UNIVERSIDADE DE SANTIAGO DE COMPOSTELA
Escola Técnica Superior de Enxeñaría
Departamento de Enxeñaría Química

DEVELOPMENT AND APPLICATION OF METHODOLOGIES TO GET SUSTAINABLE INDUSTRIAL SYSTEMS

Tesis presentada por:

LAURA CRISTÓBAL ANDRADE

Directora: Pastora María Bello Bugallo

Programa de Doctorado en Ingeniería Química y Ambiental

Santiago de Compostela, Agosto 2012

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INFORMA

Que la tesis titulada *Development and application of methodologies to get Sustainable industrial systems* que presenta **Dña. Laura Cristóbal Andrade**, ha sido realizada de forma favorable bajo su inmediata dirección en el Departamento de Ingeniería Química de la Universidad de Santiago de Compostela.

Y para que así conste, firma el presente Informe en Santiago de Compostela, a 20 de agosto de 2012.

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Doctorando	Directora
Laura Cristóbal Andrade	Pastora María Bello Bugallo

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SUMMARY

In the actual global context of limited availability of resources and increasingly restricting safety and environmental regulations, industry is in a great need of developing methodologies or strategies that facilitate facing these challenges. In the last decades uncountable methods have been developed with different purposes, being getting commercially more attractive and competitive chemical processes the main interest of the industry (Pasanen et al., 1999). These methods, often driven by safety and environmental regulations (Palaniappan et al., 2002), have contributed to the improvement of the production systems (Santos da Silva and Gonçalves Amaral, 2009), which are increasingly optimised to satisfy whether economic, environmental or social objectives (Alexander et al., 2000; Palaniappan et al., 2002).

Getting sustainable industrial systems requires the holistic consideration of the whole life cycle. However, the proper achievement of this goal requires predictive process models and optimisation of individual processes, together with the optimisation of the entire life cycle (Jayal et al., 2010). Hence the global vision of Life Cycle Thinking philosophy can be complemented considering the life cycle as a set of individual stages which can be individually analysed. These stages can be regarded as ‘systems’ or even ‘ecosystems’ under the scope of the industrial ecology.

The objective of this thesis is to develop and apply methodologies to get sustainable industrial systems on the basis of technical inventories and flow identification tools. Technical inventories are proposed regarding two different criteria: the Integrated Pollution Prevention and Control (IPPC) philosophy and the Waste Management Hierarchy (WMH), both of them derived from European policies. On the other hand two flow identification tools are suggested, namely material and energy flow analysis and process simulation. Flow identification tools are used to detect some specific flows whose qualitative and quantitative properties make them likely to be enhanced by implementing techniques from the inventories.

Initially technical inventories are proposed focussed on the IPPC philosophy and the WMH, supported by selected flow identification tools. They are individually analysed and validated to identify their benefits and limitations. Then integrated and optimised methodologies combining a technical inventory and a flow identification tool are proposed. They are developed and validated considering different criteria regarding specific industrial systems. The different methodologies are studied to evaluate their potential to improve the sustainability of the industrial systems, identifying the best combination of technical inventories and flow identification tools for any given situation.

TECHNICAL INVENTORIES

Technical inventories are proposed as a suitable basis to develop methodologies to get sustainable industrial systems. They can be defined as a set of techniques, each supported by specific information regarding specific features, selected considering certain criteria for a given industrial system. They require exhaustive information background and deep knowledge of the industrial system to provide stakeholders with a potent tool to improve the sustainability of their processes. These inventories are intended to present all the alternatives suitable and available to optimise or improve industrial systems. The alternatives are classified regarding different criteria, normally closely related to the selection criteria, which facilitates decision-making.

A methodology to develop technical inventories regarding BAT (Best Available Techniques), according to the principles of the IPPC philosophy (EU, 1996), is proposed. This methodology, BAT Analysis, is a step-by-step procedure that begins with the evaluation of the industrial system, followed by a description of the specific or generic process considered. Then the main environmental impacts, namely emissions and consumptions, are identified. An inventory of techniques candidate to be BAT is elaborated for the considered system. In the selection of techniques all the information previously analysed is regarded as well as technological features, geographical location, environmental conditions or the age of the considered installation.

BAT Analysis is validated in an industrial system: the Galician (NW Spain) heavy ceramics manufacturing industry. The methodology is applied to this system, resulting in a thorough evaluation of the sector, a generic flow diagram that identifies all the stages of the process as well as the inputs and outputs involved, and an inventory of 46 candidate techniques.

Methodologies for technical inventories, as BAT Analysis, are useful instruments for collecting and classifying all the alternatives available to get a sustainable industrial system. However, not all the available techniques can be implemented in an industrial system, as they all may not be suitable or necessary (Mavrotas et al., 2007; Samarakoon and Gudmestad, 2011). Techniques from inventories should only be applied when needed to enhance the sustainability of the industrial system, considering those elements that need to be modified and improved. It seems appropriate then to find an indicator that clearly and easily points out what elements of the system are not sustainable, and therefore should be improved.

IMPROVABLE FLOWS AND IDENTIFICATION TOOLS

A new indicator, based on material and energy flows, is defined: the Improvable Flows (IF). They are defined as quantitatively (or even qualitatively) relevant flows in an industrial system which could be improved if properly managed (Torres Rodríguez et al., 2011) by applying preventive or corrective measures. These flows are quantified and allocated regarding the industrial system they represent, so techniques from an inventory can be easily selected and implemented to effectively improve the sustainability of the system. Identification tools based on process analysis are used to detect improvable material and/or energy input, output or intermediate flows. IF detection can be also supported by literature or experience available on the analysed system.

Two tools are proposed to identify the IF of an industrial system: Material and Energy Flow Analysis (MEFA) and Process Simulation. In both cases a methodology is proposed and validated in an industrial system to evaluate the suitability of these tools to detect the IF and trace them across the system.

- **Material and Energy Flow Analysis**. MEFA is a tool derived from industrial metabolism. It comprises a whole family of tools to study the materials and energy flowing through a given system, the stocks and flows within this system and the resulting outputs from the considered system to others (Hendriks et al., 2000).

  A typical methodology (Hendriks et al., 2000) for MEFA is adapted to identify IF. It includes the definition of the targets of the study, a description of the system, the acquisition of data, modelling and scenario building using specific software, the evaluation and discussion of results, and finally the detection of the IF of the system according to the results of MEFA. The methodology provides deep knowledge about the process by qualitatively analysing all the stages and quantitatively identifying the material and energy flows involved.

  The methodology is validated in a roof-tile manufacture plant, considering the ‘transport and storage of raw materials’ stage. The application of MEFA to the case study points out transport operations as the more impactful processes. They are responsible of a great percentage of the fuel consumed and the exhaust gases released by the considered system, being lorry transport from quarry to plant the most impactful sub-stage. According to these results, fuel consumed and exhaust gases emitted in this sub-stage have been pointed out as IF for this system, as well as particulate emissions also from this sub-stage.

  MEFA is proved to be a suitable tool for IF identification. It provides quantitative information about material and energy flows, and traces them over the considered industrial system. Though quite useful as an IF identification tool, MEFA has some limitations. Not all the quantitatively relevant flows could be considered as IF, whereas some flows whose amount may not be disturbing should be avoided or reduced (due to their economic cost, or their impact over the environment) and pointed out as IF. MEFA simply quantifies and traces flows, providing valuable information to decision-makers, which are the ones who must evaluate which flows should be classified as IF, owing to their specific features. In any case it is a powerful tool on process-optimisation oriented strategies, as it can easily quantify and trace all the flows involved in a given process. Accordingly, once the major unsustainable flows have been properly identified, they can be defined as IF so that specific corrective measures could be proposed to avoid, reduce or take advantage from them.

- **Process simulation**. This tool is implemented by process simulators, defined as software specifically programmed to model process plants (Casavant and Côté, 2004). It is able to simulate and quantify material and energy flows within an industrial system, and predicts the behaviour of processes after modifying one or more variables. It is widely used with multiple purposes, as evaluating modifications on processes, predicting emissions or analysing integration potentials, to mention some.

  A methodology applying the European WMH and the IPPC philosophy criteria, together with process simulation is proposed to select suitable alternatives for waste management in an industrial system. It includes three well differentiated modules: system description, qualitative analysis and quantitative analysis. Qualitative analysis is applied to define the waste stream concerned and to elaborate an inventory techniques, representing the available management options classified in accordance with the WMH. The most appropriate technique or set of techniques is selected regarding the IPPC philosophy and respecting the hierarchical classification of the WMH. Quantitative analysis includes the selection of appropriate simulation software, data acquisition, modelling and scenario building, and simulation to quantitatively define all the material and energy streams of the process, but also the specific quantitative requirements of the units involved. This quantitative analysis leads to the identification of the IF of the system.

The suitability of the methodology is validated in a case study, which considers the waste management sector, focussing on a specific waste stream: used lubricating oil. The application of the methodology results in the selection of a recycling treatment which is quantitatively evaluated by process simulation to identify four IF.

The application of process simulation in a more complex methodology validates it as a suitable tool for IF identification. However, process simulation is a more valuable tool to evaluate the suitability of options intended to improve a given process. It allows modifying all the variables involved, process stages and equipment, or even whole sections of the process to analyse the impacts. It requires abundant and rigorous information about the simulated system to guarantee faithful models as similar to the reality as possible. Economic investments derived from process optimisation will be more justified and will be better supported if they are derived from the application of a methodology as the proposed, where improvement alternatives are validated by process simulation.

COMBINED METHODOLOGIES

After individually analysing the advantages and limitations of BAT Analysis and IF identification tools, they are combined in integrated methodologies intended to get sustainable industrial systems. Three combined methodologies are proposed.

- **Combination of BAT Analysis and MEFA.** This methodology, applied to an industrial system, seeks to identify the IF by MEFA, so that the appropriate candidate BAT can be selected by BAT analysis. Material and energy inputs, outputs and internal flows are allocated and quantified, and sustainable solutions are provided on the basis of industrial metabolism. This combined methodology involves a thorough qualitative analysis of the system, defining its limits, identifying the stages involved, and determining and allocating the associated consumptions and emissions. As a result, a complete strategy focussed on improving the unsustainable flows of the industrial system will be proposed.

  The methodology is validated in a roof-tile manufacture plant. The application of this methodology to this exemplary plant leads to the identification of 14 IF, most of them corresponding to the ‘thermal treatments’ stage. 4 BAT were already implemented in the analysed plant, and 7 candidate BAT have been proposed to reduce the IF.

  The proposed methodology provides a way to detect improvable material or energy flows in a process, whether they are inputs, outputs or internal flows, and selects the most sustainable options to enhance them. Solutions are proposed for the detected IF, and their effectiveness on improving them is roughly considered, though not specific and quantitative data about these improvements is provided. These results are very useful to enhance the process regarding resources consumption, environmental performance and, at lower level, economical aspects related to the habitual operation of the analysed process.

- **Combination of BAT Analysis and process simulation.** Both tools are jointly applied to identify the IF of the analysed process, so that the most appropriate candidate techniques from an inventory can be selected. The selected alternatives are evaluated in different scenarios by process simulation to determine the configuration that best improves the sustainability of the industrial process.

The methodology includes two modules. The first one involves a deep analysis of the process concerned, followed by a rigorous evaluation of the main environmental aspects. Then BAT Analysis is used to get an inventory of candidate techniques. Process simulation software is applied to the base case to analyse the process, quantifying all the material and energy flows. The simulation results are used to identify the IF of the process, so that candidate techniques from the inventory can be selected to improve the process. In the second module alternative scenarios implementing one or a set of candidate techniques are proposed. Each scenario is qualitatively analysed to clearly define the implementation conditions of the candidate techniques. Then process simulation software is applied to each scenario and the simulation results are compared to evaluate which one is the most appropriate to enhance the IF detected in the base case.

This methodology is validated in a case study: a H_2 production plant performing the natural gas steam reforming process. The first module of the methodology reveals three IF for the process, which have been summarised to ‘CO_2 emissions from’ and ‘energy consumption in’, associated to some stages of the process. Accordingly, three alternative scenarios are proposed and evaluated, pointing out two candidate techniques as the more suitable to improve the process. The combination of these tools in an integrated methodology is intended to help decision-makers to select the most sustainable configuration for a given process.

The previous methodologies (combining BAT Analysis with MEFA and process simulation) are validated in case studies representing different industrial systems. However both methodologies have been developed considering individual plants, not systems involving more than one plant. Moreover these methodologies are actually conceived for quite big plants whose processes can be divided into stages, their consumptions and emissions can be easily allocated, and are able to provide abundant and accurate data. Complex industrial systems and smaller plants are also in need of methodologies to improve their sustainability, which take into consideration their specific features.

- **Combination of WMH and BAT Analysis**. This methodology is intended to improve the sustainability of waste management in an industrial system represented by an atomised sector, integrated by highly dispersed small enterprises. Two of the actors involved on waste management strategies are considered: the waste producers and the intermediate waste manager. The IF between both actors are identified and techniques from an inventory are proposed to get a sustainable symbiotic system. The methodology considers the WMH and the IPPC philosophy. Both elements are combined, and the IPPC philosophy is adapted to the small and medium sized enterprises.

  The methodology is applied and validated in a system where the producers are printing plants belonging to a regional association, and represented by a reference plant. The intermediate waste manager is a local waste transfer station. This methodology provides extensive information about the considered system regarding the geographical area considered, the processes performed, the consumptions and emissions associated, and the waste flows between the waste producers and the waste manager. The IF are identified according to their amount and hazards associated. Alternatives to enhance their management are proposed on the basis of WMH and BAT Analysis, so that the waste producers focus their initiatives on prevention and preparation for re-use techniques, whereas the intermediate waste manager focuses on preparation for re-use, recycling and recovery options. Techniques and treatments are selected aiming to establish or improve the symbiosis between waste producers and intermediate managers.

The original system, integrated by a printing plant and a waste transfer station, is analysed to detect the IF. A series of alternatives are proposed to improve the system, and some of them are selected for being implemented. After implementation, the improved system is compared with the original one, showing that, besides reducing the amount of waste managed in the system, a symbiotic relationship between both actors has been settled. In this methodology, principles established considering big installations have been adapted to sectors that, in spite of being mainly integrated by small and medium-sized enterprises, generate a not negligible amount of diverse hazardous wastes.

Each methodology has its own strengths and weaknesses, and its suitability depends on the specific situation where the method is applied. In all cases qualitative analysis is initially applied to define the industrial system. This step allows stage identification and classification, which facilitates the study and comprehension of the process. It also defines the material and energy flows involved *a priori* in the process, making it easier to identify all the materials expected in each stage and the potential major energy consumers. All this information can be used in the quantitative steps of the methodologies, whether they are based on MEFA, process simulation or simpler material balances. Models are built based on the results of the qualitative part of the method, so that the process structure defined is respected through the whole analysis.

