

## ACRYLONITRILE

In the event that activity data are not available for production of secondary products (acetonitrile and hydrogen cyanide), the default values in Table 3.26 and Equation 3.19 may be applied to the activity data for primary product production to estimate secondary product production.

| Secondary Product | kg secondary product/tonne acrylonitrile produced |
|-------------------|---|
| Acetonitrile      | 18.5  |
| Hydrogen Cyanide  | 105   |

Note: The secondary product production factors in this table are based on acrylonitrile production from propylene feedstock. In the event that feedstocks other than propylene are used, the factors in this table would not apply. Process-specific factors would need to be developed in order to apply the Tier 2 mass balance approach to acrylonitrile production from feedstocks other than propylene.

Source: European IPPC Bureau, 2005 (IPPC LVOC BAT Document, Section 11.3.4, Page 27)

If no activity data are available concerning acetonitrile product recovery it may be assumed that it is not recovered as product and is burned for energy recovery to CO<sub>2</sub>. If no activity data are available concerning thermal treatment of the acetonitrile main absorber vent gas it may be assumed that the vent gas is thermally treated and combusted to CO<sub>2</sub> and is not vented to the atmosphere uncontrolled.

## **CARBON BLACK**

Emissions of CO<sub>2</sub> from carbon black production may be calculated from specific primary feedstock (e.g., carbon black feedstock) and secondary feedstock (e.g., natural gas) consumption and product (carbon black) production activity data and carbon mass balance calculations.

### **3.9.2.4 COMPLETENESS**

In estimating CO<sub>2</sub> emissions from petrochemical and carbon black processes, there is a risk of double-counting or omission in either the IPPU or the Energy Sector. Petrochemical and carbon black plants produce methane and non-methane hydrocarbon by-products that may be burned for energy recovery and such energy recovery may be reported in national energy statistics under 'other' fuels or some similar categorisation. If CO<sub>2</sub> emissions from 'other' fuel combustion include industrial process off gases that are burned for energy recovery some adjustment to the energy statistics or to the CO<sub>2</sub> emissions calculation for petrochemical production would be needed to avoid double counting of the CO<sub>2</sub> emissions.

## **METHANOL**

There may be production of methanol from biogenic (renewable) sources. Such biogenic methanol may be incorporated into methanol national production statistics, which would result in overestimation of CO<sub>2</sub> emissions from fossil fuel (e.g., natural gas) derived methanol unless adjustments are made to the methanol production activity data.

## **ETHYLENE**

There may be production of ethylene from petroleum refining processes or from petrochemical processes other than steam crackers. Such ethylene may be incorporated into ethylene national production statistics, which would result in overestimation of CO<sub>2</sub> emissions from steam cracker derived ethylene unless adjustments are made to the ethylene production activity data.

## **ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER**

Ethylene dichloride is an intermediate petrochemical product used to manufacture vinyl chloride monomer and other products. Activity data for production of ethylene dichloride may not be complete because the ethylene dichloride may be converted directly to vinyl chloride monomer in an integrated EDC/VCM plant. Therefore it may be the case that the vinyl chloride monomer production activity data are more complete with respect to industry coverage than the ethylene dichloride production activity data. However, utilisation of vinyl chloride monomer activity data as a surrogate for ethylene dichloride data also has issues related to completeness because not all of the ethylene dichloride is used to manufacture vinyl chloride monomer. Therefore adjustments to the activity data for vinyl chloride monomer may be needed to account for utilisation of ethylene dichloride in the production of other products. Based on data for North America and Europe utilisation of ethylene dichloride for products other than vinyl chloride monomer would amount to the order of 5 percent of total ethylene dichloride production.

## **ETHYLENE OXIDE**

Ethylene oxide is an intermediate petrochemical product used to manufacture ethylene glycols and other products. Activity data for production of ethylene oxide may not be complete because the ethylene oxide may be converted directly to ethylene glycol in an integrated EO/EG plant. Ethylene oxide may also be converted into other products (e.g., amines, ethers, etc.) in integrated plants. Since only on the order of 70 percent of ethylene oxide production worldwide is used in the manufacture of ethylene glycols, production activity data for chemical products of ethylene oxide may not be more complete with respect to industry coverage than the ethylene oxide production activity data.

## **CARBON BLACK**

There may be small amounts of production of carbon black from biogenic (renewable) sources such as animal black and bone black. Such biogenic carbon black may be incorporated into carbon black national production statistics, which would result in overestimation of CO<sub>2</sub> emissions from fossil fuel derived carbon black. There also may be carbon black production within the physical boundaries of petroleum refineries rather than within the chemical industry. Carbon black produced within petroleum refineries is anticipated to be incorporated into national carbon black production statistics, therefore CO<sub>2</sub> emissions from carbon black production within petroleum refineries should be reported along with other emissions from carbon black production within the chemical industry as industrial process emissions.

There may be gaps in completeness with respect to carbon black feedstock consumption activity data. Activity data for carbon black feedstock derived from coal tar products, waste gases, or acetylene may not be available,

which would result in underestimating of CO<sub>2</sub> emissions from carbon black production if a higher-tier carbon balance approach was used.

### 3.9.2.5 DEVELOPING CONSISTENT TIME SERIES

The emissions from petrochemical and carbon black production should be estimated using the same Tier and type of activity data for all years. Constructing a time series for emissions from petrochemical and carbon black production using plant specific measurement activity data will give the most accurate current emissions. However activity data on flaring and fugitive emissions will most likely not be available for previous years. If no technology upgrades have taken place calculating a plant specific emission factor based on recent measurement data related to production of petrochemicals may provide a reasonable result. Petrochemical production is often integrated in an industrial complex producing more than one chemical, or exchanges energy or chemical flows with adjacent industrial plants, and carbon black may be produced within petroleum refineries. When constructing a time series based on feedstock consumption great care should be taken to assure that the activity data includes the same flows every year in the time series. Again a Tier 1 type calculation using emission factors developed from recent plant specific emission estimates based on Tier 2 carbon balance calculation may be used. Investigations to uncover a change in choice of feedstock as well as variations in primary and secondary chemicals produced both within a single year and between years. Reconstruction of gaps in emission estimates and recalculations should follow the guidance in Volume 1, Chapter 5.

## 3.9.3 Uncertainty assessment

Uncertainty assessments for each emissions factor and activity data applicable to each process are discussed in this section. Uncertainty ranges for the emission factors and activity data included in the Tables in the previous sections are summarised in Table 3.27.

### METHANOL

Much of the uncertainty in emission estimates for methanol production is related to the difficulty in determining activity data including the quantity of methanol produced and, for higher tier methodologies, the amount of natural gas and other feedstocks consumed on an annual basis. Natural gas and other feedstock consumption may only be reported on an annual basis in national energy statistics, without any breakout of consumption for methanol production. If natural gas consumption activity data are not available then only an emission factor approach rather than a higher tier carbon balance approach is applicable. If activity data are not available for consumption of other feedstocks for methanol production, it may be assumed that all of the national methanol production is from natural gas feedstock. However, this assumption would introduce some uncertainty. Further, activity data may not be available for annual CO<sub>2</sub> feedstock consumption in methanol production plants that utilise CO<sub>2</sub> as a supplemental feedstock in the production process.

### ETHYLENE

Uncertainty in activity data for ethylene production is related to the difficulty in determining the types, quantities, and characteristics of feedstocks to the steam cracking process (e.g., ethane, naphtha) and the types, quantities, and characteristics of products from the process (e.g., ethylene, propylene). Feedstock consumption and product production may only be reported on an annual basis in national energy statistics and commodity statistics, without any breakout of feedstock consumption for ethylene production or product production from the steam cracking ethylene production process. The ability to conduct a carbon balance calculation for ethylene production depends upon the availability of both activity data for consumption of specific feedstocks and production of specific products of the steam cracking process. If only activity data for national annual ethylene production are available, the default feedstock for the country/region may be assumed and the default emission factor applied. In this case the feedstocks analysis would be conducted by utilising the default yield table for the default feedstock. However, considering the wide variability in emission factors and yield factors among the feedstocks, the unavailability of specific feedstock consumption data would introduce significant uncertainty into the emissions calculations and feedstocks analysis. If specific feedstock consumption activity data are available then a separate emissions estimate and feedstocks analysis may be conducted for each feedstock, which would reduce the uncertainty. Ideally, however, activity data would be available for both specific feedstock consumption and specific product production, allowing a higher tier carbon balance calculation to be conducted.

Another source of uncertainty is related to the difficulty in determining other details of the steam cracking ethylene process configuration, including backflows of products of the steam cracking process from the petrochemical plant to the [potentially adjacent] petroleum refinery and flows of by products to energy recovery or flaring. The unavailability of activity for refinery backflows would introduce uncertainty into the feedstocks analysis.

## **ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER**

Sources of uncertainty for ethylene dichloride include the difficulty in determining the specific process utilised for the ethylene dichloride production and in determining activity data for the consumption of ethylene feedstock in the production process. If only activity data for ethylene dichloride production are available, the emission calculation may be conducted using the default [balanced] process product yield factor and default emission factor for the process. However, considering the variability in emission factors and yield factors for the oxychlorination process, direct oxidation process, and balanced process, the unavailability of specific ethylene feedstock consumption data by process would introduce significant uncertainty into the emissions calculations

## **ETHYLENE OXIDE**

A main source of uncertainty for ethylene oxide production is the difficulty in determining activity data for the consumption of ethylene feedstock for ethylene oxide production. If ethylene consumption activity data are not available then only an emission factor approach rather than a higher tier carbon balance approach is applicable. If only activity data for national annual ethylene oxide production are available, the default product yield may be assumed and the default emission factor applied. In this case the feedstocks analysis would be conducted by utilising the default product yield factor. However, considering the range of reported product yield factors and emission factors for the ethylene oxide process, the unavailability of specific ethylene feedstock consumption data would introduce significant uncertainty into the emissions calculations.

## **ACRYLONITRILE**

Sources of uncertainty for acrylonitrile production include the difficulty in determining the specific process configuration for acrylonitrile production, in determining activity data for the consumption of propylene feedstock in the production process, and in determining activity data for the production of acrylonitrile and acetonitrile from the process. If only activity data for acrylonitrile production are available, the emission calculation may be conducted using the default process configuration (assuming no acetonitrile recovery) and default emission factor for the process. However, the assumption that acetonitrile is not recovered from the process introduces significant uncertainty in the emission and feedstocks calculations and may result in overestimation of emissions and underestimation of feedstocks flows from the acrylonitrile process. Activity data for national production of both acrylonitrile and acetonitrile from the acrylonitrile production process would allow application of the process-specific emission factor for the percentage of national acrylonitrile production from which acetonitrile is recovered. Ideally, however, activity data for propylene consumption and activity data for acrylonitrile, acetonitrile, and hydrogen cyanide production from the acrylonitrile production process would allow utilisation of a higher-tier method, which would reduce the uncertainty.