The quantitative analysis is performed using, in each case, a different IF identification tool, MEFA and process simulation, with different results. The method applying MEFA was intended to identify the IF of a process so that candidate techniques could be selected to prevent and reduce those flows. On the other hand, the method applying process simulation was meant to find the sustainable configuration for a given process by comparing the original situation with the potential future situation after applying the selected techniques. The last methodology applied material balances to roughly analyse the improvements expected after implementing the selected techniques.

Improvable Flows have been presented as a suitable indicator representing the unsustainabilities of industrial systems. They are quantifiable and allocable, and easily detected by identification tools based on process analysis. They can be prevented, reduced or enhanced by the application of an accurate selection of candidate techniques mainly defined under the principles of the IPPC philosophy and the WMH. IF have been used in three different methodologies, each combining an IF identification tool and a technical inventory, which have been validated and proved to provide sustainable industrial systems.

RESUMEN

En el contexto actual de disponibilidad limitada de recursos, y las cada vez más restrictivas políticas de seguridad y medio ambiente, la industria requiere metodologías o estrategias que permitan afrontar estos retos. En las últimas décadas se han desarrollado muchos métodos con diferentes propósitos, siendo el principal interés de la industria obtener procesos químicos más atractivos y competitivos (Pasanen et al., 1999). Estos métodos, frecuentemente motivados por la legislación en materia de seguridad y medio ambiente (Palaniappan et al., 2002), han contribuido a la mejora de los sistemas de producción (Santos da Silva and Gonçalves Amaral, 2009), cada vez más centrados en satisfacer objetivos económicos, ambientales o sociales (Alexander et al., 2000; Palaniappan et al., 2002).

Conseguir sistemas industriales sostenibles implica considerar de forma integrada el ciclo de vida. Sin embargo este objetivo requiere modelos predictivos y la optimización de procesos individuales, junto con la optimización completa de todo el ciclo de vida (Jayal et al., 2010). Por tanto, la visión global de la filosofía de Pensamiento de Ciclo de Vida (*Life Cycle Thinking, LCT*) debe complementarse considerando el ciclo de vida como un conjunto de etapas individuales que pueden analizarse individualmente. Estas etapas pueden entenderse como ‘sistemas’ o incluso ‘ecosistemas’, si se tiene en cuenta la ecología industrial.

El objetivo de esta tesis es desarrollar y aplicar metodologías para obtener sistemas industriales sostenibles basadas en inventarios de técnicas y herramientas de identificación de flujos. Los inventarios de técnicas se proponen en base a dos criterios diferentes: la filosofía de prevención y control integrados de la contaminación (*Integrated Pollution Prevention and Control, IPPC*) y la jerarquía de gestión de residuos (*Waste Management Hierarchy, WMH*), ambos derivados de políticas ambientales europeas. Por otro lado, se proponen dos herramientas de identificación de flujos: el análisis de flujo de materiales y energía (*Material and Energy Flow Analysis, MEFA*) y la simulación de procesos. Las herramientas de identificación de flujos se emplean para detectar algunos flujos específicos cuyas propiedades cualitativas y cuantitativas los hacen susceptibles de ser mejorados mediante la implementación de técnicas recompiladas en un inventario.

Inicialmente se proponen inventarios de técnicas enfocados en la filosofía *IPPC* y la *WMH*, respaldados por herramientas de identificación de flujos seleccionadas. Ambos se analizan individualmente y se validan para identificar sus ventajas y limitaciones. A continuación se proponen metodologías integradas y optimizadas que combinan un inventario de técnicas y una

herramienta de identificación de flujos. Estas metodologías se desarrollan y validan considerando diferentes criterios para sistemas industriales específicos. Las distintas metodologías se estudian para evaluar su potencial para mejorar la sostenibilidad de los sistemas industriales, identificando la mejor combinación de inventarios de técnicas y de herramientas de identificación de flujos para cada situación.

INVENTARIOS DE TÉCNICAS

Los inventarios de técnicas se proponen como base para desarrollar metodologías que permitan obtener sistemas industriales sostenibles. Pueden definirse como un conjunto de técnicas, cada una de ellas respaldada por información específica sobre determinados aspectos, seleccionadas de acuerdo a criterios definidos para cada sistema industrial. Implican un exhaustivo proceso de recopilación de información, así como conocer en profundidad el proceso industrial para proporcionar una herramienta potente que mejore la sostenibilidad de los procesos. Estos inventarios deben presentar todas las alternativas adecuadas y disponibles para optimizar o mejorar los sistemas industriales. Las alternativas se clasifican de acuerdo a diferentes criterios, normalmente relacionados con el criterio de selección, lo que facilita la toma de decisiones a la hora de seleccionar una u otra técnica.

Se ha propuesto una metodología para desarrollar inventarios de técnicas en relación con las Mejores Técnicas Disponibles (*Best Available Techniques, BAT*), de acuerdo con las principios de la filosofía *IPPC* (EU, 1996). Esta metodología, *BAT Analysis*, en un procedimiento por pasos que comienza por la evaluación del sistema industrial, seguido de una descripción del proceso considerado. A continuación se identifican los principales impactos ambientales (emisiones y consumos). Después se elabora un inventario de técnicas candidatas a ser *BAT* para el sistema considerado. Para la selección de técnicas se tiene en cuenta toda la información anteriormente analizada así como aspectos tecnológicos, localización geográfica, condiciones ambientales o la antigüedad de la instalación analizada.

BAT Analysis se ha validado en un sistema industrial: la industria gallega de producción de cerámicas pesadas. La metodología se aplica al sistema, resultando en una extensa evaluación del sector, un diagrama de flujo genérico que identifica todas las etapas del proceso, así como las entradas y salidas involucradas, y un inventario de 46 técnicas candidatas.

Las metodologías para desarrollar inventarios de técnicas, como *BAT Analysis*, son instrumentos útiles para reunir y clasificar todas las alternativas disponibles para obtener sistemas industriales sostenibles. Sin embargo no todos las técnicas disponibles pueden implementarse en un sistema industrial, ya que puede que no todas sean adecuadas o necesarias (Mavrotas et al., 2007; Samarakoon and Gudmestad, 2011). Las técnicas recogidas en los inventarios deben aplicarse únicamente cuando sean necesarias para mejorar la sostenibilidad de un sistema industrial, considerando aquellos elementos que deben modificarse o mejorarse. Por tanto se necesita un indicador que clara y fácilmente señale qué elementos del sistema no son sostenibles, y por tanto deben mejorarse.

FLUJOS MEJORABLES Y HERRAMIENTAS DE IDENTIFICACIÓN

Se ha definido un nuevo indicador basado en los flujos de materiales y energía: los flujos mejorables (*Improvable Flows, IF*). Se definen como aquellos flujos cuantitativamente (o incluso cualitativamente) relevantes en un sistema industrial que son susceptibles de ser mejorados si se gestionan adecuadamente (Torres Rodríguez et al., 2011) aplicando medidas preventivas o correctivas. Estos flujos se cuantifican y ubican en el sistema industrial que representan, de forma que las técnicas de los inventarios pueden seleccionarse e implementarse para mejorar de forma efectiva la sostenibilidad del sistema. Se emplean herramientas de identificación basadas en análisis de procesos para detectar los flujos de entrada, salida o intermedios, tanto de materia como de energía. La detección de *IF* puede estar respaldada por la bibliografía o por la experiencia disponible sobre el sector analizado.

Se proponen dos herramientas para identificar los *IF* de un sistema industrial: análisis de flujo de materiales y energía (*MEFA*) y simulación de procesos.

- **Análisis de flujo de materiales y energía**. *MEFA* es una herramienta derivada del metabolismo industrial. Abarca toda una familia de herramientas para estudiar los materiales y la energía que fluyen a través de un sistema, los *stocks*, y los flujos dentro del mismo sistema, así como los flujos desde el sistema considerado hacia otros sistemas (Hendriks et al., 2000).

  La metodología típica (Hendriks et al., 2000) de *MEFA* se ha adaptado para identificar los *IF*. Incluye la definición de los objetivos del estudio, la descripción del sistema, la colección de datos, el modelado y la construcción del escenario empleando software específico, la evaluación y la discusión de resultados, y finalmente la detección de los *IF* de acuerdo con los resultados del *MEFA*. Esta metodología aporta conocimiento sobre el proceso mediante el análisis cualitativo de todas las etapas y la identificación cuantitativa de los flujos de materiales y energía involucrados.

  Esta metodología se valida en una planta de fabricación de tejas, considerando únicamente la etapa ‘transporte y almacenamiento de materias primas’. La aplicación de *MEFA* a este caso de estudio señala que las operaciones de transporte son las que más impacto tienen sobre el resto del sistema. Son responsables de un gran porcentaje del combustible consumido y de los gases de escape emitidos, siendo el transporte desde la cantera hasta la planta la sub-etapa más impactante. De acuerdo con estos resultados, se han identificado los *IF* del sistema, que corresponden al combustible consumido y los gases de escape emitidos en esta sub-etapa, así como las emisiones de partículas, también derivadas de esta sub-etapa.

  De esta forma *MEFA* se valida como una herramienta adecuada para la identificación de *IF*. Aporta información cuantitativa sobre los flujos de materiales y energía, y los ubica dentro del sistema industrial considerado. Aunque es bastante útil como herramienta de identificación de *IF*, *MEFA* tiene algunas limitaciones. No todos los flujos cuantitativamente relevantes deben considerarse *IF*, mientras que algunos flujos cuya cantidad puede no ser relevante deben ser eliminados o reducidos (debido a su coste económico o su impacto ambiental potencial), y por tanto identificados como *IF*. *MEFA* simplemente cuantifica y localiza flujos, aportando información valiosa para los profesionales involucrados en la toma de decisiones, que son quienes evalúan qué flujos deben clasificarse como *IF*. En cualquier caso, *MEFA* es una herramienta potente para estrategias orientadas a la optimización de procesos. Una vez que los principales flujos insostenibles han sido identificados, pueden definirse como *IF* para proponer medidas correctoras específicas para evitar, reducir o aprovechar estos flujos.

- **Simulación de procesos.** Esta herramienta se aplica mediante simuladores de procesos, que se definen como software específicamente programado para modelar plantas de proceso (Casavant and Côté, 2004). Permite simular y cuantificar flujos de materia y energía en un sistema industrial, y predice el comportamiento de los procesos después de haber modificado una o más variables. Es ampliamente utilizado con múltiples propósitos, como evaluar modificaciones en procesos, predecir emisiones o analizar el potencial de integración de un proceso, entre otros.

Se ha propuesto una metodología que aplica criterios de la *WMH* y de la filosofía *IPPC* con la simulación de procesos para seleccionar alternativas adecuadas para la gestión de residuos en un sistema de industrial. Incluye tres módulos bien diferenciados: descripción del sistema, análisis cualitativo y análisis cuantitativo. El análisis cualitativo se aplica para definir la corriente de residuos considerada y así elaborar un inventario de técnicas que incluya las opciones de gestión disponibles clasificadas según la *WMH*. La técnica más apropiada, o conjunto de técnicas, se seleccionan respetando la filosofía de *IPPC* y la clasificación jerárquica establecida en la *WMH*. El análisis cuantitativo incluye la selección del software de simulación adecuado, la toma de datos, el modelado y construcción del escenario, y la simulación para definir de forma cuantitativa las corrientes de materia y energía del sistema, pero también los requerimientos cuantitativos de los equipos involucrados. Este análisis cuantitativo permite identificar los *IF* del sistema.

Esta metodología se valida en un caso de estudio que considera el sector de gestión de residuos, concentrándose en una corriente residual concreta: los aceites lubricantes usados. La aplicación de esta metodología resulta en la selección de un tratamiento de reciclado que se evalúa de forma cuantitativa mediante simulación de procesos para identificar cuatro *IF*.

La aplicación de la simulación de procesos en una metodología compleja la valida como una herramienta adecuada para la identificación de *IF*. Sin embargo la simulación de procesos es una herramienta más valiosa para evaluar la idoneidad de las opciones destinadas a mejorar un proceso. Permite modificar todas las variables involucradas, las etapas del proceso y los equipos, e incluso secciones completas del proceso para analizar los impactos. Requiere disponer de información abundante y rigurosa sobre el sistema simulado para garantizar que los modelos representan fielmente la realidad. Las inversiones económicas para la optimización de procesos estarían más justificadas y mejor respaldadas si surgieran de la aplicación de metodologías como la propuesta, donde las alternativas de mejora han sido validadas mediante simulación de procesos.

METODOLOGÍAS COMBINADAS

Después de analizar de forma individual las ventajas y limitaciones de *BAT Analysis* y de las herramientas de identificación de IF, estos instrumentos se combinan en metodologías integradas para obtener sistemas industriales sostenibles. Se han propuesto tres metodologías.

- **Combinación de *BAT Analysis* y *MEFA***. Esta metodología, aplicada a un sistema industrial, pretende identificar los *IF* mediante *MEFA*, de forma que las técnicas candidatas más apropiadas puedan seleccionarse mediante *BAT Analysis*. Las entradas, salidas y flujos intermedios de materiales y energía se localizan y cuantifican, y se proponen soluciones sostenibles en base al metabolismo industrial. Esta metodología combinada aporta un exhaustivo análisis cualitativo y cuantitativo del sistema, definiendo sus límites, identificando las etapas involucradas, y determinando y localizando los consumos y emisiones asociados. Como resultado se obtiene una estrategia completa enfocada en la mejora de los flujos insostenibles del sistema.

Esta metodología se valida en una planta de fabricación de tejas. La aplicación de la metodología en esta planta ejemplar permite identificar 14 *IF*, la mayoría de ellos correspondientes a la etapa ‘tratamientos térmicos’. 4 *BAT* ya estaban implementadas en la planta, y otras 7 técnicas candidatas de proponen para reducir los *IF* identificados.

La metodología propuesta aporta una forma de detectar los flujos mejorables de materiales o energía de un proceso, tanto si son entradas, salidas o flujos intermedios, y selecciona las opciones más sostenibles para mejorarlos. Se proponen soluciones para los *IF* detectados, considerando de forma aproximada su efectividad para mejorar estos flujos, pero sin aportar datos específicos o cuantitativos. Estos resultados son de gran utilidad para mejorar el proceso de acuerdo al consumo de recursos, el comportamiento ambiental y, en menor medida, aspectos económicos relativos a la operación habitual del proceso analizado.

- **Combinación de *BAT Analysis* y simulación de procesos.** Ambas herramientas se aplican de forma conjunta para identificar los *IF* del proceso analizado y seleccionar las técnicas candidatas más adecuadas. Las alternativas seleccionadas se evalúan en diferentes escenarios mediante simulación de procesos para determinar la configuración que mejor optimiza la sostenibilidad del proceso industrial.

  La metodología incluye dos módulos. El primero implica un profundo análisis del proceso, seguido de una evaluación rigurosa de los principales aspectos ambientales. Después se aplica *BAT Analysis* para desarrollar un inventario de técnicas candidatas. El software de simulación de procesos se aplica al caso base para analizar el proceso, cuantificando todos los flujos de materiales y energía. Los resultados de la simulación se emplean para identificar los *IF* y así seleccionar las técnicas candidatas del inventario. En el segundo módulo se proponen escenarios alternativos que implementan una o un conjunto de técnicas candidatas. Cada escenario se analiza de forma cualitativa para definir claramente las condiciones de implementación de las técnicas candidatas. A continuación se aplica a cada escenario el software de simulación de procesos, y los resultados se comparan para evaluar cuál es el más adecuado para mejorar los *IF* detectados en el caso base.

  Esta metodología se valida en un caso de estudio: una planta de producción de H_2 que aplica el proceso de reformado de gas natural con vapor. El primer módulo de la metodología identifica tres *IF* en el proceso, que se resumen como ‘emisiones de CO_2 desde’ y ‘consumo energético en’, asociados a algunas etapas del proceso. Como resultado se proponen tres escenarios alternativos y se evalúan, revelando dos técnicas candidatas como las más adecuadas para mejorar el proceso. La combinación de estas herramientas en una metodología integrada pretende ayudar a los profesionales en la toma de decisiones para seleccionar la mejor configuración para conseguir un sistema industrial sostenible.

Las metodologías anteriores (combinando *BAT Analysis* con *MEFA* y simulación de procesos) se validan en casos de estudio que representan diferentes sistemas industriales. Sin embargo ambas metodologías se han desarrollado considerando plantas individuales, no sistemas que involucren más de una planta. Además estas metodologías están concebidas para plantas bastante grandes cuyos procesos pueden dividirse en etapas, y sus consumos y emisiones pueden ser fácilmente ubicados dentro del sistema, siendo capaces de aportar abundantes y precisos datos. Los sistemas industriales más complejos, así como las plantas más pequeñas, también requieren metodologías para mejorar su sostenibilidad, teniendo en cuenta sus particularidades.

- **Combinación de *WMH* y *BAT Analysis*.** Esta metodología pretende mejorar la sostenibilidad de la gestión de residuos en un sistema industrial representado por un sector atomizado, integrado por pequeñas y medianas empresas muy dispersas en el área geográfica considerada. La metodología incluye a dos de los actores involucrados en las estrategias de gestión de residuos: los productores de residuos y el gestor intermedio. Los *IF* entre ambos actores se identifican y se proponen técnicas de inventarios para obtener un sistema simbiótico sostenible. La metodología considera la *WMH* y la filosofía *IPPC*. Ambos elementos se combinan y la filosofía *IPPC* se adapta a las pequeñas y medianas empresas.

  La metodología se aplica y valida en un sistema donde los productores son las plantas de artes gráficas pertenecientes a una asociación regional, y representadas por una planta de referencia. El gestor de residuos intermedio es una planta local de transferencia de residuos. Esta metodología aporta extensa información acerca del sistema considerado en relación al área geográfica, los procesos implicados, los consumos y emisiones asociados, y los flujos de residuos entre los productores y el gestor. Los *IF* se identifican de acuerdo con su cantidad y peligrosidad. Las alternativas para mejorar su gestión se proponen en base a la *WMH* y *BAT Analysis*, de forma que los productores de residuos centren sus iniciativas en la prevención y la preparación para la re-utilización, mientras que el gestor intermedio aplique opciones de preparación para la re-utilización, reciclado y valorización. Las técnicas y tratamientos se seleccionan con el objetivo de establecer, o mejorar, una relación simbiótica entre los productores de residuos y el gestor intermedio.

  El sistema original, integrado por una planta de artes gráficas y una estación de transferencia, se analiza para detectar sus *IF*. Una serie de alternativas se proponen para mejorar el sistema, y algunas de ellas se seleccionan para ser implementadas. Tras la implementación, el sistema mejorado se compara con el original, mostrando que además de reducir la cantidad de residuos gestionada en el sistema, se ha establecido una relación simbiótica entres ambos actores. En esta metodología, principios establecidos considerando grandes instalaciones se han adaptado a sectores que, a pesar de estar principalmente integrados por pequeñas y medianas empresas, generan una no despreciable cantidad de variados residuos peligrosos.

Cada metodología tiene sus propios puntos fuertes y débiles, y sus idoneidad depende de la situación específica en el que método se aplica. En todos los casos el análisis cualitativo se emplea inicialmente para definir el sistema industrial. Este paso permite identificar las etapas y clasificarlas, lo que facilita el estudio y la comprensión del proceso. También define los flujos de materiales y energía involucrados *a priori* en el proceso, permitiendo la identificación de todos los materiales esperados en cada etapa, así como los potenciales consumidores de energía. Toda esta información puede emplearse en la parte cuantitativa de la metodología, tanto si está basada en *MEFA*, en simulación de procesos, o en simples balances de materia. Los modelos se construyen en base a los resultados de la parte cualitativa de la metodología, de forma que la estructura definida para el proceso se respeta durante todo el análisis.

El análisis cuantitativo se desarrolla empleando, en cada caso, diferentes herramientas de identificación de *IF*, *MEFA* y simulación de procesos, con diferentes resultados. El método aplicando *MEFA* pretendía identificar los *IF* del proceso para seleccionar técnicas candidatas de un inventario que previnieran o redujeran estos flujos. Por otro lado, el método aplicando simulación de procesos debía encontrar la configuración más sostenible para un proceso comparando la situación original con las potenciales situaciones futuras tras haber aplicado técnicas seleccionadas en base a los *IF*. La última metodología aplicaba balances de materia para analizar *grosso modo* las mejoras esperadas después de aplicar técnicas previamente seleccionadas.

Los flujos mejorables se han presentado como un indicador adecuado que representa las insostenibilidades de los sistemas industriales. Son cuantificables y localizables, y pueden detectarse fácilmente mediante herramientas de identificación basadas en análisis de procesos. Estos flujos pueden prevenirse, reducirse o mejorarse mediante la aplicación de una adecuada selección de técnicas candidatas principalmente definidas considerando los principios de la filosofía *IPPC* y la *WMH*. Su utilidad se ha validado en tres metodologías diferentes, cada una combinando una herramienta de identificación de *IF* y un inventario de técnicas, que han sido validadas verificando que permiten obtener sistemas industriales sostenibles.

OBJECTIVE

The objective of this thesis is to develop and apply methodologies to get sustainable industrial systems, defining, combining and integrating two different types of tools.

The first tool is intended to provide methodologies to recompile techniques that, properly selected and implemented, could improve the sustainability of an industrial process. In developing this methodology two European policies will be considered as a basis for technique selection and method structuring: the Integrated Pollution Prevention and Control philosophy and the Waste Management Hierarchy.

The second tool represents flow identification tools based on process analysis. These tools, properly applied by means of defined methodologies, should effectively identify, quantify and allocate material and energy flows within a given system. Flow identification tools should be able to detect some specific flows whose qualitative and quantitative properties would make them likely to be enhanced by implementing the techniques recompiled by the first tool.

Initially for both tools simple methodologies will be individually defined, analysed and validated to identify their benefits and limitations. Then integrated and optimised methodologies combining the individual methodologies will be proposed. They will be developed and validated considering different criteria regarding specific industrial systems. The different methodologies will be studied to analyse their potential to improve the sustainability of the industrial systems, identifying the best combination for any given situation.

CHAPTER 1

INTRODUCTION

For many years process design has focused on technical and economic factors, being the objective low investments and operational costs, high benefits and mechanized processes for reducing costs on manpower. However, in the actual global context of limited availability of resources and increasingly restricting safety and environmental regulations, industry is in a great need of developing methodologies or strategies that facilitate facing these challenges. In the last decades uncountable methods have been developed with different purposes, being producing commercially more attractive and competitive chemical processes the main interest of the industry (Pasanen et al., 1999). These methods, often driven by safety and environmental regulations (Palaniappan et al., 2002), have contributed to the improvement of the production systems (Santos da Silva and Gonçalves Amaral, 2009), which are increasingly optimised to satisfy whether economic, environmental or social objectives (Alexander et al., 2000; Palaniappan et al., 2002).

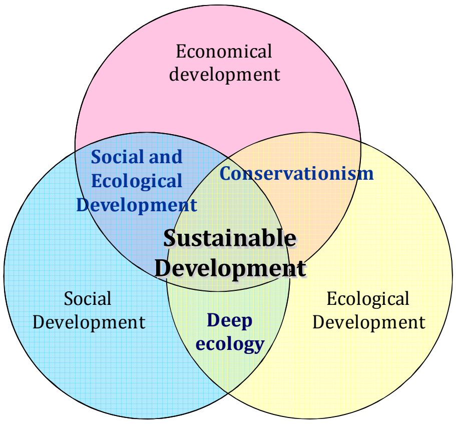


Figure 1.1: The three dimensions of sustainability (Torres Rodríguez et al., 2011)

The World Commission on Environment and Development, known as the Brundtland Commission, was assembled by United Nations in 1983 in order to, among others, consider ways and means by which the international community could deal effectively with environmental concerns and help define a long term agenda for action during the coming decades (WCED, 1987). The result was the publication in 1987 of the Report of the Brundtland Commission, “Our Common Future”. It defined, for first time in history, “sustainable development”, meaning a simultaneous economical, social and environmental growth to avoid deep ecology, conservationism or an excessive economical and social growth behind environmental consequences (Figure 1.1). So, since then and progressively, modern plants need a different focus based on technical development aiming to integrate the three dimensions of sustainability.

Some philosophies emerged from the concept of sustainable development, being Life Cycle Thinking (LCT) one of the most impactful ones. It can be understood in different ways. For the European Commission, LCT seeks to identify possible improvements to goods and services as lower environmental impacts and reduced use of resources across all life cycle stages (European Commission, 2010). On the other hand, for the United Nations LCT is about going beyond the traditional focus on production sites and manufacturing processes so that the environmental, social and economic impact of a product over its entire life cycle, including the consumption and end of use phase, is taken into account (UNEP, 2010). In spite of the focus considered, LCT is directly related to resources management under a life cycle point of view, involving not only environmental factors but the whole concept of sustainability.

LCT has been included in the EU (European Union) policies of the last decade, using as starting point the “Integrated Product Policy Communication” (Commission of the European Communities, 2003b), as well as the “Thematic Strategies on the Sustainable Use of Natural Resources” (Commission of the European Communities, 2005b) and the “Prevention and Recycling of Waste” (Commission of the European Communities, 2005a). All these strategies and methodologies are integrated in the “Sustainable Consumption and Production Action Plan” (Commission of the European Communities, 2008), which aims to reduce the overall environmental impact and consumption of resources across all life cycle stages of products.

According to Joint Research Centre (European Commission, 2010), LCT drives towards sustainable consumption and production. Its system-oriented approach (Allan et al., 2008) and life cycle perspective helps process designers to consider the resources consumed and the environmental impacts associated with the supply, use, and end-of-life of products (European Commission, 1995-2010). Besides this new approach for process designing, LCT provides a series of tools that ease the complex task of integrating sustainability concepts in process design. That is the case of Environmental Management System (EMS), Design for Environment (DfE), Life Cycle Assessment (LCA) and Material and Energy Flow Analysis (MEFA) (Torres et al., 2008) among others. These are well known and globally applied tools, really useful when the project focuses on the environmental dimension of sustainability. Other methods, such as Life Cycle Costing (LCC) or Cost-Benefit Analysis (CBA) focus on the economics, whereas others, like Social Life Cycle Assessment (SLCA) or Environmental Impact Assessment (EIA), combine environmental factors with social ones. This wide range of possibilities proves that the available tools are focused on specific dimensions of the sustainability (Jeswani et al., 2010), but none integrates the three of them. Therefore, there is a need to develop methodologies under the LCT philosophy aiming the optimal integration of the social, economic and environmental aspects of the system through the application of tools that include novel technical concepts.

1. LCT and Industrial Ecology

Though Industrial Ecology (IE) derives from the earlier concepts of sustainable development (Korhonen, 2004) and industrial metabolism (introduced in the 1970s by Robert Ayres (Ayres and Kneese, 1969)), it is assumed that it was introduced in 1989 by Frosch and Gallopoulos in a special issue of the journal Scientific American. In this paper they stated that “the traditional model of industrial activity in which individual manufacturing processes taking in raw materials and generating products to be sold plus waste to be disposed of should be transformed into a more integrated model: an industrial ecosystem” (Frosch and Gallopoulos, 1989). This metaphor of industry behaving as a natural ecosystem gives rise to the concept of IE. IE suggests that industrial systems should rely on the sustainable use of renewable natural resources, instead of upon the unsustainable use of non-renewable fossil fuels, employing energy cascades and using material cycles including waste utilisation (Korhonen et al., 2004), creating a holistic system of inter-connected material and energy flows. As major materials and energy consumers, process industries are responsible of facilitating material and energy cycling in industrial ecosystems (Casavant and Côté, 2004).

IE studies physical, chemical and biological interactions and interrelationships within and between industrial and ecological systems (Basu and van Zyl, 2006), so that processes and industries can be seen as interacting systems (or ecosystems) rather than comprising isolated components in a system of linear flows (Gibbs and Deutz, 2007; Tibbs, 1992). Research in the field of IE has been mainly focussed on the flow aspects, though the interdependence aspects related with industrial symbiosis are getting growing attention (Ehrenfeld, 2004). The truth is that to achieve a more sustainable industry, a more holistic view on production, processes and products (Jørgensen, 2008) is needed in all the systems involved in the life cycle.

Industry is directly affected by sustainable development initiatives. It causes and determines flows of materials and energy through the human economy (Azapagic and Perdan, 2000) and is widely recognized as a source of environmental and social impacts (Wallner, 1999). The standardized indicators developed by Azapagic and Perdan (2000) can determine the sustainability of an industrial system, though keeping in mind that not a single indicator, but a substantial number of them, is necessary to fully consider all the aspects of sustainable development (Al-Sharrah et al., 2010). It is an accurate procedure demanding a great amount of data about the analysed system.

Initiatives and technologies that mitigate the inherent negative effects of the industrial activity have been lately developed and applied. However, in many cases, end-of-pipe pollution control and management is the major practice, mostly triggered by environmental regulations that limit, but not eliminate, pollution (Harris and Khare, 2002), which is not a sustainable solution in the long term (Hossain et al., 2008). Therefore, nowadays research is increasingly focusing on techniques where pollution is prevented before being generated (Hossain et al., 2008; Lindsey, 2011), being sustainability oriented design procedures an important asset on prevention.

Some authors are already working on new methodologies based on the LCT philosophy combining known tools in such a way that one supplies the lacks of the other. That is the case of the ‘process design for sustainability’, a pioneer methodology proposed by Azapagic et al. (2006) that enables the identification of relevant sustainability criteria systematically integrating sustainability into process design, or the most recent ‘life cycle assessment for sustainability’ proposed by Heijungs et al. (2010), which combines LCA and sustainability analysis to get a wide perspective of the analysed item. Most of these methodologies follow a pattern that includes abnormal situations detection, causes diagnosis, and elimination of these causes by process improvement (Lee et al., 2004). All these elements of typical process improvement methodologies can be performed by applying different individual tools or combinations of some, ranging from the conventional LCA (Azapagic and Clift, 1999; Azapagic et al., 2006; Löfgren et al., 2011), DfE methods and tools (Sarigiannis, 1996; Vargas Hernandez et al., 2012) or process simulation (Cabezas et al., 2005, Halim and Srinivasan, 2008). Literature provides numerous examples of such methodologies, exhaustively analysing their benefits and limitations. The challenge now is developing industry-focussed integrated methodologies that effectively combine these benefits so that both existing and new plants are optimised, improving the sustainability of industrial systems.