## **CARBON BLACK**

Uncertainty in activity data for carbon black production is related to the difficulty in determining the types, quantities, and characteristics of primary and secondary feedstocks to the carbon black process, and in determining the type of process used for the carbon black production and the characteristics of the carbon black product from the process. Primary and secondary feedstock consumption and carbon black production may only be reported on an annual basis in national energy statistics and commodity statistics, without any breakout of feedstock consumption for carbon black production for each carbon black production process. Most worldwide production of carbon black is by the furnace black process, therefore if feedstock consumption activity data are not available by process, all of the carbon black production may be assumed to be from the furnace black process without introducing a large amount of uncertainty.

Also, if activity data are available for primary carbon black feedstock consumption, the data may be reported in generic terms as 'carbon black feedstock' without any indication of whether the feedstock is a petroleum-based feedstock produced at petroleum refineries or a coal tar-based feedstock produced from metallurgical coke production. Activity data may also not be available for other primary carbon black feedstocks (e.g., acetylene). Also, specific activity data may be available for natural gas consumption as secondary carbon black feedstock, however, activity data may not be available for other secondary feedstocks that may be used in carbon black production (e.g., coke oven gas). Unavailability of specific primary and secondary feedstock consumption data would add uncertainty to the feedstocks analysis.

The ability to conduct a carbon balance calculation for carbon black production depends upon the availability of activity data for the consumption and the characteristics of primary and secondary feedstocks. If only activity data for national annual carbon black production are available, the default feedstock characteristics and product yield may be assumed and the default emission factor may be applied. However, considering the variability in feedstock characteristics and origin, the unavailability of specific feedstock consumption and composition activity data would introduce significant uncertainty into the emissions and feedstocks calculations. If specific feedstock consumption and characteristics activity data and associated carbon black production activity data are

available then a separate carbon balance and feedstocks analysis may be conducted for each feedstock and process using a higher tier method, which would reduce the uncertainty.

## UNCERTAINTY RANGES

Uncertainty ranges for Tier 1 emission factors and Tier 2 activity data and Tier 3 activity data for each process are provided in Table 3.27. The source of the data or expert judgement used in preparing the uncertainty estimate is identified in the table for each factor or activity data. Expert judgement elicitation was conducted by evaluating the range of available data. In many cases process-specific data were available only for several plants; the relatively large uncertainty ranges are the result of the relatively few data available and the expected variability of process configurations and feedstock utilisation efficiency among petrochemical and carbon black plants.

| Method | Reference  | Factor  | Uncertainty Range | Source  |
|--------|------------|---|-------------------|---|
| Tier 3 |            | Direct measurement of fuel consumption together with gas composition samples for all substances | - 5 to + 5 %      | Expert judgement by Lead Authors of Section 3.9, on the basis of discussions with national industry January 2005. |
| Tier 1 | Table 3.12 | Methanol production CO <sub>2</sub> emission factors  | -30% to +30%      | Expert judgement by Lead Authors of Section 3.9.  |
| Tier 1 | Table 3.13 | Methanol Production Feedstock Consumption Factors   | -30% to +30%      | Expert judgement by Lead Authors of Section 3.9.  |
| Tier 1 |            | Methane Emission Factor for Methanol Production   | -80% to +30%      | Expert judgement by Lead Authors of Section 3.9 on the basis of Methanex plant data.                              |
| Tier 1 | Table 3.14 | Ethylene Production CO <sub>2</sub> Emission Factors  | -30% to +30%      | IPPC LVOC BAT Document, Figure 7.10,  |
| Tier 1 | Table 3.15 | Geographic Adjustment Factors For CO <sub>2</sub> Emissions Factors For Ethylene Production     | -10% to +10%      | Expert judgement by Lead Authors of Section 3.9.  |
| Tier 1 | Table 3.16 | Methane Emission Factors for Ethylene Production  | -10% to +10%      | Expert judgement by Lead Authors of Section 3.9.  |
| Tier 1 | Table 3.17 | Ethylene Dichloride/Vinyl Chloride Production Process Vent CO <sub>2</sub> Emission Factors     | -20% to +10%      | IPPC LVOC BAT Document, Tables 12.6 and 12.7  |
| Tier 1 | Table 3.17 | Ethylene Dichloride/Vinyl Chloride Production CO <sub>2</sub> Emission Factors                  | -50% to +20%      | IPPC LVOC BAT Document, Tables 12.6 and 12.7  |
| Tier 1 | Table 3.18 | Ethylene Dichloride/Vinyl Chloride Monomer Process Feedstock Consumption Factors                | -2% to +2%        | IPPC LVOC BAT Document, Section 12.3.1, Page 300  |
| Tier 1 | Table 3.19 | Ethylene Dichloride/Vinyl Chloride Monomer Process CH <sub>4</sub> Emission Factors             | -10% to +10%      | IPPC LVOC BAT Document, Section 12.3.1, Table 12.4, Page 300  |
| Tier 1 | Table 3.20 | Ethylene Oxide Production Feedstock Consumption and CO <sub>2</sub> Emission Factors            | -10% to +10%      | Expert judgement by Lead Authors of Section 3.9.  |
| Tier 1 | Table 3.21 | Ethylene Oxide Production CH <sub>4</sub> Emission Factors                                      | -60% to +60%      | IPPC LVOC BAT Document, Table 9.6, Page 233; Table 9.8, Page 236; Table 9.9, Page 236                             |
| Tier 1 | Table 3.22 | Acrylonitrile Production CO <sub>2</sub> Emission Factors                                       | -60% to +60%      | IPPC LVOC BAT Document, Section 11.3.1.1, Table 11.2, Page 274.   |

**TABLE 3.27 (CONTINUATION)**  
**UNCERTAINTY RANGES FOR EMISSION FACTORS AND ACTIVITY DATA**

| Method | Reference  | Factor  | Uncertainty Range | Source   |
|--------|------------|---|-------------------|--|
| Tier 1 |            | Acrylonitrile Production CH <sub>4</sub> Emission Factors                 | -10% to +10%      | Boustead, 2003b (Eco-Profiles of the European Plastics Industry Methodology I. Boustead, Report prepared for APME, July 2003, Page 40) |
| Tier 1 | Table 3.23 | Carbon Black Production CO <sub>2</sub> Emission Factors                  | -15% to +15%      | Draft IPPC LVIC BAT Document, Table 4.11, Page 214   |
| Tier 1 | Table 3.24 | Carbon Black Production CH <sub>4</sub> Emission Factors                  | -85% to +85%      | Draft IPPC LVIC BAT Document, Table 4.8, Page 209  |
| Tier 2 | Table 3.25 | Ethylene Steam Cracking Feedstock-Product Matrix                          | -10% to + 10%     | Expert judgement by Contributing Authors of Section 3.9  |
| Tier 2 | Table 3.26 | Secondary Product Production Factors for Acrylonitrile Production Process | -20% to +20%      | Expert judgement by Lead Authors of Section 3.9.   |

## 3.9.4 Quality Assessment/Quality Control (QA/QC), Reporting and Documentation

### 3.9.4.1 QUALITY ASSESSMENT/QUALITY CONTROL

Quality Assurance/Quality Control for emissions factors and activity data involves methods to improve the quality or better understand the uncertainty of the emissions estimates. It is *good practice* to conduct quality control checks for the Tier 1 method as outlined in Volume 1, Chapter 6. More extensive quality control checks and quality assurance procedures are applicable, if Tier 2 or Tier 3 methods are used to determine emissions. Inventory compilers are encouraged to use higher tier QA/QC for key categories as identified in Volume 1, Chapter 4.

#### Evaluation of Tier 1 and Tier 2 method activity data

The Tier 1 and Tier 2 methods both depend upon the application of activity data for petrochemical and carbon black production and/or activity data for feedstock consumption. These activity data should not be expected to vary by more than about +/- 10 percent year to year, barring significant changes in the overall economic output of the country, the construction of new petrochemical production capacity, or other similar factors. If the activity data vary by more than about +/-10 percent year to year, it is *good practice* to assess and document the country-specific conditions that account for the differences.

#### Evaluation of Tier 1 method emission factors

Inventory compilers that develop country-specific emission factors for petrochemical and carbon black production and apply the Tier 1 method should assess whether the estimated emission factors are within the range of the default emission factors and process-specific emission factors provided for the Tier 1 method in this guidance. If the emission factors are outside of the range of factors reported in this Guidance, then the reasons why this is the case should be investigated (e.g., the process configuration differs from that for the emission factors reported in this guidance; the feedstock is a unique material not considered in this Guidance.) Inventory compilers should also ensure that the country-specific emission factors are consistent with the values derived from analysis of the process chemistry. For example, for methanol production from natural gas the carbon content of the CO<sub>2</sub> generated, as estimated using the emission factor, should equal approximately the difference between the carbon content of the natural gas feedstock and the carbon content of the methanol product. If the emission factors are outside of the estimated ranges, it is *good practice* to assess and document the plant-specific conditions that account for the differences. It is also *good practice* for inventory compilers using Tier 1 method emission factors included in this Guidance to conduct quality control checks to assess whether the data characteristics of the emission factor conform to the characteristics of the petrochemical and carbon black production processes in the country in which the emission factor is applied.

### Evaluation of Tier 2 method mass balance calculations

Application of the Tier 2 mass balance method depends upon the identification and characterisation of process flows. For the Tier 2 method, failure to identify all carbon-containing process flows or mischaracterisation of the flow rates or carbon contents of such process flows could result in significant deviation of the estimated CO<sub>2</sub> emissions from the actual CO<sub>2</sub> emissions. The quality of Tier 2 mass balance calculation results are generally more dependent upon the quality of the activity data than are Tier 1 calculation results because in general a greater number of activity data need to be applied to the Tier 2 method than to the Tier 1 method. Therefore, it is *good practice* to assess and document the quality of each activity data applied to the Tier 2 method and the completeness of the activity data prior to applying the Tier 2 method. If the data quality or completeness are deemed not adequate for application of the Tier 2 method then the Tier 1 method should be applied.

### Evaluation of Tier 3 method plant-specific data

The Tier 3 method is based on the application of plant-specific emissions data. It is *good practice* for inventory compilers that conduct audits of plant-specific emissions estimates used in the inventory. This involves evaluating whether the plant-specific data are representative of plant emissions and, if plant-specific data for a specific plant are applied to the national inventory, evaluating whether the plant-specific data representative of petrochemical and carbon black production processes in the country as a whole. Audits of plant-specific data would involve the evaluation of:

- Documentation of plant-specific measurement methodology;
- Documentation of plant-specific measurement results;
- Emissions estimation method and calculations;
- Process feedstock(s) and product(s)
- Activity data employed in emissions calculations;
- Documentation of process technology and configuration;
- List of assumptions;

If the specific process for which plant-specific data are obtained is deemed not to be representative of other plants in the country producing the same petrochemical (e.g., if the feedstock differs or the process configuration differs) then the plant-specific data should not be applied to the overall inventory but only to the activity data for the specific plant. If emission measurements from individual plants are collected, inventory compilers should ensure that the measurements were made according to recognised national or international standards and the quality control methods were applied to the emissions measurement. Quality control procedures in use at the plant should be directly referenced and included in the quality control plan. If the measurement practices were not consistent with quality control standards or if the measurement procedures and results cannot be adequately documented, the inventory compiler should reconsider the use of the plant-specific data.