Methodologies to improve industrial systems should consider the legal requirements in force. In Europe potentially polluting industrial systems are affected by legislation intended to get sustainable systems with minimised impact over the environment. Two remarkable pieces of legislation regarding the environmental performance of industrial systems have derived in philophies to be considered in this type of methodologies: the Integrated Pollution Prevention and Control philosophy and the Waste Management Hierarchy. Both derive from European policies, so they are supported by legal documents which lay down binding rules that should be applied by an important percentage of the industry.

1.1. Integrated Pollution Prevention and Control Philosophy

On the 24th September 1996, the Council of the EU issued the Directive 96/61/EC (EU, 1996), laying down the Integrated Pollution Prevention and Control (IPPC) philosophy. The integrated approach set by this directive implies firstly that all the stages of the productive process are considered, and secondly that a relationship between the quantity of pollutants and the features of the receiving medium is established, considering the transference of pollutants from one medium to the other (air, water and land). Directive 96/61/EC was one of the most ambitious initiatives of the EU to apply the pollution prevention principle in industrial systems.

Directive 96/61/EC was updated in 2008 by Directive 2008/1/EC (EU, 2008a), promptly repealed to be refunded and updated by Directive 2010/75/EU (EU, 2010), which combines several legal texts. Directive 2010/75/EU, from now on the IPPC Directive, aims to prevent or, where not practicable, to reduce emissions into air, water and land and to prevent the generation of waste, in order to achieve a high level of protection of the environment taken as a whole (EU, 2010), the same as its predecessors. It affects to a series of industrial sectors, more than the original Directive, meeting some specific conditions (normally referred to the production capacity of the process), listed in its Annex I.

The IPPC Directive proposes pollution minimisation at source by implementing Best Available Techniques (BAT) in the productive processes considered. Though firstly defined by the EU under the scope of Directive 96/61/EC (EU, 1996), BAT are still defined by the IPPC Directive as "the most effective and advanced stage in the development of activities and their methods of operation which indicates the practical suitability of particular techniques for providing the basis for Emission Limit Values designed to prevent and, where that is not practicable, to reduce emissions and the impact on the environment as a whole" (EU, 2010). Accordingly, BAT are intended to provide integrated pollution prevention and control if properly implemented in the industrial system considered.

The installations affected by the Directive are required an environmental permit which shall include, among others, the sources of emissions, the nature and quantities of foreseeable emissions, and the measures and/or techniques implemented or provided to prevent and/or reduce pollution. This permit joins a dispersed and varied group of licences into a unique document, turning the integrated licensing into the primary mechanism of environmental regulation and enforcement for the affected installations (Styles et al., 2009). Permits must be periodically revised, and substantial changes must be updated (Silvo et al., 2002).

There were precisely the environmental permits the ones that give rise to the first collections of techniques candidate to be BAT for industrial systems and/or sectors. The administrative procedure of obtaining (for the installation) and granting (for the competent authority) an environmental permit requires knowledge about the sectorial existing techniques. Techniques already implemented by the installation have to be compared with others that may be feasible for implementing, considering technical, environmental and economical criteria. Furthermore, both new and existing installations are required environmental permits, which in some cases involves implementing techniques or technologies that facilitate meeting the requirements of the directive. Accordingly competent authorities and industry require information about the available techniques, so that they can make responsible decisions regarding BAT implementation.

As a result, research centres and institutions, as the EIPPCB (European IPPC Bureau), the Ireland EPA (Environmental Protection Agency), the UK Environmental Agency, the US EPA or the OSPAR Commission (Convention for the Protection of the Marine Environment of the North-East Atlantic), to mention some, launched documents collecting and analysing techniques intended to be BAT for different industrial systems, normally classified by sectors. These initiatives derived in different research works where candidate techniques were collected for specific situations, as the fruit and vegetal processing industry (Derden et al., 2002), the adhesives production sector (Geldermann et al., 2004), the textile sector (Li Rosi et al., 2007), the surface treatment industry (Barros et al., 2008) or the seafood processing industry (Barros et al., 2009), among others. Though applying different strategies, all these works identify the most suitable techniques candidate to be BAT for specific situations, resulting in lists or sets of techniques.

The unstoppable evolution of technology and the constant emergence of techniques make it necessary to develop simple methodologies that efficiently determine whether a technique can be considered as BAT and under what conditions. IPPC philosophy should be carefully observed to guarantee that the selected candidate BAT respect the principles under which they were defined, regarding technical, environmental and economical criteria.

1.2. Waste Management Hierarchy Philosophy

The first European policy on waste emerged as a result of some scandals regarding waste manipulation on the 70s and 80s. Member States started to take measures at national level that finally led to the first Framework Directive on waste (EU, 1975) and to the Directive on hazardous waste (EU, 1978), both from the late 70s, and shortly after to the Council Regulation on the supervision and control of shipments of waste within, into and out of the European Community (EU, 1993). These three pieces of legislation set the basis for the European regulatory structure on waste, ensuring that waste was handled without causing damage to the environment or human health, and imposing controlled conditions for moving waste throughout the EU (European Commission, 2006a).

In an attempt to break the link between economical growth and waste generation, the EU improved the legal framework for waste, focussing on recycling and recovery. The objective of this new framework was to control the whole waste lifecycle, from generation to disposal (EU, 2009a). The Fifth European Community Environment Programme in 1990 and the Sixth Environment Action Programme (EU, 2002) in 2002 changed the waste management philosophy. These programmes promoted sustainable development, highlighted the need of ensuring that the consumption of renewable and non-renewable resources did not exceed the carrying capacity of the environment, and demanded to achieve a decoupling of resource use from economic growth through significantly improved resource efficiency and waste reduction. The next step was the initiative "Towards a thematic strategy on the prevention and recycling of waste" (Commission of the European Communities, 2003a). It established that the optimal waste management strategy to minimise environmental impacts should effectively combine waste prevention, material recycling, energy recovery, and disposal options.

These new philosophies were applied to waste management, thus the old directives were updated by Directive 2006/12/EC on waste (EU, 2006), which was intended to encourage first the prevention and reduction of waste production and second the recovery of waste and its use as a source of energy. However this policy was soon updated, and in 2008 the European Framework Directive on waste, Directive 2008/98/EC (EU, 2008b), was launched. It lays down measures to prevent or reduce the adverse impacts of the generation and management of waste, aiming to improve the efficiency of the use of resources.

Directive 2008/98/EC has also set down the new Waste Management Hierarchy (WMH) that shall apply as priority order in waste prevention and management activities, strategies and initiatives (EU, 2008b):

1. Prevention: measures taken before a substance, material or product has become waste. These measures reduce:
   - the quantity of waste, including through the re-use of products or the extension of the life span of products;
   - the adverse impacts of the generated waste on the environment and human health;
   - the content of harmful substances in materials and products.
2. Preparing for re-use: checking, cleaning or repairing recovery operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing.
3. Recycling: any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes.
4. Recovery: any operation whose principal result is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy.
5. Disposal: any operation which is not recovery, even where the operation has as a secondary consequence the reclamation of substances or energy.

Waste management is a complex task whose performance has to meet the requirements of sustainable development (Generowicz et al., 2011). Stakeholders should be provided with information about the alternatives available to apply the WMH, avoiding waste when possible and enhancing the sustainability of the processes performed. The application of the WMH requires methodologies to select, evaluate and classify the available options. These methodologies should provide techniques to turn waste into valuable by-products that could be used in the proper industrial system but also in other systems, integrating the concept of industrial symbiosis with waste management.

2. System evaluation tools

The philosophies concerning IPPC and WMH, intended to improve the sustainability and environmental performance of industrial processes, demand tools to analyse these processes.

Industrial systems perform processes that require the physical or chemical transformation of raw materials and energy into valuable products (Casavant and Côté, 2004) by means of input, output and internal flows of materials and energy. Process improvement demands adequate tools that quantitatively evaluate the environmental performance of the process to identify the enhancement opportunities (Hossain et al., 2008). Some of these tools are material flow analysis (Clift, 2006), process simulation (Nourai et al., 2000), WAR (waste reduction) algorithm (Cabezas et al., 1997), LCA (Azapagic and Clift, 1999) or total site analysis and net work synthesis technique (Hossain et al., 2008), all of them involving the quantitative assessment of material and energy flows. Given their relevance in the whole performance and management of an industrial system, material and energy flows can be considered as indicators of the unsustainability of a process. Two typical system evaluation tools are Material and Energy Flow Analysis and process simulation.

2.1. Material and Energy Flow Analysis

Material and Energy Flow Analysis (MEFA) comprises a whole family of tools to study the materials and energy flowing through a given system, the stocks and flows within this system and the resulting outputs from the considered system to others (Hendriks et al., 2000). Computer software with various degrees of complexity is available to facilitate this analysis. It is a tool of assessment of environmental issues and a decision-support method in resource, waste and environmental management.

MEFA is especially useful when applied in environmental management and engineering, resource and waste management, or anthropogenic metabolism (Brunner and Rechberger, 2004), but also in IE. MEFA is a useful tool for the practical implementation of the IE concept, as it allows tracing materials and energy on industrial systems, balancing industrial input and output to the capacity of the natural systems. Though not quite suitable for predicting the behaviour of a system beyond marginal perturbations (Suh, 2005), MEFA is perfectly appropriate to understand and quantitatively define an industrial system, as it can detect both material and energy flows with a good degree of traceability.

2.2. Process simulation

In the context of the chemical engineering, process simulation is used to interpret process flowsheet, to identify malfunctions, and to predict the performance of processes (Seider et al., 2004). Simulation tools are based on a set of equations that relate multiple variables, involving material and/or energy balances, profitability analysis and so on. Simulation is implemented by process simulators, which are software specifically programmed to model process plants (Casavant and Côté, 2004). They are widely used by engineers to evaluate modifications on a certain process, predict emissions, analyse integration potentials or assess economic possibilities, among others. In fact, engineers rely on process simulation to answer what-if questions posed by stakeholders (Sharma, 1996).

Process simulation is a useful tool to identify and trace flows of materials and energy, considering not only individual operations but also interconnected units, entire plants or even more complex industrial systems. It allows manipulating the operating conditions and the structure of an industrial system without risk, minimising production losses (Alves Santos et al., 2008; Bezzo et al., 2004). Therefore, it can be used to test the effect of modifications of different nature over the system, so that it can predict the consequences of implementing improvement measures.

CHAPTER 2

BAT ANALYSIS

Summary

This chapter presents a methodology to develop technical inventories candidate to be BAT in sustainable industrial systems, based on the integrated pollution prevention and control principles. The proposed methodology, BAT Analysis, aims to facilitate the implementation and evaluation of the techniques candidate to be BAT under the principles of the IPPC philosophy.

The proposed methodology is a step-by-step procedure that begins with the evaluation of the industrial system, followed by a thorough description of the specific or generic process considered. Then the main environmental impacts, namely emissions and consumptions, are identified. An inventory of techniques candidate to be BAT is elaborated for the considered system. In the selection of techniques all the information previously analysed is regarded as well as technological features, geographical location, environmental conditions or the age of the considered installation.

The resulting inventory is an exhaustive list including the preventive and abatement techniques candidate to be BAT and the so-called Best Environmental Practices (BEP). An informative technical data sheet is presented for each candidate technique to support decision-making. The technical data sheets include information about the environmental aspects related, technical descriptions, benefits and environmental data, secondary effects, implementation, applicability and characterization, economical aspects and example plants where the technique has already been implemented.

BAT Analysis is validated in an industrial system: the Galician (NW Spain) heavy ceramics manufacturing industry, a sub-sector of the ceramics manufacture industry producing building materials and refractory products. The methodology is applied step-by-step to this system, resulting in a thorough evaluation of the sector, a generic flow diagram that identifies all the stages of the process as well as the inputs and outputs involved, and an inventory of 46 candidate techniques supported by a variety of BEP.

Though useful for collecting candidate techniques, BAT Analysis fails to identify which set of techniques are necessary and where they should be implemented. Identification tools are required to get a potent method to get a sustainable industrial system on the basis of BAT.

1. Introduction

BAT are generically defined under the scope of the IPPC Directive as the most effective and advanced stage in the development of activities and their methods of operation (EU, 2010). But the EU further refines this definition by specifying the terms involved:

- *Techniques* include the technology used but also the way in which the installation is designed, built, maintained, operated and decommissioned.
- *Available techniques* implies that the techniques have already been developed on a scale that allows implementation under economically and technically viable conditions.
- *Best* involves the technique being the most effective in achieving a high level of protection of the environment as a whole.

According to this definition, BAT are firstly intended for pollution prevention. Only when pollution prevention is not practicable, techniques for emission reduction can be considered as BAT. Furthermore, the so-called ‘techniques’ are not just technology, but also good practices, procedures or configurations that provide integrated pollution prevention and control. This variety of elements has led the EU to set twelve criteria to determine whether a given technique is really the ‘best available’ (Figure 2.1). The potential costs and benefits of the candidate techniques are considered regarding the principles of precaution and prevention. Techniques selected with these criteria ensure the minimum environmental impact without compromising the economic performance of the installation (Georgopoulou et al., 2008), and so they set the basis to fix the Emission Limit Values (ELV) for the industry.

1. Using low-waste technology.
2. Using less hazardous substances.
3. Furthering the recovery and recycling of substances generated and used in the process, and of waste where appropriate.
4. Comparable processes, facilities or methods of operation which have been tried with success on an industrial scale.
5. Technological advances and changes in scientific knowledge and understanding.
6. The nature, effects and volume of the emissions concerned.
7. The commissioning dates for new or existing installations.
8. The length of time needed to introduce the best available technique.
9. The consumption and nature of raw materials (including water) used in the process and energy efficiency.
10. The need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risks to it.
11. The need to prevent accidents and to minimise the consequences for the environment.
12. The exchange of information, published every three years, between Member States and the industry concerning best available techniques, associated monitoring, and developments.

Figure 2.1: EU criteria for the qualification of a technique as ‘best available’ (EU, 2010)

ELV are defined by the EU as "the mass, expressed in terms of certain specific parameters, concentration and/or level of an emission, which may not be exceeded during one or more periods of time" (EU, 2010). The IPPC Directive states that the ELV should be based on BAT without prescribing the use of any specific technology, but taking into account the technical characteristics of the concerned installation, its geographical location and the local environment conditions. Likewise, ELV must be specifically established for the considered process (Cunningham, 2000; Geldermann and Rentz, 2004). Both, BAT and ELV must be checked and periodically updated so that the latest technical developments can be taken into account. BAT have associated BAT-AEL (BAT-Associated Emission Limits), which are the emission values considered achievable by implementing BAT. These emission values set the basis for the authorities to fix the ELV for an installation applying for an environmental permit, as required by the IPPC Directive.