## 3.9.4.2 REPORTING AND DOCUMENTATION

Combustion emissions from combustion of off gases generated by petrochemical production processes are attributed to the IPPU Sector source category which produces them, and are reported as industrial process emissions. However, if any portion of the off gases generated by an IPPU Sector source category is combusted within a different IPPU Sector source category, or combusted within an Energy Sector source category, the corresponding emissions are reported as fuel combustion emissions rather than as industrial process emissions. This means that if the combustion emissions occur within the IPPU Sector source category which produced the off gases, then the emissions are reported as industrial process emissions attributed to that IPPU Sector source category. However, if the off gases are transferred out of the process to another source category in the IPPU Sector or a source category in the Energy Sector, then the emissions from the combustion of the off gases are reported as fuel combustion emissions within that source category. When the total emissions from the combustion of the off gases are calculated, the quantity transferred to and reported in the Energy Sector and the quantity transferred to and reported in a different IPPU Sector source category should be clearly quantified in the IPPU Sector source category calculations and in the Energy Sector source category calculations. If a country-specific emission factor was developed, the corresponding data should be provided as how the emission factor was developed and applied in the emission factor calculation, including reporting of the production process configuration upon which the emission factor and calculation are based.

### METHANOL

The amount of methanol produced, the amount of natural gas feedstock consumed in methanol production, and the amount of supplemental CO<sub>2</sub> feedstock consumed in methanol production are to be reported when available.



If a default emission factor is used, this should be noted in the reporting documentation, and the methanol production process configuration should be reported in the event that the default process configuration is not used.

### **ETHYLENE**

The amount of each feedstock consumed in ethylene production and the amounts of ethylene and each other primary product produced and recovered as product are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the ethylene production process configuration and feedstock(s) should be reported in the event that the default process configuration and default feedstock for the country/region are not used.

### **ETHYLENE DICHLORIDE**

The amount of ethylene dichloride produced and ethylene feedstock consumed in ethylene dichloride production are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the ethylene dichloride production process configuration should be reported in the event that the default process configuration is not used.

### **ETHYLENE OXIDE**

The amount of ethylene oxide produced and ethylene feedstock consumed in ethylene oxide production are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the ethylene oxide production process configuration should be reported in the event that the default process configuration is not used.

### **ACRYLONITRILE**

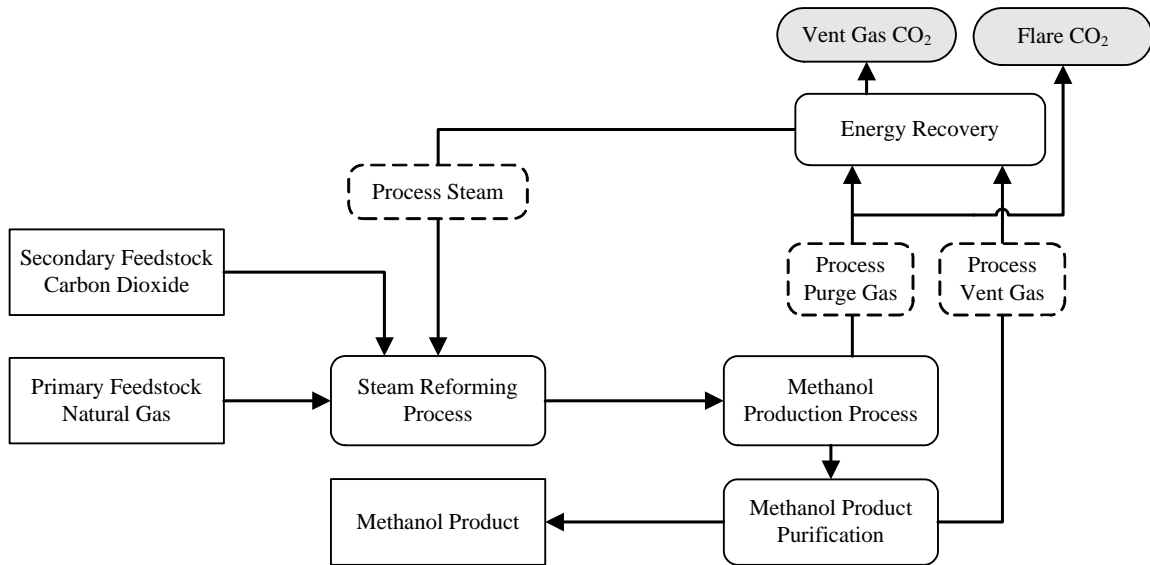
The amount of propylene feedstock consumed in acrylonitrile production and the amounts of acrylonitrile, acetonitrile, and hydrogen cyanide produced and recovered as product are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the acrylonitrile production process configuration should be reported in the event that the default process configuration is not used.

### **CARBON BLACK**

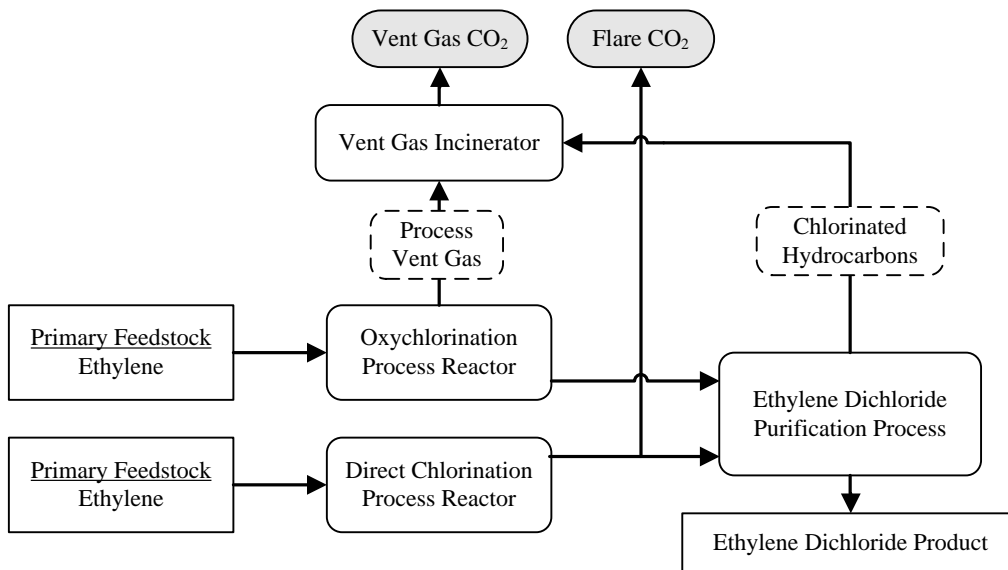
The amount of carbon black produced and the amounts and characteristics (carbon content) of each primary and secondary feedstock consumed in carbon black production are to be reported when available. If a default emission factor is used, this should be noted in the reporting documentation, and the carbon black production process configuration should be reported in the event that the default process configuration is not used.

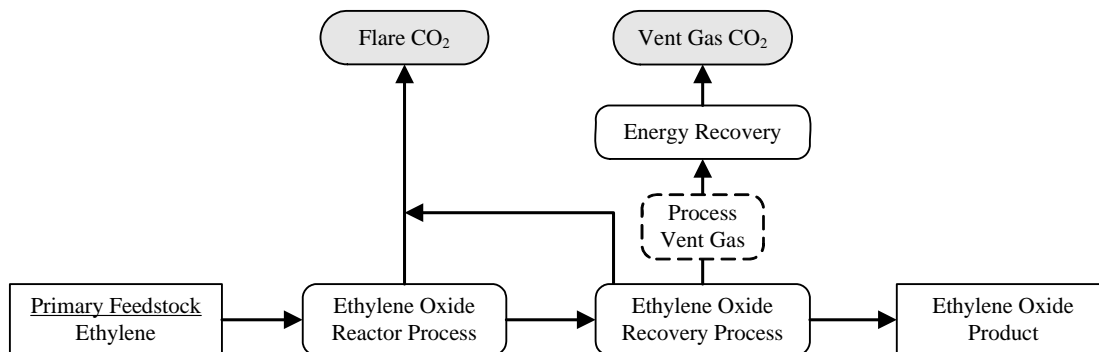
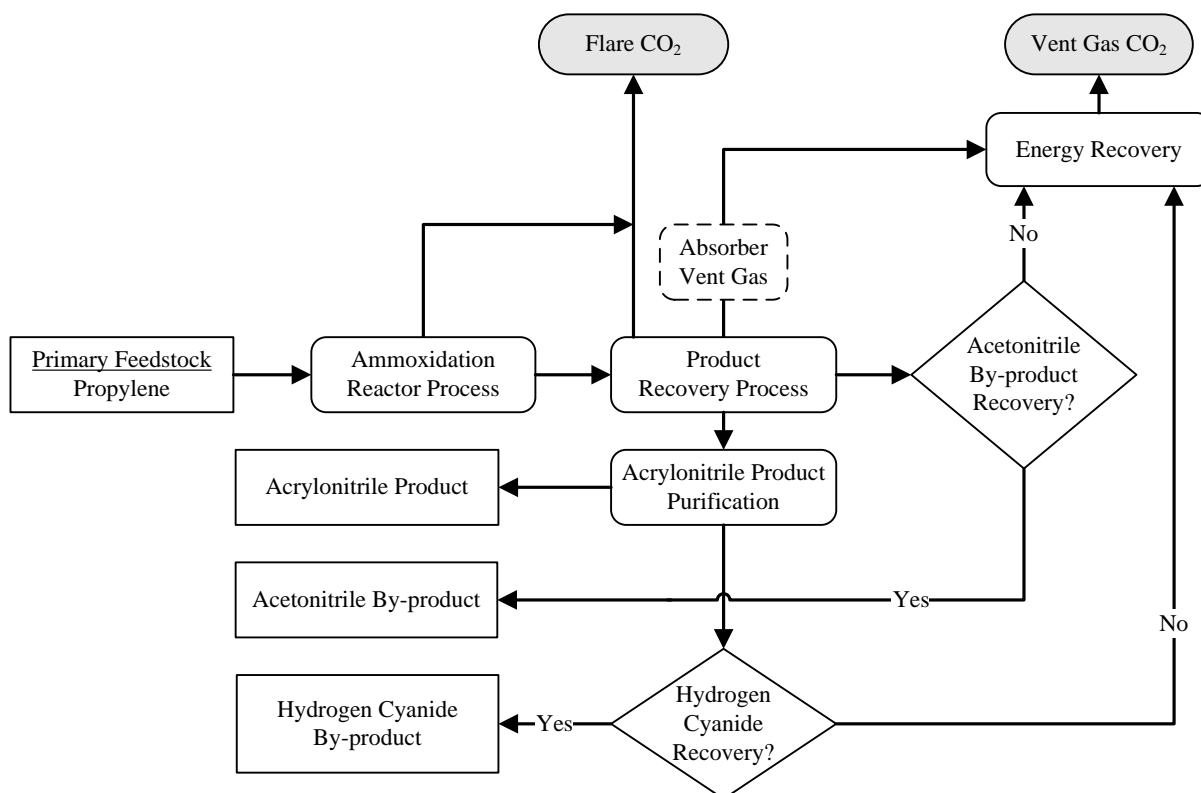
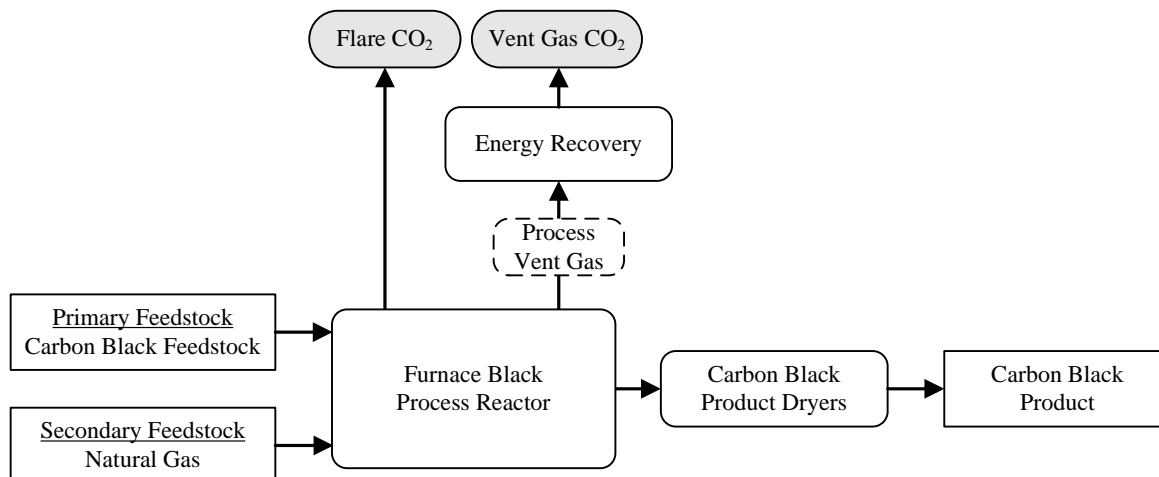
## Annex 3.9A Feedstock-product flow diagrams

**Figure 3.11 Methanol production feedstock-product flow diagram**



**Figure 3.12 Ethylene dichloride production feedstock-product flow diagram**



**Figure 3.13 Ethylene oxide production feedstock-product flow diagram****Figure 3.14 Acrylonitrile production feedstock-product flow diagram****Figure 3.15 Carbon black production feedstock-product flow diagram**

## 3.10 FLUOROCHEMICAL PRODUCTION

### 3.10.1 HFC-23 emission from HCFC-22 production

#### 3.10.1.1 INTRODUCTION

Trifluoromethane (HFC-23 or  $\text{CHF}_3$ ), is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22 or  $\text{CHClF}_2$ ).<sup>3</sup> Materials such as HFC-23 (and other HFCs, PFCs and  $\text{SF}_6$ ) are not significantly removed by aqueous (acidic, neutral or alkaline) scrubbing processes and will be released into the atmosphere. It is estimated that in 1990 the HFC-23 released from HCFC-22 plants was at most 4 percent of the production of HCFC-22 (U.S. EPA, 2001), in the absence of abatement measures. There are a small number of HCFC-22 production plants globally and thus a discrete number of point sources of HFC-23 emissions. While the methodology described here is applicable to by-product emissions of any fluorinated greenhouse gas, it has been written specifically for HFC-23. The methodology for emissions of fluorinated by-products in general and 'fugitive emissions' is covered by Section 3.10.2.

#### 3.10.1.2 METHODOLOGICAL ISSUES

##### CHOICE OF METHOD

There are two broad measurement approaches to estimating HFC-23 emissions from HCFC-22 plants. These are described in IPCC (2000), DEFRA (2002a and 2002b), EFCTC (2003) and UN (2004) and have been translated into Tier 2 and 3 methodologies described below. National emissions using either of these methodologies are the sum of those from the individual facilities. Tier 1 (default) methodology can be applied to individual plants or, if there is no abatement by destruction, to the total national output of HCFC-22. Accounting for HFC-23 emissions is not simply mechanistic but requires information on the process operations responsible for producing and emitting HFC-23, so that the most appropriate methodology and factors can be adopted. Therefore, it is *good practice*, to the extent possible, to establish contacts with plant managers in order to obtain the necessary data.

The Tier 1 method is relatively simple, involving the application of a default emission factor to the quantity of HCFC-22 produced. This method can be applied at the plant level or the national level. Tier 2 and Tier 3 methodologies are suitable only for plant level calculations because they rely on data that are only available from plants. In cases where there are Tier 3 data available for some plants, the Tier 1 or Tier 2 methods can be applied to the remainder to ensure complete coverage.

It is *good practice* to estimate national emissions by summing measured parameters from all HCFC-22 plants in a country. Tier 3 plant emission measurements are the most accurate, followed by Tier 2 measurements based on plant efficiencies. Direct measurement is significantly more accurate than Tier 1 because it reflects the conditions specific to each manufacturing facility. In most cases, the data necessary to prepare Tier 3 estimates should be available because facilities operating to good business practice perform regular or periodic sampling of the final process vent or within the process itself as part of routine operations. The Tier 1 (default) method should be used only in cases where plant-specific data are unavailable and this subcategory is not identified as significant subcategory under *key category*. (See Section 4.2 of Volume 1.) Modern plant using process optimization will need to keep accurate HFC-23 generation data as part of this optimization, so plant-specific data should be available to most countries in most cases.

The choice of *good practice* method will depend on national circumstances. The decision tree in Figure 3.16 describes *good practice* in adapting the methods in these *Guidelines* to country-specific circumstances.

Procedures to abate emissions include destruction of HFC-23 in a discrete facility and, in this case, emissions occur only when the destruction facility is not in operation. The tiers of methodology provide estimates for the quantity of HFC-23 that is produced and the share of production that is ultimately emitted depends on the length of time that the destruction facility is not operated. For facilities using abatement techniques such as HFC-23 destruction, verification of the abatement efficiency is also done routinely. It is *good practice* to subtract abated HFC-23 emissions from national estimates where the abatement has been verified by process records on every plant.

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<sup>3</sup> HCFC-22 is used as a refrigerant in several different applications, as a blend component in foam blowing, and as a chemical feedstock for manufacturing synthetic polymers.

**Tier 1**

In the Tier 1 methodology, a default factor is used to estimate production (and potential emissions) of HFC-23 from the total HCFC-22 production from each facility (for both potentially dispersive uses, as reported under the Montreal Protocol, and feedstock uses, which are reported separately to the Ozone Secretariat). See Equation 3.30.

**EQUATION 3.30**  
**TIER 1 CALCULATION OF HFC-23 FROM HCFC-22 (PRODUCED) USING DEFAULT FACTOR**

$$E_{\text{HFC-23}} = EF_{\text{default}} \cdot P_{\text{HCFC-22}}$$

Where:

$E_{\text{HFC-23}}$  = by-product HFC-23 emissions from HCFC-22 production, kg

$EF_{\text{default}}$  = HFC-23 default emission factor, kg HFC-23/kg HCFC-22

$P_{\text{HCFC-22}}$  = total HCFC-22 production, kg

This methodology is suitable where plant-specific measurements are not available and, in that case, the default condition is that all of the estimated HFC-23 production is released into the atmosphere.

**Tier 2**

In the Tier 2 methodology, the HFC-23 emission factor is derived from records of process efficiencies and used in the calculation shown as Equation 3.31. This is a material balance approach and relies on calculating the difference between the expected production of HCFC-22 and the actual production and then assigning that difference to loss of raw materials, loss of product (HCFC-22) and conversion to by-products, including HFC-23. These parameters will be different for each plant and so should be assessed separately for each facility reporting into the national data.

**EQUATION 3.31**  
**TIER 2 CALCULATION OF HFC-23 FROM HCFC-22 (PRODUCED) USING FACTOR(S) CALCULATED FROM PROCESS EFFICIENCIES**

$$E_{\text{HFC-23}} = EF_{\text{calculated}} \cdot P_{\text{HCFC-22}} \cdot F_{\text{released}}$$

Where:

$E_{\text{HFC-23}}$  = by-product HFC-23 emissions from HCFC-22 production, kg

$EF_{\text{calculated}}$  = HFC-23 calculated emission factor, kg HFC-23/kg HCFC-22

$P_{\text{HCFC-22}}$  = total HCFC-22 production, kg

$F_{\text{released}}$  = Fraction of the year that this stream was released to atmosphere untreated, fraction

The emission factor can be calculated from both the carbon efficiency (Equation 3.32) and the fluorine efficiency (Equation 3.33) and the value used in Equation 3.31 should normally be the average of these two values unless there are overriding considerations (such as a much lower uncertainty of one of the efficiency measures) that can be adequately documented. Annual average carbon and fluorine balance efficiencies are features of a well-managed HCFC-22 plant and are either normally available to the plant operator or may be obtained by examination of process accounting records. Similarly, if there is a vent treatment system, the length of time that this was in operation, and treating the vent stream from the HCFC-22 plant, should be available from records.

Total HCFC-22 production includes material that is used as a chemical feedstock as well as that which is sold for potentially dispersive uses.

**EQUATION 3.32**  
**CALCULATION OF HFC-23 EMISSION FACTOR FROM CARBON BALANCE EFFICIENCY**

$$EF_{\text{carbon\_balance}} = \frac{(100 - \text{CBE})}{100} \cdot F_{\text{efficiency loss}} \cdot FCC$$

Where:

$EF_{\text{carbon\_balance}}$  = HFC-23 emission factor calculated from carbon balance efficiency, kg HFC-23/kg HCFC-22

CBE = carbon balance efficiency, percent

$F_{\text{efficiency loss}}$  = factor to assign efficiency loss to HFC-23, fraction

FCC = factor for the carbon content of this component (= 0.81), kg HFC-23/kg HCFC-22

and

**EQUATION 3.33**  
**CALCULATION OF HFC-23 EMISSION FACTOR FROM FLUORINE BALANCE EFFICIENCY**

$$EF_{\text{fluorine\_balance}} = \frac{(100 - FBE)}{100} \cdot F_{\text{efficiency loss}} \cdot FFC$$

Where:

$EF_{\text{fluorine\_balance}}$  = HFC-23 emission factor calculated from fluorine balance efficiency, kg HFC-23/kg HCFC-22

FBE = fluorine balance efficiency, percent

$F_{\text{efficiency loss}}$  = factor to assign efficiency loss to HFC-23, fraction

FFC = factor for the fluorine content of this component (= 0.54), kg HFC-23/kg HCFC-22

The factor to assign the efficiency loss to HFC-23 is specific to each plant and, if this method of calculation is used, the factor should have been established by the process operator. By default, the value is 1; that is all of the loss in efficiency is due to co-production of HFC-23. In practice, this is commonly the most significant efficiency loss, being much larger than losses of raw materials or products.