BAT have a strong dynamic character, as they are highly affected by scientific and technical progress (Schoenberger, 2009). The European Commission organises exchange-of-information meetings between experts from the EU and agents from the industry and environmental organizations to identify BAT. This work is coordinated, synthesized and edited by the EIPPCB (European Commission, 2005), who has divided the whole task on areas related with productive sectors and horizontal activities. Each area is examined by a Technical Working Group (TWG) and it takes about two years to complete the work and to produce a draft of the so-called BREF (BAT Reference document). The draft is then examined and discussed in the Information Exchange Forum (IEF) (integrated by representatives from all Member States, Accession Countries, industry and the European Commission), which draws up the final BREF. The EIPPCB has published in the last decade around 35 documents recompiling and analysing BAT for all sectors concerned, as well as for horizontal activities, most of which are currently being updated. European governments (DEFRA, 2011; EPA, 2011; *MARM*, 2011) and environmental groups (Envirowise, 2011; *IHOBE*, 2011) have also developed documents concerning BAT, which support the information provided by the BREF, facilitating their diffusion between the stakeholders.

1.1. BAT methodologies

According to their definition (EU, 2010), BAT should be "best" for the environment as a whole and economically "available" for the industrial sector concerned (Dijkmans, 2000). Literature provides abundant examples of the benefits of implementing BAT on the industry: the textile processing industry, benefited of important water and energy savings (Kocabas et al., 2009); the Irish pharmaceutical industry, which registered high rates of reduction of emissions, mainly of heavy metals and air pollutants (Styles et al., 2009); or the partial improvements on the energy efficiency and resources consumption in the Greek paper manufacturing industry (Karavanas et al., 2009); to mention some. These are all examples of successful implementation of BAT, though in the last case the selected techniques did not reduce all the environmental impacts of the analysed system. They were not properly selected or not properly implemented. Candidate techniques do not always work as BAT (Shoenberger, 2011), as their suitability depends on the specific conditions of the analysed process. BAT are normally referred to specific industrial sectors and do not consider the particularities of every individual case or single installation (Schoenberger, 2009). This leads to the question of which technique or set of techniques are the most appropriate for any specific case.

BAT selection involves identifying the most suitable system (Samarakoon and Gudmestad, 2011) to mitigate the potential environmental impacts. There is, in general, not a single best available technique but a best combination of available techniques to be used (Bréchet and Tulkens, 2009). Normally BAT are selected on the basis of technical feasibility, environmental benefits and economic profitability (Generowicz et al., 2011; Samarakoon and Gudmestad, 2011; Schollenberger et al., 2008), although other authors suggest a life cycle oriented approach that considers off-site associated impacts (Nicholas et al., 2000). Literature provides several methodologies for BAT evaluation and selection (Table 2.1). The different approaches seek to identify the best combination of candidate techniques to improve processes regarding different criteria, which is normally based on the emission and consumption levels achieved by the techniques applied and on the economical viability (Silvo et al., 2009). Although these approaches have been successfully validated in different systems, the *VITO* methodology (a four-step procedure to evaluate technical, environmental and economic factors) by Dijkmans (2000) and the Reference Installation Approach (based on the ISO 14040, it considers the same abatement options for all the installations of a category) by Geldermann and Rentz, (2004), are the most widely used methodologies (Bréchet and Tulkens, 2009; Samarakoon and Gudmestad, 2011). Both methods are quite similar and provide structured methods that can be easily applied, being the final verdict strongly influenced by expert judgements (Schoenberger, 2009). In any case, the proper and effective evaluation of alternatives involves the analysis of a large amount of data on the basis of quantitative and qualitative criteria (Giner-Santonja et al., 2012), as qualifying a technique as “best available” involves technical, environmental and economic aspects.

Though not so widely known, other approaches for BAT determination and evaluation have been developed in the last years (Bréchet and Tulkens, 2009; Georgopoulou et al., 2008; Mavrotas et al., 2007; Nicholas et al., 2000; Samarakoon and Gudmestad, 2011). As the methodologies described before, the criteria these other methods use for BAT selection includes environmental benefits, technical availability and economic feasibility. These aspects are useful to evaluate the viability of a technique in the industrial sector as a whole, but not the specific conditions of individual plants (Schoenberger, 2011), so techniques must be characterised and evaluated on process level (Geldermann et al., 2004).

In spite of these approaches, the EIPPCB has set its own procedure for BAT selection. It considers, for each technique, environmental aspects, technical description of the technique, benefits derived from its implementation, secondary effects, implementation considerations, applicability and economical aspects, which are illustrated by example plants where the technique has already been implemented (European Commission, 2005). Although strongly affected by the opinions of experts, this method takes into account a wide range of elements, apart from the typical technical, environmental and economic ones, which condition the suitability of a given technique for being a BAT.

1.2. BAT limitations

In spite of the availability of methods to select candidate techniques and the successful trajectory of BAT over industry, some companies still fail to incorporate new technologies or have not fulfilled the expectations of their implementation (Shehabuddeen et al., 2006). On the other hand, it is quite striking that, although the IPPC philosophy claims to favour prevention techniques over reduction ones, companies often choose pollution control techniques over preventive measures (Honkasalo et al., 2005).

BAT implementation is generally associated to economic investment, as normally new equipment or machinery is required (Giner-Santonja et al., 2012). Economic requirements for prevention techniques are normally lower than for control ones. However, preventive measures normally demand deeper analysis of the process to be improved, being the expertise of the decision-makers more relevant than in the case of control techniques. The selection of candidate techniques cannot be simply based on the reduction of emissions, as this criterion tends to result on end-of-pipe solutions, which is not the priority objective of the IPPC philosophy. The potential unsustainable sources of the process should be identified, so that the proper techniques can be proposed and implemented to avoid the problems derived. Furthermore, according to the life cycle perspective, environmental impacts cannot be simply reduced to emissions and waste generation. The inefficient use of resources, both material and energetic, should also be regarded as another factor to take into account when selecting candidate techniques.

Other limitation of BAT selection is that, normally, the geographical location and the local environmental conditions of the analysed installation are not considered (Giner-Santonja et al., 2012), which is an important decision criteria, especially in environmentally sensitive areas (Samarakoon and Gudmestad, 2011). Although the IPPC Directive does not prescribe the use of any specific technique, it does recommend the consideration of the technical characteristics of the installation concerned, its geographical location and the local environmental conditions (EU, 2010). Accordingly, when selecting candidate techniques these elements should be regarded as determinant factors when deciding whether a given technique could be or not a BAT for the situation concerned.

These limitations when selecting BAT compromise the efficiency of the techniques implemented. Besides knowledge about the candidate techniques, knowledge about the process concerned is also needed. The disturbing elements of the process should be clearly identified, as well as the potential impacts they may cause over the specific environment, in order to provide a coherent set of candidate techniques for each specific situation.

The objective of this chapter is to develop and validate a methodology, BAT Analysis, to perform inventories of techniques candidate to BAT in sustainable industrial systems. The criteria suggested for the selection of techniques is the IPPC philosophy. The selected candidate techniques are examined, evaluated and collected in the inventory, each of them supported by a technical data sheet. The proposed methodology is based on the standard procedure applied by the EIPPCB (European Commission, 2005), including deep evaluations of the system and its potential impacts. The methodology is validated an industrial system, the heavy ceramics industry of Galicia (NW Spain).

Table 2.1: Tools for BAT selection and evaluation

Author	**Basis**	**Selection criteria**	**Limitations**	**Validation**
Schramm (1998)	Comparative assessment	Cleaner production targets about reducing resources consumption, emissions and waste, hazards and risks	Targets essentially correspond to prevention criteria. Ambiguous results that fail to clearly identify the best candidate techniques.	Textile dyeing process
Nicholas et al. (2000)	Life Cycle Assessment	Reduced environmental impacts	Evaluation of techniques randomly selected. Not economic issues considered.	Glass manufacturing
Mavrotas et al. (2007)	Multi-objective optimisation by goal programming and Pareto optimal solutions.	Economic and environmental criteria	Environmental criteria limited to the reductions of emissions of specific pollutants.	Athens industrial area
Bréchet and Tulkens (2009)	Linear programming modelling	Technical and economic viability	Highly focussed on economic parameters, almost neglecting environmental issues.	Limestone industry
Samarakoon and Gudmestad (2011)	Best ‘qualified’ technique	Risk –based assessment of the candidate techniques	Difficulty of identifying the potential failures of the analysed techniques.	Offshore oil and gas installations
Liu and Wen (2012)	Data Envelopment Analysis	Emissions reduction and energy conservation potential	Results are highly influenced by the alternatives compared, and data accuracy.	Thermal power techniques

2. Case study

Epigraph 3.5 of Annex I of the IPPC Directive quotes the mineral industries that accomplish the manufacture of ceramic products by firing as follows: “manufacture of ceramic products by firing, in particular roofing tiles, bricks, refractory bricks, tiles, stoneware or porcelain with a production capacity exceeding 75 tonnes per day and/or with a kiln capacity exceeding 4 m^3 and with a setting density per kiln exceeding 300 kg/m^3” (EU, 2010).

The TWG for the ceramic industry sector was organised for the purposes of information exchange under Article 16.2 of the Directive 96/61/EC. On the 1st and 2nd December 2003, the EIPPCB, part of the Institute for Prospective Technological Studies (IPTS) of the Joint Research Centre, organised the kick off meeting in Seville. The TWG agreed that due to the wide variety of ceramic products, the various ceramic sub-sectors should be summarised regarding the application of the different types of products in two groups: heavy and fine ceramics (European Commission, 2004a). The lack of information at European level had lead to different countries to analyse their own state of the art in several reports (*Cérame-Unie*, 2004; Dutch Government, 2003; Huybrechts et al., 1999; Rentz et al., 2001; Spanish Government, 1999) in order to support and contribute to the process of establishing the identification of BAT for the ceramic sector in the EU. A final BREF for the ceramic manufacturing industry was set in 2005, though it was shortly updated by a new version (European Commission, 2007a) in 2007, being the document available nowadays.

They industrial system considered to validate the proposed methodology is the Galician (NW Spain) heavy ceramics manufacturing industry. Although it is a well-established and complex sector in the considered region, not much information on pollution prevention is available, so it is in need of a deep examination to determine the techniques candidate to be BAT and accurately apply the IPPC philosophy.

3. Methodology

Technical inventories are proposed as a suitable basis to develop methodologies to get sustainable industrial systems. They can be defined as a set of techniques, each supported by specific information regarding particular features, selected considering certain criteria for a given industrial system. They require exhaustive information background and deep knowledge to provide stakeholders with a potent tool to improve the sustainability of their processes. These inventories are intended to present all the alternatives suitable and available to optimise or improve industrial systems. The alternatives are classified regarding different criteria, normally closely related to the selection criteria, which facilitates decision-making.

The evaluation of methodologies for BAT selection reveals that the one developed by the EIPPCB (European Commission, 2005) is maybe the one that better fits the definition of BAT. It considers a wider variety of aspects and, in spite of being strongly affected by the opinions of experts; it takes into account the necessities of each single plant by determining the implementation conditions for each technique. For that reason this approach has been selected as a reference to develop the sustainability-oriented methodology ‘BAT Analysis’, proposed in this chapter.

BAT Analysis evaluates techniques candidate to be BAT following the method set by the EIPPCB (European Commission, 2005). It is a sustainability-oriented procedure involving a deep knowledge of the process considered to develop technical inventories. Each technique included in the inventory has its own technical data sheet including technical, environmental and economical information about the technique. Based on this information, techniques for the specific situations can be selected for implementation.

BAT Analysis involves the consecutive application of the steps defined below:

1. Analysis of the sector. The considered sector is deeply analysed, considering its technical requirements and regional particularities.
2. Description of the process. Identification, definition and description of the stages of the generic or specific process considered.
3. Environmental aspects. Evaluation of the consumptions (materials and energy) and emissions (atmospheric emissions, liquid effluents and waste) derived from the process, regarding the specific stage of the process where they take place.
4. Inventory of candidate techniques. Recompilation and inventory of techniques candidate to be BAT for the selected industrial system, based on the evaluation of environmental aspects. Technological features, the geographical location, the environmental conditions and the age of the installation are considered, as well as the elements recommended by the IPPC Directive (Figure 2.1). A technical data sheet is incorporated for each technique of the inventory, including the following information:
   - Environmental aspects. Main environmental impacts to be addressed by the technique.
   - Technical description. Description of the technique considered, including drawings or figures to help the understanding of the text.
   - Benefits/environmental data. Performance data on emissions/waste, consumption levels, and emission values for different pollutants as stated in legislation. Benefits derived from the use and/or implementation of the technique.
   - Secondary effects. Any indirect effects and disadvantages, as well as details on environmental problems by applying the technique.
   - Implementation. Driving forces to take into account for implementing the technique.
   - Applicability and characterization. Consideration of the factors involved in applying and retrofitting the technique, including useful information on how to operate, maintain and control the technique (i.e., space requirements, specific process and so on).
   - Economical aspects. Information on costs (investment and operation) and savings.
   - Plants where the technique is already implemented. Examples or reference plants.
5. Identification of already implemented techniques. The detected implemented techniques can be compared with the items of the technical data sheet, concluding whether it is BAT or not. The not implemented techniques are evaluated and selected as candidates to be BAT for the process regarding the needs of the analysed process.

4. Application of the methodology

The methodology is applied, step by step, to the case study for validation. The Galician heavy ceramics manufacture industry is thoroughly analysed to evaluate the suitability of BAT Analysis.

4.1. Analysis of the sector

Generally the term ceramics refers to inorganic materials, possibly with some organic content, made up of non-metallic compounds (normally clay) hardened by a firing process. Besides the traditional clay-based materials, ceramics today include a multitude of products containing small fractions of clay or none at all, that can be glazed or unglazed, porous or vitrified (European Commission, 2004a).

The ceramic industry is included in the European NACE (Classification of Economic Activities in the European Community), Division 26, corresponding to the manufacture of other non-metallic mineral products. This division includes some of the following related groups:

26.2. Manufacture of ceramic goods other than for construction, which comprises refractory ceramic products and non-refractory ceramic goods for purposes other than construction.
    26.21. Manufacture of ornamental ware and household ceramics.
26.3. Manufacture of ceramic tiles and flags.
26.4. Manufacture of clay construction products, which includes bricks, tiles and other construction products made of clay.

An alternative classification of the ceramic products is based on the key environmental aspects associated to the product, in addition to issues as the raw materials additives used, the production techniques applied and properties of the final product, resulting in the following groups (European Commission, 2004a):

- Heavy ceramics, which includes the sub-sectors bricks and roof tiles, vitrified clay pipes, refractory products and calcined clays.
- Fine ceramics, which includes the sub-sectors wall/floor tiles, tableware and other household ceramics, sanitary ware and technical ceramics.