The factors for carbon and fluorine contents are calculated from the molecular compositions of HFC-23 and HCFC-22 and are common to all HCFC-22 plants at 0.81 for carbon and 0.54 for fluorine.

### Tier 3

Tier 3 methodologies are potentially the most accurate. The Tier 3 methodologies provided here give equivalent results and the choice between them will be dictated by the information available in individual facilities. In each case, the national emission is the sum of factory specific emissions, each of which may be determined using a Tier 3 method to estimate the composition and flowrate of gas streams vented to atmosphere (either directly and continuously – as in Tier 3a - or by continuous monitoring of a process parameter related to the emission - Tier 3b - or by monitoring the HFC-23 concentration continuously within the reactor product stream - Tier 3c):

**EQUATION 3.34**  
**TIER 3a CALCULATION OF HFC-23 EMISSIONS FROM INDIVIDUAL PROCESS STREAMS**  
**(DIRECT METHOD)**

$$E_{\text{HFC-23}} = \sum_i \sum_j \int_t C_{ij} \cdot f_{ij} \quad \left[ \int_t \text{ means the quantity should be summed over time.} \right]$$

Where:

$E_{\text{HFC-23}}$  = total HFC-23 emissions: the sum over all  $i$  plants, over all  $j$  streams in each plant of the emitted mass flows  $f$  and concentrations  $C$  is integrated over time  $t$ . (See Equation 3.37 for calculation of ‘instantaneous’ HFC-23 emissions in an individual process stream.)

or, where proxy methodology is used:

**EQUATION 3.35**  
**TIER 3b CALCULATION OF HFC-23 EMISSIONS FROM INDIVIDUAL PROCESS STREAMS**  
**(PROXY METHOD)**

$$E_{\text{HFC-23}} = \sum_i \sum_j \int_t E_{ij} \quad \left[ \int_t \text{ means the quantity should be summed over time.} \right]$$

Where:

$E_{\text{HFC-23}}$  = total HFC-23 emissions:  $E_{ij}$  are the emissions from each plant and stream determined by the proxy methods. (See Equation 3.38 for calculation of HFC-23 emissions in an individual process stream.)

or, where the HFC-23 concentration within the reactor product stream is used:

**EQUATION 3.36**  
**TIER 3c CALCULATION OF HFC-23 EMISSIONS FROM INDIVIDUAL PROCESS STREAMS**  
**(BY MONITORING REACTOR PRODUCT)**

$$E_{\text{HFC-23}} = \sum_i \int_t C_i \cdot P_i \quad \left[ \int_t \text{ means the quantity should be summed over time.} \right]$$

Where:

$E_{\text{HFC-23}}$  = total HFC-23 emissions;  $P_i$  is the mass flow of HCFC-22 product from the plant reactor at the plant  $i$ , and  $C_i$  is the concentration of HFC-23 relative to the HCFC-22 product at the plant  $i$ . (See Equation 3.40 for calculation of HFC-23 emissions at an individual facility by in-process measurement.)

**Tier 3a**

The Tier 3a method is based on frequent or continuous measurement of the concentration and flow-rate from the vent at an individual plant. So that the quantity emitted to atmosphere is the mathematical product of the mass concentration of the component in the stream, the flowrate of the total stream (in units compatible with the mass concentration) and the length of time that this flow occurred:

**EQUATION 3.37**  
**TIER 3a CALCULATION OF ‘INSTANTANEOUS’ HFC-23 EMISSIONS IN AN INDIVIDUAL PROCESS**  
**STREAM (DIRECT METHOD)**

$$E_{ij} = C_{ij} \cdot f_{ij} \cdot t$$

Where:

$E_{ij}$  = ‘instantaneous’ HFC-23 emissions from process stream  $j$  at plant  $i$ , kg

$C_{ij}$  = the concentration of HFC-23 in the gas stream actually vented from process stream  $j$  at plant  $i$ , kg HFC-23/kg gas

$f_{ij}$  = the mass flow of the gas stream from process stream  $j$  at plant  $i$  (generally measured volumetrically and converted into mass flow using standard process engineering methods), kg gas/hour

$t$  = the length of time over which these parameters are measured and remain constant, hours

If any HFC-23 is recovered from the vent stream for use as chemical feedstock, and hence destroyed, it should be discounted from this emission; material recovered for uses where it may be emitted may be discounted here, if the emissions are included in the quantity calculated by the methods in Chapter 7. Because emissions are measured directly in this tier, it is not necessary to have a separate term for material recovered, unlike Tiers 3b and 3c.

The total quantity of HFC-23 released is then the annual sum of these measured instantaneous releases. Periods when the vent stream is processed in a destruction unit to remove HFC-23 should not be counted in this calculation. If it is necessary to estimate the quantity destroyed at each facility, the operator should calculate this based on the difference between the operating time of the plant and the duration of release ( $t$  above).

**Tier 3b**

In many cases, measurements are not continuous but were gained during an intensive process survey or plant trial, and the results of the trial may be used to provide a proxy for calculating emissions during normal plant operation. In this case, the emission rate of the by-product is related to a more easily (or accurately) measurable parameter, such as feedstock flow rate. The trial(s) must meet the following conditions:

- There should have been no major process design, construction or operating changes that affect the plant upstream of the measurement point and so could render relationships between emissions and production invalid. (See also Box 3.14)
- The relationship between emissions and plant operating rate must be established during the trial(s), together with its uncertainty.

For almost all cases the rate of plant operation is a suitable proxy and the quantity of HFC-23 emitted depends on the current plant operating rate and the length of time that the vent flow was released.

**EQUATION 3.38**  
**TIER 3b CALCULATION OF HFC-23 EMISSIONS IN AN INDIVIDUAL PROCESS STREAM**  
**(PROXY METHOD)**

$$E_{ij} = S_{ij} \cdot F_{ij} \cdot POR_{ij} \cdot t - R_{ij}$$

Where:

- $E_{ij}$  = the mass emission of HFC-23 in vent stream  $j$  at plant  $i$ , kg
- $S_{ij}$  = the standard mass emission of HFC-23 in vent stream  $j$  at plant  $i$  per 'unit' of proxy quantity, such as process operating rate (described in Equation 3.39, below), kg/'unit'
- $F_{ij}$  = a dimensionless factor relating the measured standard mass emission rate to the emission rate at the actual plant operating rate. In many cases, the fraction produced is not sensitive to operating rate and  $F_{ij}$  is unity (i.e., the emission rate is proportional to operating rate). In other cases the emission rate is a more complex function of the operating rate. In all cases  $F_{ij}$  should be derived during the plant trial by measuring HFC-23 production at different operating rates. For situations where a simple function relating the emissions to the operating rate cannot be determined from testing, the proxy method is not considered appropriate and continuous measurement is desirable.
- $POR_{ij}$  = the current process operating rate applicable to vent stream  $j$  at plant  $i$  averaged over  $t$  in 'unit/hour'. The units of this parameter must be consistent between the plant trial establishing the standard emission rate and the estimate of ongoing, operational emissions (described in Equation 3.39, below).
- $t$  = the actual total duration of venting for the year, or the period if the process is not operated continuously in hours. Annual emissions become the sum of all the periods during the year. The periods during which the vent stream is processed in a destruction system should not be counted here.
- $R_{ij}$  = the quantity of HFC-23 recovered for vent stream  $j$  at plant  $i$  for use as chemical feedstock, and hence destroyed, kg. Material recovered for uses where it may be emitted potentially may be counted here if the emissions are included in the quantity calculated by the methods for ODS substitutes in Chapter 7 of this volume.

**EQUATION 3.39**  
**TIER 3b CALCULATION OF STANDARD EMISSION FOR PROXY METHOD**

$$S_{T,ij} = C_{T,ij} \cdot f_{T,ij} / POR_{T,ij}$$

Where (for each test T):

- $S_{ij}$  = the standard mass emission of HFC-23 in vent stream  $j$  at plant  $i$ , kg/'unit' (in units compatible with the factors in Equation 3.38, see  $POR_{T,ij}$  below)
- $C_{T,ij}$  = the average mass fractional concentration of HFC-23 in vent stream  $j$  at plant  $i$  during the trial, kg/kg
- $f_{T,ij}$  = the average mass flowrate of vent stream  $j$  at plant  $i$  during the trial, kg/hour
- $POR_{T,ij}$  = the proxy quantity (such as process operating rate) at plant  $i$  during the trial, 'unit'/hour. The 'unit' depends on the proxy quantity adopted for plant  $i$  vent stream  $j$  (for example, kg/hour or m<sup>3</sup>/hour of feedstock)

**Tier 3c**

It is a relatively simple procedure to monitor the concentration of HFC-23 in the product of a reaction system relative to the amount of HCFC-22. This provides a basis for estimation of the quantity of HFC-23 released as the mathematical product of the monitored concentration and the mass flow of HCFC-22 made. If there is no vent treatment to abate emissions, this is a simple procedure. However, where there is abatement then it must be shown that this actually treats all streams that may be released into the atmosphere, including direct gas vents and the outgassing of aqueous streams. The latter, especially, may not be passed to the destruction facility. If all potential vent streams are not treated, the method cannot be used.