The sector of non-metallic mineral products performs the intermediate role of taking minerals that have been mined or quarried and transforming them into products that can be used in several industries (building industry, civil engineering, metallurgical processes, cement manufacture, glass, incinerators, sanitary ware and tableware). The features of ceramic products include long service life, wear resistance, chemical inertness and low toxicity, fire and heat resistance and, in many cases, aesthetic appeal (*Cérame-Unie*, 2004).

This sector has a relatively high reliance on energy, as high temperatures are often required as part of the manufacturing process. Some manufacturers have responded to this challenge by developing and investing in cleaner and more efficient production processes, as well as encouraging the use of recycled materials (European Commission, 2003a).

Spain is one of the leading countries of the ceramic manufacture in the EU, being fifth and fourth in the ranking of the manufacture of ceramic building materials (bricks, roof tiles and so on) (Figure 2.2) and refractory products (Figure 2.3), respectively. Regarding Spain, the production of building materials in 2010 was 7.7 million tonnes (*CEPCO*, 2012), a value that has been quite reduced since 2007, when the production was up to 28.8 million tonnes (*CEPCO*, 2012). This reduction is caused by the economic crisis, which has highly affected the Spanish ceramics manufacture sector. However, in spite of the decrease on the production of building materials, the sector still plays an important role in the Spanish economy, representing 4.2% of the Spanish industrial market (*INE*, 2010a). Among the Spanish regions, Galicia is the seventh regarding the total turnover (in million €) of the sector, accounting for 5.4% (*INE*, 2010a).

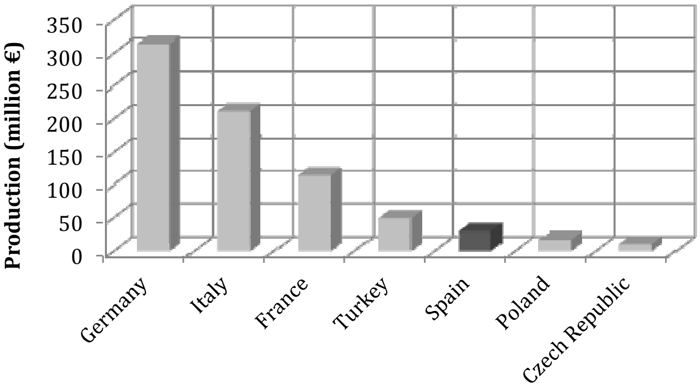


Figure 2.2: Ceramic building materials production (million €) in the EU in 2010 (Eurostat, 2010)

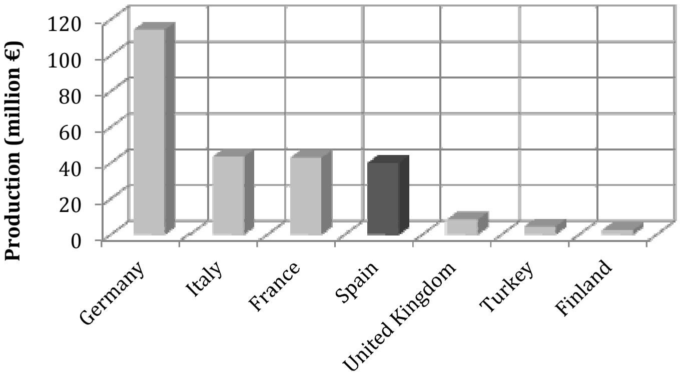


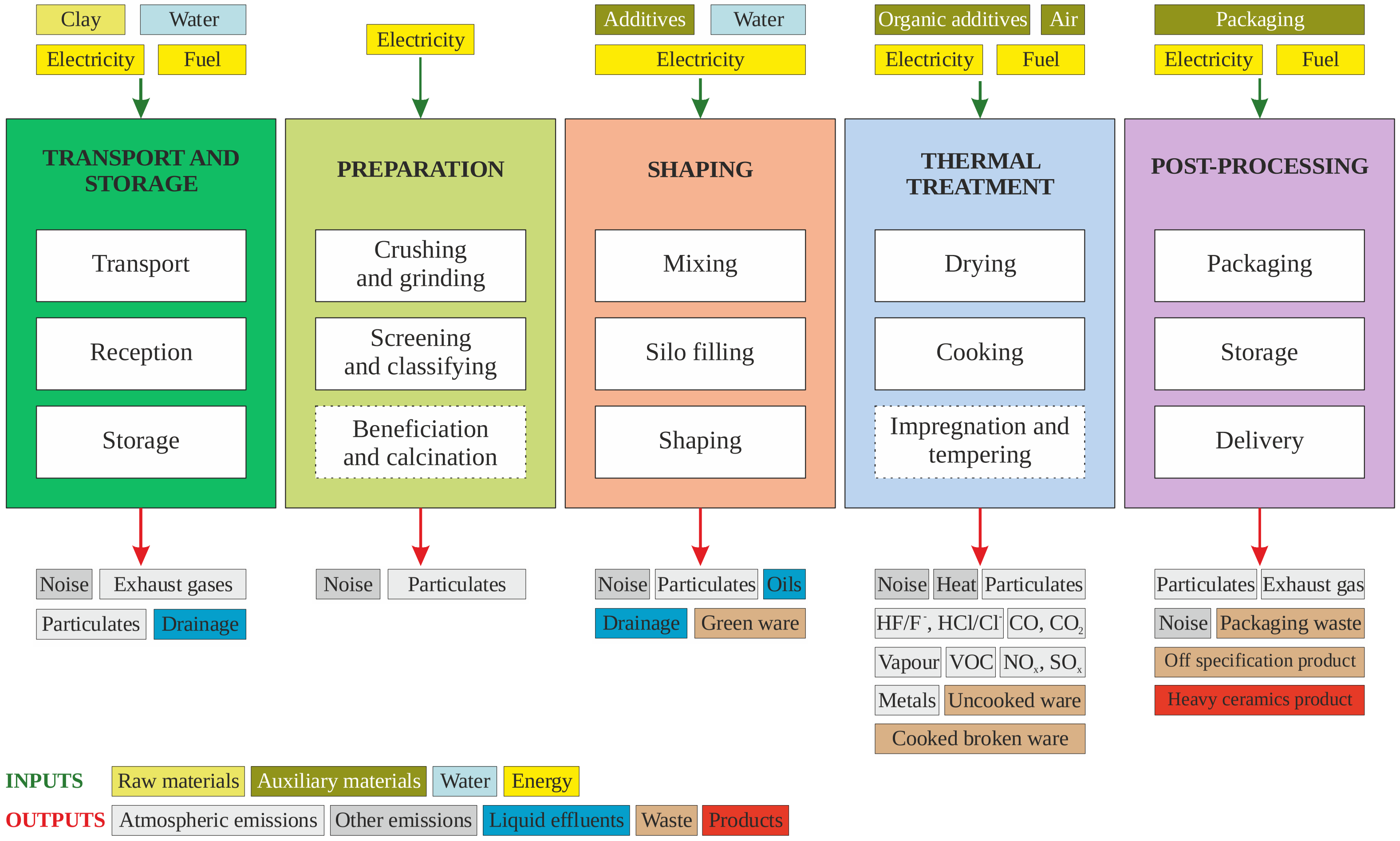
Figure 2.3: Refractory products production (million €) in the EU in 2010 (Eurostat, 2010)

The Galician ceramics manufacture sector is characterised by (Varela, 2003):

- A heterogeneous group of sub-sectors of small or medium-sized enterprises located in Galicia, benefited from plenty of raw materials of high quality.
- Familiar enterprises at first, although some evolved to anonymous sites and other were absorbed by financial groups with higher economical capacity.
- A good technological level, though mainly imported.
- Export capacity depending on the quality and the added value of their products.

4.2. Description of the process

Heavy ceramics category mainly covers ceramic building materials and refractory products, where clay raw materials are moulded into shaped structural products. The productive process for the general manufacture of heavy ceramics (Figure 2.4) can be divided into five main stages: transport and storage, preparation, shaping, thermal treatment and post-processing.


Clay
Water
Electricity
Fuel
Electricity
Additives
Water
Electricity
Organic additives
Air
Electricity
Fuel
Packaging
Electricity
Fuel
TRANSPORT AND STORAGE
Transport
Reception
Storage
PREPARATION
Crushing and grinding
Screening and classifying
Beneficiation and calcination
SHAPING
Mixing
Silo filling
Shaping
THERMAL TREATMENT
Drying
Cooking
Impregnation and tempering
POST-PROCESSING
Packaging
Storage
Delivery
Noise
Exhaust gases
Particulates
Drainage
Noise
Particulates
Noise
Particulates
Oils
Drainage
Green ware
Noise
Heat
Particulates
HF/F⁻, HCl/Cl⁻
CO, CO₂
Vapour
VOC
NOₓ, SOₓ
Metals
Uncooked ware
Cooked broken ware
Particulates
Exhaust gas
Noise
Packaging waste
Off specification product
Heavy ceramics product
INPUTS
Raw materials
Auxiliary materials
Water
Energy
OUTPUTS
Atmospheric emissions
Other emissions
Liquid effluents
Waste
Products

4.2.1. Transport and storage

Initially raw materials are transported to the plant, where they are received and stored in piles before further use.

4.2.1. Preparation

Raw materials are crushed, grinded, screened and classified. The beneficiation and calcination of clay only occurs when refractory products are manufactured. The calcination consists of heating a ceramic material to a temperature below its melting point to liberate undesirable gases and compounds, in order to perform a structural transformation to get the desired composition for the product. Calcination usually is carried out in rotary kilns (US EPA, 1996).

4.2.2. Shaping

After selecting the required raw materials, they are mixed with water to produce a clay body of the required characteristics. Auxiliary materials (additives) may be added to the clay body to give certain qualities to finished product (shrinkage, porosity, strength, colour and refractoriness) (*Cérame-Unie*, 2004). The clay body is then stored in silos and subdued to different shaping methods such as soft or stiff-mud moulding, extrusion or pressing (Environmental Agency, 2004), depending on the kind of material, the water content, and the desired properties of the final product.

Most bricks are made by stiff-mud extrusion process, although others are processed on soft-mud and dry-press processes. The green clay tubes are shaped in vertical de-gasifying extruders, while roof tiles and refractory products are conformed by isostatic or hydraulic pressing. Some refractory products are also made by extrusion.

4.2.3. Thermal treatment

After shaping, the conformed ceramics are thermally treated. The first step is drying, which can be outdoors though it is often performed in tunnel kilns. Driers are heated mainly by waste heat recovered from the cooling zone of the kiln, and in some cases by natural gas or fuel oil burners (Varela, 2003), which make the temperature arise up to 120 ºC over a 24 hour period (Environmental Agency, 2004).

Cooking takes place in gas heated tunnel kilns predominantly in an oxidizing atmosphere, otherwise in roller, Hoffman or shuttle kilns. The kilns can be programmed to modify different parameters such as cooking temperature or time, according to the specific requirements of the final product. Bricks and roof tiles are heated up to a maturing temperature between 900-1200 ºC, vitrified clay pipes need 1150-1250 ºC, and the wide variety of refractory products ranges from 1250-1800 ºC (Rentz et al., 2001). The manufacture of impregnated refractory shapes using pitch involves special procedures that require low temperature (250–300 ºC) tempering in a kiln (*Cérame-Unie*, 2004; Environmental Agency, 2004; Rentz et al., 2001).

4.2.4. Post-processing

In the last stage, the finished products are sent to the storage facility for selection and quality inspection, packaging, dispatch, and distribution (Environmental Agency, 2004).

4.3. Environmental aspects: consumptions and emissions

Diverse raw materials, natural and synthetic, are used to manufacture a broad range of ceramic goods applying various production techniques. Hence, the ample variation in materials, products, properties, and production techniques, leads to widely varying levels of consumption and emission (Environmental Agency, 2004). The typical consumptions (inputs) and emissions (outputs) of the generic process are qualitatively shown in Figure 2.4.

4.3.1. Consumptions

The typical consumptions associated to the generic heavy ceramics manufacture process are:

- Raw materials. The main raw material is red clay, being more than 13 Mt produced in Spain in 2009 (*IGME*, 2009). However the refractory industry uses other materials, such as alumina, bauxite, magnesite, graphite, silicon carbide, dolomite or refractory clays, depending on the type of refractory product to be manufactured, representing 175 thousand tonnes in 2009 (*IGME*, 2009).
- Water. It is thoroughly used in all the production process, during the preparation of clay cases and clay bodies for shaping, in wet beneficiation or in grinding processes. The average consumption in brick manufacturing is about 0.187 m^3/t, while for vitrified clay pipes and chromate refractory products is around 150 and 5.0 kg/t, respectively (Rentz et al., 2001).

  Besides the water used in the production process, cleaning water is also required. The volume of water used is quite variable (around 5 l/t of product (Spanish Government, 1999)), depending on the applied techniques and the water pressure, or on whether water recycled from the process is used.
- Energy. It is an energy intensive sector, since a key part of the process involves drying followed by cooking at temperatures between 800 and 2000 ºC. The energy consumption depends on the raw materials used, the manufacturing process and the final product, in addition to the cooking techniques employed.

  Diesel fuel is required for in-site transportation. In terms of specific energy consumption, the bricks/roof-tile sub-sector ranges from 1710 to 2805 kJ/kg, while the energy consumption of the vitrified clay pipes rises as they increase in size (Rentz et al., 2001). There has been a progressive move to cleaner fuels (natural gas or electricity) and away from coal and heavy oils within the last decades. It has resulted in a substantial reduction of the emissions to air, especially sulphur compounds and organic substances. Natural gas is now mostly used and accounts for nearly 90% of the total energy consumption (*Cerámе-Unie,* 2004).

  Machinery used for crushing and mixing of raw materials and shaping of ware requires electricity, as well as other equipment as conveyor belts, fan systems or engines.
- Auxiliary materials. They are packaging material, involving around 0.5-1.0 g per kg of brick manufactured (Rentz et al., 2001).

4.3.2. Emissions

Typical emissions derived from the heavy ceramics manufacture process are described below:

- Atmospheric emissions. They represent the major environmental aspect of the heavy ceramics industry, including a wide variety of pollutants.

  Particulate matter (PM_{10}) may arise during handling or processing of raw materials (grinding operations, screening, shaping, drying, cooking and calcination), specifically the dry ones. Also, fugitive emissions can be produced on the whole installation by broken wares or dusty spillages, as vacuum cleaning systems are not always available on-site. Particulates from tunnel kilns may reach values ranging 80 mg/m^3 (Rentz et al., 2001).

  Gaseous compounds released during drying, calcination and cooking are mainly derived from the raw materials (including additives), though the fuels employed also contribute to the emissions to air. These compounds, identified in the kiln exhaust gases, are SO_x, NO_x, CO, CO_2, VOC (Volatile Organic Compounds), chlorine and fluorine and their compounds, and metals as trace elements.