**EQUATION 3.40**  
**TIER 3c CALCULATION OF HFC-23 EMISSIONS FROM AN INDIVIDUAL FACILITY BY IN-PROCESS MEASUREMENT**

$$E_i = C_i \cdot P_j \cdot t_F - R_i$$

Where:

$E_i$  = HFC-23 emissions from an individual facility  $i$ , kg

$C_i$  = the concentration of HFC-23 in the reactor product at facility  $i$ , kg HFC-23/kg HCFC-22

$P_j$  = the mass of HCFC-22 produced at facility  $i$  while this concentration applied, kg

$t_F$  = the fractional duration during which this HFC-23 is actually vented to the atmosphere, rather than destroyed, fraction

$R_i$  = the quantity of HFC-23 recovered from facility  $i$  for use as chemical feedstock, and hence destroyed, kg

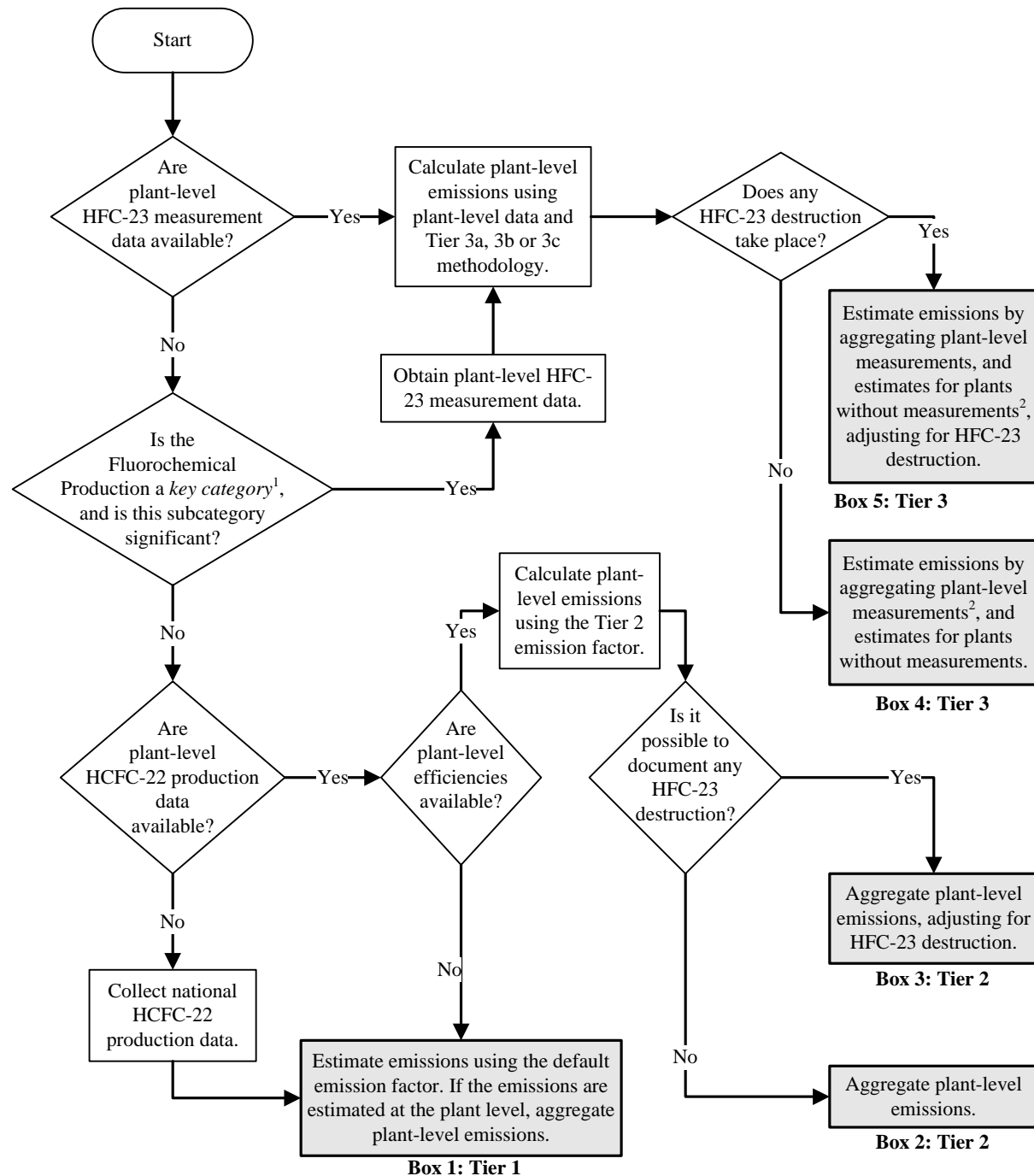
Material recovered for uses where it may be emitted potentially may be counted here if the emissions are included in the quantity calculated by the methods in Chapter 7 of this volume.

The total quantity of HFC-23 released into the atmosphere is the sum of the quantities from the individual release periods and individual reaction systems.

HFC-23 that is recovered for use as chemical feedstock should be subtracted from the total quantity estimated here.

In summary, the Tier 1 method is relatively simple, involving the application of a default emission factor to the quantity of HCFC-22 produced. This method can be applied at the plant level or the national level. Tier 2 and Tier 3 methodologies are suitable only for plant level calculations. In cases where there are Tier 3 data available for some plants, the Tier 1 or Tier 2 methods can be applied to the remainder to ensure complete coverage. Uncertainty in the national emission is then calculated using production weighted uncertainties of the individual sources and standard statistical techniques. Regardless of the method, emissions abated should be subtracted from the gross estimate from each plant to determine net emissions before these are added together in the national estimate.

**Figure 3.16 Decision tree for HFC-23 emissions from HCFC-22 production (or other similar by-product emissions from fluorochemical production)**



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.

2. If there are Tier 3 data available for some plants, the Tier 1 or Tier 2 methods can be applied to the remainder to ensure complete coverage.

It is *good practice* to use the Tier 3 method if possible. Direct measurement is significantly more accurate than Tier 1 because it reflects the conditions specific to each manufacturing facility. In most cases, the data necessary to prepare Tier 3 estimates should be available because facilities operating to good business practice perform regular or periodic sampling of the final process vent or within the process itself as part of routine operations. For facilities using abatement techniques such as HFC-23 destruction, verification of the abatement efficiency is also done routinely. The Tier 1 (default) method should be used only in rare cases where plant-specific data are unavailable and this subcategory is not identified as significant subcategory under *key category*. (See Section 4.2 of Volume 1.)

## CHOICE OF EMISSION FACTORS

There are several measurement options within the Tier 3 method relating to the location and frequency of the sampling. In general, direct measurement of the emissions of HFC-23 may provide the highest accuracy but continuous or frequent measurement of parameters within the production process area itself may be more pragmatic and can be equally accurate. In both cases, the frequency of measurement must be high enough to represent the variability in the process (e.g., across the life of the catalyst). Issues related to measurement frequency are summarised in Box 3.14, Plant Measurement Frequency. General advice on sampling and representativeness is provided in Volume 1, Chapter 2.

In cases where plant-specific measurements or sampling are not available and Tier 1 methods are used, the default emission factor should be used, assuming no abatement methods. For plants in operation prior to 1995 the default emission factor is 0.04 kg HFC-23/kg HCFC-22 (4 percent) (IPCC, 1996; USEPA, 2001). This is a default to be used when there are no measurements and describes the output of HFC-23 from a typical HCFC-22 plant in the absence of recovery or destruction of HFC-23. The value is consistent with atmospheric observations of HFC-23 concentrations in the 1978-1995 time period (Oram *et al.*, 1998). These showed globally averaged emissions to be equivalent to 2 percent of the total quantity of HCFC-22 produced at a time when significant HFC-23 was being recovered and converted into Halon 1301 (McCulloch, 1992) and abatement was required practice in several countries where there was significant production.

It is possible, by process optimisation, to reduce the production to between 0.014 and 0.03 kg HFC-23/kg HCFC-22 (1.4 to 3 percent) but it is not possible to completely eliminate HFC-23 formation this way (IPCC, 2000). Furthermore, the extent of the reduction is highly dependent on the process design and the economic environment (measures to reduce HFC-23 can often reduce the process output). In an optimised process HFC-23 production and emissions will, invariably, have been measured; it is not possible to optimise process operation without such measurements and so default values have no meaning in this context for an individual plant. However, the state of the technological art has been advanced by optimisation of individual plants and that art should have been built into the design of recent plants, suggesting a default emission factor of 0.03 kg HFC-23/kg HCFC-22 (3 percent). These default values have a large uncertainty (in the region of 50 percent). For more accurate assessments, the actual emissions should be determined by Tier 2 or Tier 3 methodology and, if necessary, assigned to previous years using the guidance provided in Chapter 7 of this volume.

| <b>Technology</b>  | <b>Emission Factor<br/>(kg HFC-23/kg HCFC-22 produced)</b> |
|--|--|
| Old, unoptimised plants (e.g., 1940s to 1990/1995)                     | 0.04   |
| Plants of recent design, not specifically optimised                    | 0.03   |
| Global average emissions (1978 - 1995) <sup>4</sup>                    | 0.02   |
| <i>For comparison:</i>   |  |
| <i>Optimised large plant- requiring measurement of HFC-23 (Tier 3)</i> | <i>Down to 0.014</i>                                       |
| <i>Plant with effective capture and destruction of HFC-23 (Tier 3)</i> | <i>Down to zero</i>  |

<sup>4</sup> The global average is calculated from the change in atmospheric concentration of HFC-23. It does not discriminate between plant emissions, which range from nothing to greater than 4 percent of the HCFC-22 production.

**Box 3.14****PLANT MEASUREMENT FREQUENCY**

The accuracy and precision of the estimates of annual HFC-23 emissions depend on the number of samples (the frequency of sample collection) together with the accuracy of measurement of flowrates and the extent to which discrete flow measurements can represent the total quantity vented. Since production processes are not completely static, the greater the process variability, the more frequently plants need to measure. As a general rule, sampling and analysis should be repeated whenever a plant makes any significant process changes. Before choosing a sampling frequency, the plant should set a goal for accuracy and use statistical tools to determine the sample size necessary to achieve the goal. For example, a study of HCFC-22 producers indicates that sampling once per day is sufficient to achieve an extremely accurate annual estimate. This accuracy goal should then be revised, if necessary, to take into account the available resources. (RTI, Cadmus, 1998)

**CHOICE OF ACTIVITY DATA**

When using the Tier 1 method, production data should be obtained directly from producers. There are several ways producers may determine their production levels, including shipment weights and measuring volume-times-density, using flow meters. These data should account for all HCFC-22 production for the year, whether for sale or for use internally as feedstock, and the plant should describe how the HCFC-22 production rate is determined. In some circumstances, producers may consider plant production data to be confidential. For national-level activity data, submission of HCFC-22 production data is already required under the Montreal Protocol.

**COMPLETENESS**

It should be possible to obtain complete sampling data because there are only a small number of HCFC-22 plants in each country, and it is standard practice for each plant operator to monitor process efficiencies and hence HFC-23 losses, leading to the adoption of Tier 2 methodology. The destruction efficiencies of thermal oxidisers used to abate HFC-23 are generally high (>99 percent) but it is important to establish the composition of the exit gas in order to ensure that account is taken of emissions of fluorinated greenhouse gases from this point.

**DEVELOPING A CONSISTENT TIME SERIES**

Emission of HFC-23 from HCFC-22 production should be estimated using the same method for the entire time series and appropriate emission factors. If data for any years in the time series are unavailable for the Tier 3 method, these gaps should be filled according to the guidance provided in Volume 1, Chapter 5.