  The concentration of SO_x (mainly SO_2) in waste gas streams is closely related to the sulphur content of the raw material and fuels. In brick and roof-tile industries 10–500 mg/m^3 are emitted (depending on the type of fuel employed for cooking), whereas refractory production plants emit around 10–580 mg/m^3 (Rentz et al., 2001). Nitrogen compounds are present in fuels and in organic additives, and they form NO_x during combustion. NO_2 emissions are around 20–120 mg/m^3 for brick/roof-tile industry, and up to 30–470 mg/m^3 in the refractory industry (Rentz et al., 2001).

  CO and CO_2 not only arise from the combustion of organic matter in the ceramic body, but also from fossil fuels and thermal dissociation of carbonates during cooking. The CO emission concentration ranges from 10-180 mg/m^3 in refractory products (Rentz et al., 2001).

  Ceramic raw materials may contain organic matter, and a wide range of organic materials are added, especially in the refractory industry, where pitch impregnation of fired ware is performed to achieve carbon enrichment (*Cérame-Unie*, 2004). During the early heating process, carbonisation of organic compounds occurs with the release of a complex range of VOC, and also later, when special treatments as tempering in refractory products take place.

  Nearly all earth materials contain fractional amounts of fluoride, which substitutes OH^- groups in clays and hydrous mineral, generating emissions up to 0.5–120.0 mg/m^3 (Rentz et al., 2001). These fluoride emissions can be lower if lime or other fluoride reactive compounds are added to the clay mixture, as they enhance the retention of some potential pollutants by forming a more stable compound within the fired ceramic (Envirowise, 1999a). Clay also may contain trace levels of chloride, originated while marine formation, which gives concentrations over 20 mg/m^3 in emissions (Rentz et al., 2001).

  The heavy metal content of most ceramic material is very low, and causes no emission problems (*Cérame-Unie*, 2004).

- Liquid effluents. They are normally wastewater polluted with insoluble particulates derived from material processing, which can be separated by settling/filtrating, allowing reusing.

- Waste. Most waste generated in ceramic processing is recycled within the process, or find secondary uses (tennis sand, filling material for roadways or quarries, etc.) (*Cérame-Unie*, 2004), whereas other scrubbing waste needs a specific post-treatment.
- Other emissions. Heat is lost in thermal treatments. Besides noise and odours are produced, though they have a minimal impact on the installations.

Table 2.2 shows an overview of all the potential emissions to the different media. It also includes their environmental effects, which may be harmful to human health or to the quality of the environment, result in damage to material property, or interfere with amenities and other legitimate uses of the environment.

Table 2.2: Potential emissions to different media and their associated environmental effects

Type of emissions		**Environmental effects**
To air	Particulates Diffusive emissions CO, CO_2 NO_x, SO_2 HF/F^-, HCl/Cl^- VOC Metals	Increasing global warming (greenhouse gases) Ozone layer depletion Air quality reduction Acidification Photochemical smog Effects on health
To water	Suspended particulates Anions (F^-, Cl^-, SO_4^{-2}) Heavy metals Organic additives traces	Changes of pH Accumulation of heavy metals Water pollution
To land	Suspended particulates Anions (F^-, Cl^-, SO_4^{-2}) Heavy metals Organic additives traces	Changes of pH Accumulation of heavy metals Water pollution
Others	Odours Noise and vibration Light and irradiative heat	Effects on health and local environment

4.4. Inventory of candidate techniques

After defining the industrial system and its potential environmental impacts, it is possible to act upon the specific sources of pollution to prevent and/or reduce pollution. All the potential preventive and reduction measures are evaluated using different sources of information as books, journals, reports, personal communications from industry, experts' opinions, etc. It is worth remarking the contribution of several heavy ceramics plants from Galicia. This gives rise to a list of measures for the sector to consider in the initial analysis of BAT.

The definitive inventory of candidate BAT was achieved after undertaking a screening of the previous list, taking into account the following aspects for considering in the selection:

- Design or re-design of the equipment used for the thermal treatment of the ceramic pieces in order to minimise the emissions to atmosphere coming from them.
- Low polluting additives and combustibles.
- Waste minimisation by control measures, raw materials inventories, recycling and re-use, etc.

Table 2.3: Inventory of techniques candidate to be BAT for the heavy ceramics manufacture (techniques in italics are exclusively applicable in the case of refractory products production) (part I)

Stage	**Techniques**	**Environmental aspects**
General	T.1.1 Environmental Management Systems (EMS)	Atmospheric emissions, liquid effluents and waste
	T.1.2 Best Environmental Practices (BEP)	
Transport and storage	T.2.1 Bulk storage areas for dusty materials enclosed with walling	Particulates and dust emissions
	T.2.2 Circulating through paved roads	
	T.2.3 Limiting vehicles speed	Fuel consumption, exhaust gases and particulates
	T.2.4 Minimising transport distances	
Raw materials preparation	T.3.1 Energetic optimisation	Electricity consumption
	T.3.2 Selection of raw materials and additives	Particulates and polluting gases (F, S, C and Cl derivates)
	T.3.3 Techniques for reducing fugitive emissions	Fugitive emissions
	T.3.4 Cleaning systems T.3.4.1 Centrifugal force separators (cyclones) T.3.4.2 Bag filters T.3.4.3 Electrostatic precipitators	Particulates and fugitive emissions
	T.3.5 Isolation and acoustic barriers	Noise
	T.3.6 Neutralization and settlement	*Effluents and toxic waste*
Shaping	T.4.1 Water usage optimisation	Water consumption
	T.4.2 Energetic optimisation	Electricity consumption
	T.4.3 Management of effluents T.4.3.1 Serial settling tanks T.4.3.2 Management of equipment drainage	Wastewater management
	T.4.4 Management of waste	
	T.4.4.1 Reprocessing of green and unfired ware	Green ware
	T.4.4.2 Management of empties	Empties
	T.4.4.3 Management of used oils	Used oils
Thermal treatment	T.5.1 Selection of fuel T.5.1.1 Free or low sulphur fuels T.5.1.2 Natural gas (low ash fuels)	Particulates and exhaust gases

Table 2.3: Inventory of techniques candidate to be BAT for the heavy ceramics manufacture (techniques in italics are exclusively applicable in the case of refractory products production) (part II)

Stage	Techniques		Environmental aspects
Thermal treatment	T.5.2	Cleaning systems	
		T.5.2.1 Bag filters with injection of $NaHCO_3$	Particulates and acid gases
		T.5.2.2 Electrostatic precipitators with injection of $NaHCO_3$	
	T.5.3	Process optimisation	
		T.5.3.1 Cogeneration system	Fuel consumption
		T.5.3.2 Using calcium-rich additives	HF/F^- emissions
		T.5.3.3 Optimisation of kiln parameters	
		T.5.3.4 Exhaust gas recirculation	Heat recovery (fuel consumption)
		T.5.2.5 Heat recovery from flue gases and recirculation to drier	
	T.5.4	Reduction of inorganic compounds on exhaust gases	
		T.5.4.1 Low NO_x burners	NO_x
		T.5.4.2 Granulated bed absorber operate with $CaCO_3$	
		T.5.4.3 Cascade-type packed-bed absorber	
		T.5.4.4 Dry scrubber with bag filters or electrostatic precipitator	Acid gases (SO_2, HF, HCl)
		T.5.4.5 Honeycomb shaped module absorber system	
		T.5.4.6 Wet scrubber	
	T.5.5	*Management of scrubbing waste*	*Toxic waste*
	T.5.6	*Reducing organic compounds from impregnation and tempering*	
		T.5.6.1 Carbonisation gas post-combustion in the kiln	
		T.5.6.2 Carbonisation gas post-combustion in counter-current kilns	
		T.5.6.3 External thermal post-combustion with regenerator columns	*VOC*
		T.5.6.4 Catalytic post-combustion	
		T.5.6.5 VOC adsorption and destruction systems	
		T.5.6.6 Special installations	*Odours*
Post-processing	T.6.1	Recycling fired and broken ware	Fired ware
	T.6.2	Limiting vehicles speed	Fuel consumption, exhaust gases and particulates
	T.6.3	Minimising transport distances	

The measures of the candidate BAT inventory are classified in Best Environmental Practices (BEP) and techniques (preventive or abatement ones). The last ones will be individually evaluated to define them as candidate BAT and to elaborate the corresponding technical data sheet. The information included in these sheets is classified as specified in the methodology.

The techniques to be considered as candidate BAT and the environmental aspects they act upon, according to the process stages of the generic heavy ceramics manufacture process, are summarised in Table 2.3. BEP also represent an essential part, as their application minimises the environmental impacts of the process. They are characterized by their utility, simplicity and low cost, as well as for the quick results they provide. In general, BEP for a heavy ceramics installation should be based on (Spanish Government, 2000; Valencian Government, 2000):

- Information campaigns to promote environmental awareness among the staff of the plant.
- Records of raw materials, auxiliary materials, water and energy, as well as the quantity, typology, destination and costs of waste and its management to set reduction targets.
- Assess the possible environmental impacts caused by accidents or unexpected emissions.
- Adequately training equipments and materials before operating in order to prevent defective pieces on the start-up.
- Operate at a suitable processing speed to optimise production and minimise waste.
- Optimise heating processes for avoiding waste heat and making best use of combustible.

Moreover, an Environmental Management System (EMS) is also a generic technique related to the continuous improvement of environmental performance of an installation, and should also be considered as a candidate BAT.

Candidate BAT and BEP are explained below. The explanation includes several example technical data sheets.

4.4.1. Transport and storage

The candidate techniques to improve the first stage of the heavy ceramics manufacturing process are the following:

- Install bulk storage areas for dusty materials enclosed with walling to avoid particulates and dust emissions.
- When possible, circulate though paved roads instead of unpaved ones, to reduce dust emissions derived from transport.
- Limiting vehicles speed to reduce the emissions of dust and particulates but also to limit fuel consumption and exhaust gases.
- Proper planning of transport operations to minimise transport distances.

4.4.2. Preparation

The specific techniques selected for this stage are briefly described below.

RAW MATERIALS EXTRACTION/RECEPTION

Prior to the extraction of raw materials in clay pits, it is necessary have on mind several measures to minimise the impacts they produce on the environment and how optimise their usage, as follows (Environmental Agency, 2004):

- Adequately selection of raw materials considering the emissions and waste they cause.
- Maintain an inventory covering the principal types of raw materials and additives used.
- Annually review alternatives for the principal types of raw materials and additives used with regard to their environmental impact.
- Substitution of organic additives for inorganic ones.
- Control the specification of raw materials and additives used in order to minimise any potential environment impact.
- Reduce the usage of chemicals and other polluting materials.

STORAGE, CRUSHING AND GRINDING OF CLAYS

The general measures to be employed during the storage, crushing and grinding of clays aiming to avoid fugitive emissions are (Environmental Agency, 2004):

- Ensure that, where there is vehicular movement, storage areas have a consolidated surface which is kept in good conditions.
- Wet stockpiles where necessary to minimise dust emission and install fixed water sprays for long term stocking areas if appropriate.
- Provide adequate protection against wind whipping.
- Clean all process buildings regularly, according to a written maintenance programme to minimise fugitive emissions.
- Use closed and independent warehouses to control emission sources.

The techniques selected for the efficient removal of PM_{10} and dust are:

- Cleaning systems as centrifugal force separators, bag filters and electrostatic precipitators (Environmental Agency, 2004; Rentz et al., 2001; Spanish Government, 1999, 2000).
- Isolation and acoustic barriers for the minimisation of acoustic emissions.

BENEFICIATION AND CALCINATION OF CLAYS

The measures to be considered during the beneficiation and calcination of clays are:

- Optimise the calcination process using accurate residence times, kiln lengths, time–temperature profiles, etc.
- Installing cleaning systems for particulates and acidic gases coming from the calcination kiln, as centrifugal force separators, bag filters and electrostatic precipitators, which include alkaline reactives to neutralise the acidic emissions.

- Segregate solid and toxic waste, guarantying adequate storage in special containers clearly labelled in secured places.
- Segregate toxic effluents when the purification of raw materials is carried out by wet processes. These liquid effluents need a physicochemical treatment including homogenisation, pH adjustment, coagulation, flocculation, sedimentation, treatment, and sludge stabilization. Later, a sludge analysis is required before disposal to landfill, to check whether they have hazardous heavy metals forcing them into a safety storage tank (Huybrechts et al., 1999).

4.4.3. Shaping

The techniques considered for reducing emissions in this stage are:

- Water usage and energetic optimisation.
- Mechanical dosing systems for the mixture of raw materials and water, improving resources and quality at maximum.
- Installation of isolation and acoustic barriers for minimising and/or preventing acoustic emissions and vibrations from machinery.
- Re-use of green and unfired wares within the process, saving raw materials (Figure 2.5).

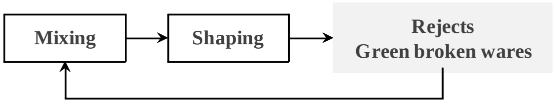
T.4.4.1 **REPROCESSING OF GREEN WARE**

ENVIRONMENTAL ASPECTS

Re-using rejects and waste green ware.

TECHNICAL DESCRIPTION

Reusing green ware by directly feeding it back to the mixing stage. Efficient clay collection systems are required to prevent ware contamination in case of falling to the floor.



BENEFITS / ENVIRONMENTAL DATA

Reduction of natural resources consumption (mainly raw materials) and waste generation.

SECONDARY EFFECTS

If rejects are not properly selected the paste can be polluted, affecting the quality of the final product.

IMPLEMENTATION

Suitable for both new and existing plants.

APPLICATION AND CHARACTERIZATION

The average humidity of the green ware (18-25%) makes it plastic and malleable enough to be directly reincorporated to the process, without any further processing (Spanish Government, 1999).

ECONOMICAL ASPECTS

Cost-effective, as raw materials are fed back to the process. A single plant can save about 150000 €/y by installing a guttering system to collect green ware for re-use. The capital cost is about 750 € (Churchman-Davies, 2001).

PLANTS WHERE THE TECHNIQUE IS ALREADY IMPLEMENTED

Usual practice in Galician installations.

Figure 2.5: Technical data sheet of the candidate technique 'Reprocessing of green ware'

- Cleaning systems for particulates: centrifugal force separators, bag filters and electrostatic precipitators.
- Management of packaging and used oils.
- Recycling of industrial effluents (equipment drainage and cleaning), firstly treating them if needed. When treatment is not practicable, they should be recycled to another part of the process which has a lower water quality requirement. Moreover, sludge can be reincorporated to the mixture of raw materials.

4.4.4. Thermal treatment

Techniques candidate to be BAT in this stage are classified as ‘drying and cooking’ techniques, which apply in all heavy ceramics production processes, and ‘impregnation and tempering’ techniques, which only apply in the case of refractory products.