**3.10.1.3 UNCERTAINTY ASSESSMENT****TIER 1**

Unlike the other Tiers, where uncertainties are based on measurements and statistics, Tier 1 uncertainties are assessed through expert judgement and an error of approximately 50 percent could be considered for Tier 1 based upon knowledge of the variability in emissions from different manufacturing facilities. An error of this magnitude will completely outweigh the uncertainty in the activity.

**TIER 2**

Uncertainty of the Tier 2 result is calculated by the root-squared sum of the individual uncertainties in production mass quantity and efficiencies, assuming the carbon and fluorine uncertainties are the same. Where the uncertainties in carbon and fluorine efficiency differ significantly (enough to cause a material difference to the calculated emission), the value with the lower uncertainty should be used throughout the calculation.

Uncertainty in the value derived by Tier 2 methods is much larger than that expected from Tier 3 but is, nevertheless, quantifiable. Typically, for a plant producing about 4 percent HFC-23, the carbon efficiency is in the region of 95 percent and the fluorine efficiency 92 percent. If these efficiencies can be measured to within 1 percent, then the error in the Tier 2 HFC-23 estimate would be less than 20 percent. Estimating efficiencies to this degree of accuracy will require rigorous accounting procedures and that all raw materials and product for sale should be weighed in or out of the facility. Such a regime sets the expected accuracy of the overall activity (for both Tiers 1 and 2); with good accounting and measurement of production by weight, it should be possible to reduce the error in the activity to below 1 percent.

### TIER 3

For HFC-23, the Tier 3 method is significantly more accurate than either the Tier 2 measured or Tier 1 default methods. Regular Tier 3 sampling of the vent stream can achieve an accuracy of 1-2 percent at a 95 percent confidence level in HFC-23 emissions and the uncertainty of the Tier 3 (proxy) result may be similar. In both cases, the uncertainty may be calculated statistically from the uncertainties of the input parameters and, because these methods do not rely on emission factors or activities, the concept of subdividing uncertainty has no validity.

Uncertainty of the estimate is expressed as a coefficient of variance (percent) and, for each of these streams, there will be an uncertainty as a consequence of uncertainties in measured concentration and flowrate and uncertainty in the duration of the flow. The combined uncertainty can be determined analytically and should be calculated using the standard methodology described in Chapter 3 of Volume 1.

#### 3.10.1.4 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

##### QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, and quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

In addition to the guidance in Volume 1, specific procedures of relevance to this sub-source category are outlined below:

##### Comparison of emissions estimates using different approaches

Inventory compilers should compare reported plant emissions estimates against those determined using the Tier 1 default factor and production data. If only national production data are available, they should compare aggregated plant emissions to a national default estimate. If significant differences are found in the comparison, they should answer the following questions:

1. Are there inaccuracies associated with any of the individual plant estimates (e.g., an extreme outlier may be accounting for an unreasonable quantity of emissions)?
2. Are the plant-specific emission factors significantly different from one another?
3. Are the plant-specific production rates consistent with published national level production rates?
4. Is there any other explanation for a significant difference, such as the effect of controls, the manner in which production is reported or possibly undocumented assumptions?

##### Direct emission measurement check

- Inventory compilers should confirm that internationally recognised, standard methods were used for plant measurements. If the measurement practices fail this criterion, then the use of these emissions data should be carefully evaluated. It is also possible that, where a high standard of measurement and QA/QC is in place at sites, the uncertainty of the emissions estimates may be revised downwards.
- Each plant's QA/QC process should be evaluated to assess if the number of samples and the frequency of sample collection is appropriate given the variability in the process itself.
- Where possible, inventory compilers should verify all measured and calculated data through comparison with other systems of measurement or calculation. For example, emissions measurement within the process itself can be verified periodically with measurement of the vent stream. Inventory compilers should verify abatement system utilisation and efficiency.
- With a periodic external audit of the plant measurement techniques and results, it is also possible to compare implied emission factors across plants and account for major differences.

##### REPORTING AND DOCUMENTATION

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11.

Some examples of specific documentation and reporting relevant to this source category are provided below:

- To provide for completely transparent reporting, emissions of HFC-23 from HCFC-22 production should be reported as a separate item, rather than included with other HFC emissions.
- Documentation should also include:
  - (i) Methodological description;
  - (ii) Number of HCFC-22 plants;
  - (iii) HCFC-22 production (if multiple producers);
  - (iv) Presence of abatement technology;
  - (v) Process descriptions, operating parameters; and
  - (vi) Related emission factors.

### **Confidentiality**

- The use of the Tiers 2 and 3 methods would mean that the plant emissions of HFC-23 are reported separately from the production of HCFC-22. By de-coupling the HFC-23 emissions and HCFC-22 production, the emission data on HFC-23 cannot be considered to be of commercial confidence as it does not reveal the levels of production of HCFC-22 without detailed and confidential knowledge of the individual manufacturing facility.
- The application of the Tier 1 method to total national production of HCFC-22 would enable this to be calculated from published emissions of HFC-23 and, if there were less than three producers, such production data could be considered confidential business information. In such cases, steps should be taken to protect confidentiality through, for example, the aggregation of all HFC emissions. For transparency reasons, whenever there is aggregation, a qualitative discussion of HCFC-22 production should be included.
- When national emissions are calculated as the sum from individual facilities and these have been calculated using different methodologies, it is not possible to recalculate the HCFC-22 production from these data alone and there should be no problems concerning confidentiality.

## **3.10.2 Emissions from production of other fluorinated compounds**

### **3.10.2.1 INTRODUCTION**

A large number of fluorine containing greenhouse gases can be produced as by-products of fluorochemical manufacture and emitted into the atmosphere. For example, in a recent national inventory, significant by-product emissions of SF<sub>6</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>10</sub>, C<sub>5</sub>F<sub>12</sub> and C<sub>6</sub>F<sub>14</sub> were reported for a fluorochemical plant (UNFCCC, 2005). Other examples include the release of by-product CF<sub>4</sub> from the production of CFC-11 and 12 or of SF<sub>6</sub> from the production of uranium hexafluoride in the nuclear fuel cycle.

Emissions of a chemical occur during its production and distribution or as a by-product during the production of a related chemical (HFC-23 from HCFC-22 production is covered specifically in Section 3.10.1 above). There may also be emissions of the material that is being produced; the so-called 'fugitive emissions'. Both by-product and fugitive emissions are calculated in the same way. In this section, emissions associated with use are not addressed specifically, being counted in the emissions related to consumption (see Chapters 4.5, 6, 7 and 8 in this volume). Typically, fluorochemicals may be released from chemical processes involving a broad range of technologies and processes<sup>5</sup>:

- Telomerization Process used in the production of fluorochemicals fluids and polymers
- Photooxidation of tetrafluoroethylene to make fluorochemical fluids
- Direct Fluorination often used in SF<sub>6</sub> production
- Halogen Exchange Processes to make low boiling PFCs like C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub>, HFC 134a and 245fa
- NF<sub>3</sub> manufacturing by direct fluorination
- Production of uranium hexafluoride

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<sup>5</sup> This list is illustrative.

- Production of fluorinated monomers like tetrafluoroethylene and hexafluoropropylene
- Production of fluorochemical agrochemicals
- Production of fluorochemical anesthetics

Halogen exchange processes are extensively used for HFC manufacture, while most PFCs and SF<sub>6</sub> require elemental fluorine, generated electrochemically. In 'electrochemical fluorination' processes, the fluorine is not separated but makes the desired product in the electrochemical cell. In other processes it is separated and subsequently used, either as the elemental gas or as a component of a carrier system, such as CoF<sub>3</sub>. Each process will have a different spectrum of emissions, in terms of both chemical nature and quantities, and so a common default emission function is of relatively little value. It is essential that the existence of potentially emissive plants is identified within each country, hence this step is first in the decision tree (Figure 3.17). The common factor for these plants is the use of anhydrous hydrogen fluoride, which is the source of fluorine in halogen exchange processes and in processes that use elemental fluorine. The production and importation of anhydrous hydrogen fluoride can therefore be used as a means of tracing significant producers of fluorochemicals. Further enquiries (see Figure 3.17) can then elucidate whether or not there are significant fluorochemical greenhouse gas emissions.

### 3.10.2.2 METHODOLOGICAL ISSUES

#### CHOICE OF METHOD

It is *good practice* to choose the method using the decision tree shown in Figure 3.17. If the Category 2B9 Fluorochemical Production is identified as *key* and this subcategory is judged to be significant, inventory compilers should consider whether or not emissions are dominated by the production of a sub-set of chemicals, and focus more sophisticated data collection efforts on production of these chemicals. The number of major producers of these fluorinated greenhouse gases is quite small: in the case of SF<sub>6</sub>, there are globally about 6 companies with about 10 production facilities world-wide (Preisegger, 1999). The number of smaller producers may grow in the near future, particularly in developing economies. However, a survey of national producers should not be difficult to compile.

#### Tier 1

In the Tier 1 methodology, a default emission factor, or a similar number derived for the particular country's circumstances, can be used to estimate national production-related emissions of individual HFCs, PFCs, SF<sub>6</sub> and other fluorinated greenhouse gases.

**EQUATION 3.41**  
**TIER 1 CALCULATION OF PRODUCTION-RELATED EMISSIONS**

$$E_k = EF_{default,k} \cdot P_k$$

Where:

$E_k$  = production-related emissions of fluorinated greenhouse gas  $k$ , kg

$EF_{default,k}$  = default emission factor, kg/kg

$P_k$  = total production of fluorinated greenhouse gas  $k$ , kg

Problems of confidentiality arising from reporting specific component data can be circumvented by providing a single number for total national emissions of each HFC, PFC and SF<sub>6</sub>. This may be facilitated if data are collected by a third party and reported only as this total.

#### Tier 2

The method based on process efficiencies, which works for HFC-23 emissions from HCFC-22 plants, is of less value for other types of plants. This is due in part to the lower inefficiency expected from these other by-product emissions; the uncertainty in measurement of efficiencies is likely to be much greater than the by-product emission factor. Furthermore, a range of by-products may be responsible for process inefficiency (unlike the case for HCFC-22 where one by-product predominates). However, production efficiency data should exist for each process and, in the absence of a more rigorous estimate, the quantity of emissions estimated from process inefficiencies may be used in a qualitative decision as to whether or not these emissions are a significant subcategory under a *key category* (in which case, Tier 3 methodology is specified).

### Tier 3

The Tier 3 methodology is potentially the most accurate estimate and is the sum of factory specific emissions of *each* by-product fluorinated greenhouse gas determined using standard methods to estimate the composition and flowrate of gas streams actually vented to atmosphere after any abatement technology. In this case:

#### EQUATION 3.42

##### TIER 3 DIRECT CALCULATION OF PRODUCTION-RELATED EMISSIONS

$$E_k = \sum_i \sum_j \int_t C_{ijk} \cdot f_{ijk} \quad \left[ \int_t \text{ means the quantity should be summed over time.} \right]$$

Where:

$E_k$  = total production-related emissions of fluorinated greenhouse gas  $k$ : the sum over all  $i$  plants, over all  $j$  streams in each plant of the emitted mass flows  $f$  and concentrations  $C$  integrated over time  $t$ .

or, where proxy methodology is used, for example where the emission rate of the by-product is normalised to a more easily (or accurately) measurable parameter, such as feedstock flow rate, as described in Equation 3.35 in Section 3.10.1:

#### EQUATION 3.43

##### TIER 3 PROXY CALCULATION OF PRODUCTION-RELATED EMISSIONS

$$E_k = \sum_i \sum_j \int_t E_{ijk} \quad \left[ \int_t \text{ means the quantity should be summed over time.} \right]$$

Where:

$E_k$  = total production-related emissions of fluorinated greenhouse gas  $k$ :  $E_{ijk}$  = the emissions of fluorinated greenhouse gas  $k$  from each plant and stream determined by the proxy methods, described in Equations 3.38 and 3.39 in Section 3.10.1

Note that, generally, flows are measured volumetrically and should be converted into mass flow (kg/hour) based on the ideal gas law, temperature, pressure and composition, similarly concentration should be converted into compatible units (e.g., kg/kg).

In this case, the flowrates, concentrations and duration should be calculated separately for the periods when the abatement technology is or is not operating and only those that lead to actual emissions should be summed and reported.

## CHOICE OF EMISSION FACTORS

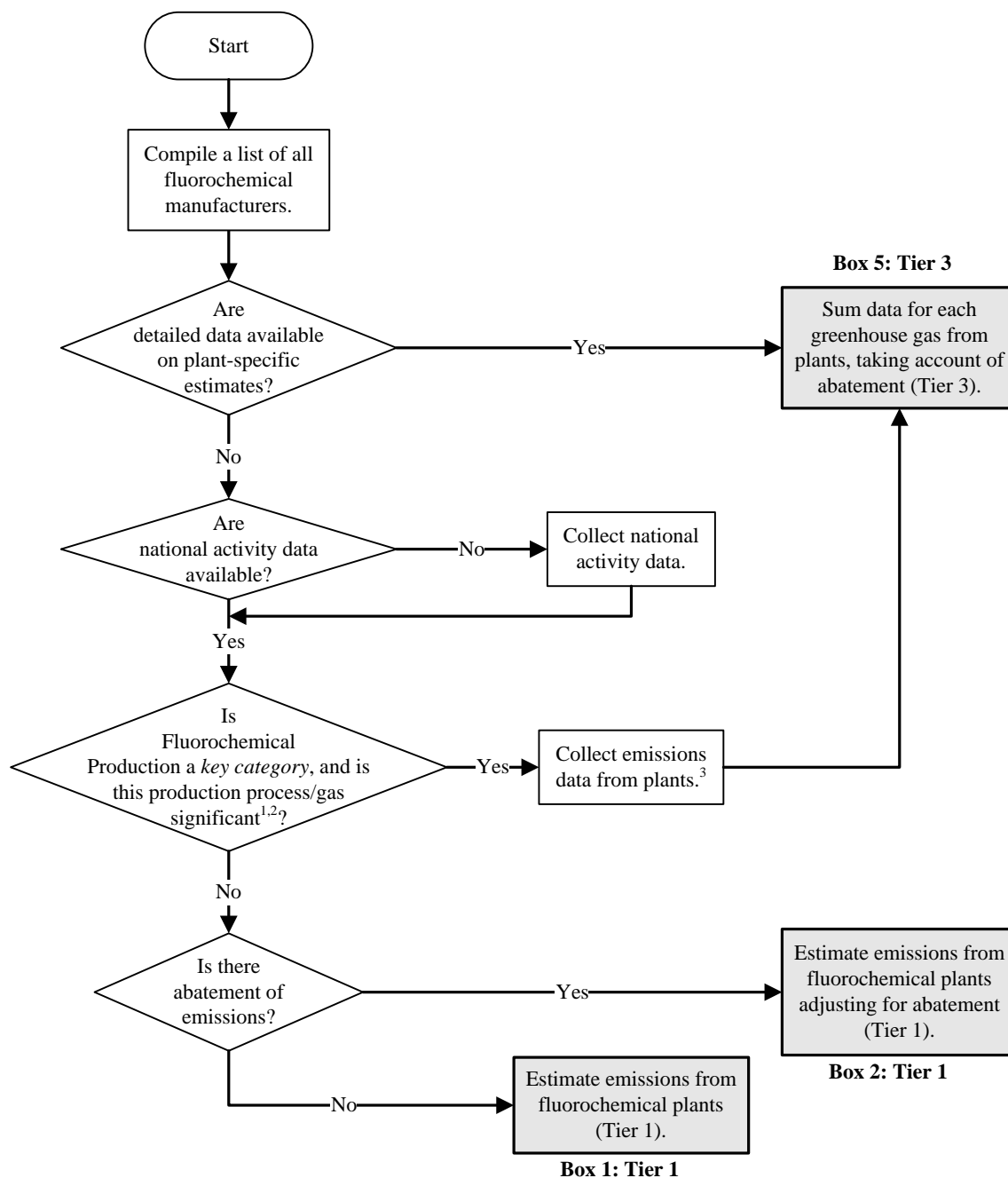
Tier 3 relies on measurements of the quantities of individual materials that are released into the atmosphere and neither Tier 2 nor Tier 3 relies on emission factors. For Tier 1, in the absence of abatement measures, a default emission factor of 0.5 percent of production, not counting losses in transport and transfer of materials, is suggested for HFCs and PFCs, based on data supplied to AFEAS (2004). There is a wide range of substances that may potentially be released. However, the AFEAS data showed that the components that were lost during production of a particular fluorochemical had, in general, radiative forcing properties similar to those of the desired fluorochemical. Consequently, for sources that are not significant subcategories under *key category*, fugitive and by-product emissions are the same and are included in the 0.5 percent emission factor.

In the case of SF<sub>6</sub>, based on German experience, a default emission factor of 0.2 percent of the total quantity of SF<sub>6</sub> produced is suggested for those countries in which the predominant end use does not require highly purified SF<sub>6</sub> gas (e.g., electrical equipment, insulated windows) (Preisegger, 1999). Based on experience in Japan, in countries where the major uses require highly purified SF<sub>6</sub> gas (e.g., semiconductor manufacturing), the default value should be 8 percent because of handling losses during disposal of residual gas (i.e., the 'heel' that is not used or recycled) in returned cylinders (Suizu, 1999). If national data are available, these should be used, particularly for other materials not specifically listed here.

The default emission factors are based on situations where no abatement measures are employed. If the quantity of gas emitted to the atmosphere is reduced by, for example, thermal oxidation of the vent stream, the quantity emitted should be adjusted to account for the destruction efficiency of the oxidiser and the length of time that it is in service. Based on the experience in the destruction of HFC-23, a default destruction efficiency of 100 percent is suggested but the on-line time of the destruction process will have a greater effect on emissions and should be recorded.



**Figure 3.17** Decision tree for emissions of fluorinated greenhouse gases from production processes, applicable to both fugitive and by-product emissions



Note:

1. See Volume 1 Chapter 4, Methodological Choice and Identification of Key Categories (noting Section 4.1.2 on limited resources), for discussion of *key categories* and use of decision trees.
2. Tier 2 methodology may be used at this point to establish whether or not this is a *key category* but, as explained in Section 3.10.2.2, this is the only use for Tier 2.
3. Data may be collected as a country study by a third party in order to preserve confidentiality.

## CHOICE OF ACTIVITY DATA

Again, activity data has no role in the Tiers 3 and 2 estimates, which are based on measurements. For Tier 1, the activity is the annual mass of the desired fluorochemical that is produced.

## Recycling

Recycling of used gas may be done by the producers of new gas or by other recycling firms. Emissions may occur during handling and purification of old gas and handling of recycled gas. Specific emission factors are not available. Thus, *good practice* is to use the same default factor as for new production.

## COMPLETENESS

For some inventory compilers, identifying smaller producers and, in particular, recycling firms may be a difficult task. However, initial estimates based on the national mass balance of these fluorinated greenhouse gases should identify if production related emissions from such entities provide a sizeable contribution to total national emissions.

## DEVELOPING A CONSISTENT TIME SERIES

Both by-product and fugitive emissions of fluorocompounds from production processes should be estimated using the same method for the entire time series and appropriate emission factors. If data for any years in the time series are unavailable for the Tier 3 method, these gaps should be filled according to the guidance provided in Volume 1, Chapter 5.

### 3.10.2.3 UNCERTAINTY ASSESSMENT

For Tier 1, the uncertainty in activity data needs to be determined for the reporting country and statistically combined with the uncertainty in the default emission factor. Typically, in a well operated facility, the default uncertainty in activity data should be in the region of 1 percent, assuming that rigorous accounting records are maintained and that production is monitored by weight. The actual emission factor may range from well in excess of the default value to zero. The default uncertainty of the default emission factors is therefore set at 100 percent, for example  $0.5 \pm 0.5$  (%).

For Tier 3 emissions, the uncertainty of the measurements should be determined individually and combined (using standard statistical methods) to provide a total uncertainty for the estimate. The methodology is identical to that described for HFC-23 from HCFC-22. In the Tier 2 methodology, the uncertainty both of the measurements of efficiencies and the assignment of losses to individual compounds should be assessed. Because these are liable to produce a much larger uncertainty than that from Tier 3, the utility of Tier 2 is likely to be limited to assessing whether or not by-product fluorochemical emissions are a significant subcategory under *key category*.

### 3.10.2.4 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC), REPORTING AND DOCUMENTATION

#### QUALITY ASSURANCE/QUALITY CONTROL

It is *good practice* to conduct quality control checks as outlined in Volume 1, Chapter 6, and an expert review of the emissions estimates. Additional quality control checks as outlined in Volume 1, Chapter 6, quality assurance procedures may also be applicable, particularly if higher tier methods are used to determine emissions from this source category. Inventory compilers are encouraged to use higher tier QA/QC for *key categories* as identified in Volume 1, Chapter 4.

#### Comparison of emissions estimates using different approaches

Inventory compilers should compare the estimate based on aggregated producer-level data to an estimate based on national production data and the suggested default emission factors. They should investigate significant discrepancies in cooperation with the producers to determine if there are unexplained differences.

#### REPORTING AND DOCUMENTATION

Confidentiality issues may arise where there are limited numbers of manufacturers. In these cases more aggregate reporting of total national emissions may be necessary. If survey responses cannot be released as public information, third-party review of survey data may be necessary to support data verification efforts.

It is *good practice* to document and archive all information required to produce the national emissions inventory estimates as outlined in Volume 1, Section 6.11. It is not practical to include all documentation in the national inventory report. However, the inventory should include summaries of methods used and references to source data such that the reported emissions estimates are transparent and steps in their calculation may be retraced.

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