DRYING AND COOKING

The candidate techniques to optimise the process and reduce the emissions are (*Cérame-Unie*, 2004; Rentz et al., 2001):

- Installing cleaning systems for particulates and acid gases from the kiln: bag filters or electrostatic precipitators with alkaline reactives injection to neutralise acid gases (Figure 2.6).
- Using low-polluting fuels, as free-sulphur fuels or natural gas.
- End-of-pipe technologies for reducing inorganic compounds existing when the abatement measures at source are not enough to achieve the emission values set: scrubbers, low NO_x burners, etc.
- Management of scrubbing wastes.
- General process optimisation of:
  (i) fluoride reactive compounds;
  (ii) cogeneration systems;
  (iii) exhaust gases internal recirculation and recovery of waste heat to drier;
  (iv) kiln parameters, altering the time–temperature profile, reducing the air flow, increasing the turbulence in the pre-heat zone, increasing the interaction between the product and the flue gas, or re-using flue gas (Figure 2.7). Each parameter gives a different percentage of reduction in fluoride emissions (Envirowise, 1999a, 1999b).

IMPREGNATION AND TEMPERING

When refractory products are required to work in extremely hostile working environments, it is necessary to perform special treatments by means of impregnating fired ware with petroleum based pitch. In that case, several measures for minimising emissions of organic compounds to the atmosphere are proposed:

- Special installations to avoid odour emissions by impregnating the refractory products.
- End-of-pipe technologies for reducing VOC from cooking (Environmental Agency, 2004).
- General optimisation of the tempering kiln parameters.

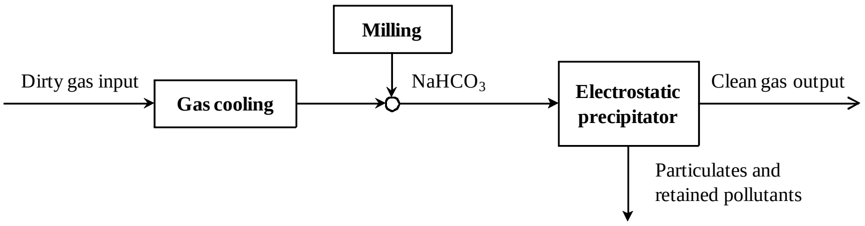
T.5.2.2 ELECTROSTATIC PRECIPITATORS WITH INJECTION OF $NaHCO_3$

ENVIRONMENTAL ASPECTS

Emissions of particulates and acid gases in cooking processes.

TECHNICAL DESCRIPTION

$NaHCO_3$ is injected into the dirty gas stream to neutralise the acid compunds. On the other hand, particulates get electrically charged by ionisation by means of an electrode and a collector with a high potential difference (50-100 kV). Electrically charged particulates are deposited on the collecting electrode. The particulate layer formed on the collector is removed by periodic shaking.



BENEFITS / ENVIRONMENTAL DATA

Reduces particulate and acid gases emissions to the atmosphere, with efficiencies up to 99%. Dust clean gas concentrations of less than 50 mg/m^3 are achievable (European Commission, 2007a).

SECONDARY EFFECTS

Electricity consumption around 0.05 – 2 kWh/1000 m^3.

IMPLEMENTATION

Re-designing of the plant and acquisition and installation of new equipment.

APPLICATION AND CHARACTERIZATION

Collected particulates can be re-used as raw materials with limitations, as they may contain high concentrations of F and S that could increase the emissions of these compounds during cooking. The technique is only suitable for high volume flows at high temperatures, and has low energy demand.

ECONOMICAL ASPECTS

Investment cost 1-3 million euro, operating cost 0.1-0.2 €/t (European Commission, 2007a).

PLANTS WHERE THE TECHNIQUE IS ALREADY IMPLEMENTED

Common practice.

Figure 2.6: Technical data sheet of the candidate technique 'Electrostatic precipitators with injection of $NaHCO_3$'

4.4.5. Post-processing

The measures adopted in the last stage refer to the management of rejects (fired and broken wares) and/or products out of specification, whose recycling as secondary raw material is the best option.

4.4.6. Integrated technologies and techniques

They are based on systems that utilize the natural resources very efficiently, with input flows of low environmental costs, generating little or no residues (which are recycled), and releasing non-toxic effluents. Moreover, the industrial symbiosis and industrial ecosystems must be also taken into account, considering the integration of the plant in industrial complexes where material and energy by-products are employed as secondary raw materials.

The integrated technologies and techniques that might be applied in a heavy ceramics manufacture installation are:

- Using vegetal oil wastes from the food industry for energy generation in thermal treatments.
- Benefiting from contaminated soils, particularly those of argillaceous nature, having identical compositions to the ones of the raw materials used in the ceramic manufacturing industry (Elías Castells, 2000).
- Ceramic valorisation of WWTP (Wastewater Treatment Plant) sludge (IRC Network, 2006), wastes from heavy fuel-oil spillages on the sea, red mud from the alumina manufacturing (Guitián, 2003), etc.

T.5.3.3 OPTIMISATION OF KILN PARAMETERS

Environmental Aspects

HF/F^- emissions from cooking.

Technical Description

Pollution prevention by increasing the interaction between exhaust gases and final products; reducing the air flow through the kiln; modifying temperature profiles; favouring turbulence in pre-heating areas; adding alkaline compounds that react with fluorides.

Benefits / Environmental Data

Reduces HF emissions to the atmosphere.

Minimisation technique	HF reduction %
Modifying temperature-time profiles	10
Interaction between exhaust gas and products	53
Reducing air flow through the kiln	63
Favouring turbulence in pre-heating areas	86
Adding alkaline compounds	75
Reusing hot exhaust gas for drying	94

Secondary Effects

None.

Implementation

Suitable for both new and existing plants.

Application and Characterization

Heating curves are optimised in line with product quality and energy consumption.

Economical Aspects

Minimisation technique	Investment cost (€/t)	Operating cost (€/t)
Modifying temperature-time profiles	<30000	0
Interaction between exhaust gas and products	30000-150000	0
Reducing air flow through the kiln	<30000	0
Favouring turbulence in pre-heating areas	30000-120000	<0.075
Adding alkaline compounds	30000-150000	0.75-4.5
Reusing hot exhaust gas for drying	>75000	<0.3

Plants where the Technique is Already Implemented

Ibstock Building Products Ltd (United Kingdom)

Figure 2.7: Technical data sheet of the candidate technique 'Optimisation of kiln parameters'

4.5. Identification of the already implemented techniques

A rough evaluation of the existing Galician heavy ceramics manufacture plants affected by the IPPC Directive concludes that they have implemented very few candidate techniques. There is no evidence of the implementation of techniques regarding the management of liquid effluents, as they are not very abundant. Techniques regarding atmospheric emissions are the most implemented ones.

In Galicia relatively few plants are affected by epigraph 3 (mineral industry) of Annex I of the IPPC Directive. Only 25 plants out of the more than 250 plants affected by the Directive belong to the mineral industry. All of them have their corresponding environmental permit, and some of them have already updated it. Around 60% of these plants belong to epigraph 3.5, regarding the production of ceramic products.

5. Results and discussion

This chapter has presented a new methodology, BAT Analysis, to perform technical inventories recompiling techniques candidate to be BAT regarding the principles of the IPPC philosophy. It is a five-step procedure that involves the qualitative analysis of the sector concerned, a thorough description of the process, an identification of the environmental aspects related, the selection of candidate techniques regarding the IPPC principles and gathering them in a technical inventory, and the detection of the techniques that have already been implemented in the industrial system.

BAT Analysis applied to the Galician heavy ceramics manufacture industry has provided a structured overview of its particularities and special conditions in the considered region. The generic productive process performed by such installations has been evaluated, dividing it by main stages. The potential environmental aspects (namely consumptions and emissions) have been qualitatively analysed, identifying the main consumptions and pollutants, assigning them to specific stages, and defining their main environmental consequences.

On determining specific BAT for these installations, the principles set by the IPPC Directive have been taken into account. Furthermore, the local environmental conditions, geographical location and distinctive technical characteristics of installations have been regarded. Consequently, an inventory of 46 candidate techniques (all of them provided by a technical data sheet) has been developed, supported by several BEP. Some examples of technical data sheet have been included to show the simple and practical procedure described in the methodology, and enlighten different types of prevention and mitigation techniques in the heavy ceramics industry (recycling of waste, end-of-pipe improvement and prevention of emissions by process optimisation). These technical data sheet include complete information regarding some technical, environmental and economic aspects, as suggested by the EIPPCB. They can be used by decision-makers to evaluate whether to implement or not a given technique, or to decide if the technique is really BAT for the considered process.

Finally, a rough evaluation of the techniques that are predominantly implemented in the sector has been carried out, to illustrate the last step of the methodology. However this step is more useful when BAT Analysis is applied to a single plant instead of a whole sector, as it is intended to evaluate the state of the process before implementing further techniques. In this case this stage gives a general idea of the degree of implementation of BAT in the Galician heavy ceramics manufacture sector. However, if applied to a single plant, it could provide information about the suitability of the implemented techniques and the necessity of updating the implemented ones or introducing others.

6. Conclusions

BAT Analysis is a suitable method to obtain inventories of techniques candidate to be BAT and therefore candidate to improve the sustainability of industrial systems. The IPPC approach used as selection criteria gives this methodology a further use, as it can help applicants of IPPC environmental permits to identify process-related information and techniques available to meet the ELV set by the Directive. It is quite useful for the technical teams in charge of gathering data, regulators analysing the documentation, and the public in general.

This methodology can be applied to any industrial system to get exhaustive technical inventories recompiling techniques candidate to be BAT, focussing on the processes performed and their environmental aspects. Though the methodology derives from a philosophy established with the IPPC Directive, it can be applied to any sector, affected or not by the Directive. It includes simple qualitative methods that can be extrapolated to any productive system. In any case, techniques should be evaluated regarding the specific aspects, as stated in the methodology, of the sector concerned.

However this methodology presents some limitations. It accurately proposes techniques candidate to get a sustainable industrial system, but it fails to identify which ones are required or where they should be implemented. It does not make sense to apply all the techniques from the inventory, as they may not be all necessary or they may not be BAT for a specific situation. The methodology requires introducing an element that helps detecting the needs of the industrial system. Some of the available options are briefly described below:

- Environmental Impact Assessment (EIA) to evaluate planned projects.
- LCA to perform environmental impact assessments related to the whole life cycle.
- Sequential procedures such as cross-media guidelines, costing methodology, evaluating alternatives and economic viability of the sector including in the BREF on Economics and Cross-Media Effects (European Commission, 2004b).
- Combined methodologies, as the one proposed by Breedveld et al. (2007), where a unique end-of-pipe technique is analysed by means of a simplified LCA, an eco-efficiency calculation and the additional cost per unit reduction of emissions.
- Expert judgement, focusing scores on the technical feasibility, cross media environmental performances and economic feasibility (Derden et al., 2002; Dijkmans, 2000). It has the advantage to be simple and convenient, but more profound quantitative analysis is needed to evaluate the impact of candidate BAT.
- Environmental assessment method for cleaner production technologies (Fijal et al., 2007). It is based on material and energy flow evaluations that use a set of profile indices, based on raw material, energy, waste, product, and packaging profiles related to the technology under investigation for determining an integrated index.

All these options suggest the idea that material and energy flows must be analysed before deciding if a technique should be applied or not. But the problem underlying goes beyond, as it is also necessary to identify where in the system the candidate technique is required. It seems obvious that further steps focussed on the identification of needs are required to complement BAT Analysis. These needs can be pointed out by a new indicator.

The technical inventories proposed classify the candidate techniques regarding the stage of the process where they should be implemented and the environmental aspect they affect, by avoiding, reducing or taking advantage of it. Accordingly the new indicator should effectively identify the unsustainable stage of the process and the environmental aspect that requires improvement. With that purpose a new concept, which will be further developed in the next chapter, is proposed as an indicator of the unsustainable elements of an industrial system: the Improvable Flows. This indicator will be intended to accurately identify which stages of the process require implementing measures to reduce their environmental impacts. Improvable Flows will actually be unsustainable material or energy flows attached to a specific stage and causing avoidable environmental impacts, which could be prevented or reduced by implementing a suitable technique or set of techniques from an inventory.

CHAPTER 3

IMPROVABLE FLOWS IDENTIFICATION TOOLS

Summary

In the previous chapter a methodology to develop inventories of techniques candidate to be BAT was proposed. However its validation pointed out the necessity of an indicator that detects which techniques are needed and where they should be implemented to get a sustainable industrial system. This indicator has been defined in terms of material and energy flows as the Improvable Flows (IF).

This chapter presents the two tools proposed to identify the IF of an industrial system: MEFA and Process Simulation. In both cases a methodology is proposed and validated in an industrial system to evaluate the suitability of both tools to detect the IF and to trace them across the system.

Though they differ in some aspects, both methodologies include a qualitative description of the industrial system followed by the modelling and simulation of the system. This step of both methodologies results in the identification of the IF of the system. This information is very useful, as it points out the unsustainable elements of the system and provides specific information about how and where improvement measures should be implemented.

Both methodologies are validated, though in different industrial systems. The first one, MEFA, is validated in a roof-tile manufacture plant by applying it to the first stage of the production process. As a result, 3 IF are identified for this industrial system, regarding energy consumption and atmospheric emissions. MEFA is also proved to be useful to allocate flows, as transport (especially from quarry to plant) is pointed out as the most unsustainable sub-stage, as it holds the three IF identified.

The second one, process simulation, is applied to the waste management sector. In this case process simulation is aimed to identify the IF of a treatment for recycling used lubricating oil, previously selected from a technical inventory regarding the WMH. In this case four IF are identified. Three of them are referred to energy consumption, which points out the most energy-

demanding sub-stages of the proposed process. The other IF refers to a waste stream, revealing that, though it cannot be prevented, its management can be improved.

Though both of them are suitable tools to identify IF, the methods and usefulness of results is different in each case. MEFA is more appropriate for existing plants, where a lot of data is available. It easily quantifies and allocates flows, and provides quantitative information which can be easily analysed to identify IF. On the other hand, although process simulation also identifies IF, it is more suitable to predict the behaviour of industrial systems after implementing corrective measures. In any case, it can be a valuable tool for IF identification and evaluation if properly integrated in a methodology.

1. Definition of the Improvable Flows

BAT Analysis has provided a useful method to develop technical inventories for BAT and therefore, suitable to get sustainable industrial systems. However this method fails to decide which technique or set of techniques are required in each specific situation. BAT Analysis requires being complemented by tools to identify the deficiencies and unsustainable elements of industrial systems so that techniques can be accurately proposed. It seems that some kind of indicator is required to identify the needs of the system in terms of sustainability.

Indicators, specifically environmental indicators, allow decision-makers to make informed judgements regarding policies, programs, plans and projects (Cloquell-Ballester et al., 2006; Henri and Journeault, 2008). As defined by the European Environment Agency (EEA), indicators are ‘measures, generally quantitative, that can be used to illustrate and communicate complex phenomena simply, including trends and progress over time’ (EEA, 2005). They reduce the volume and complexity of the information managed by decision-makers (Donnelly et al., 2007; Niemeijer and de Groot, 2008), and so they should be measurable, scientifically valid and representative of the situation or phenomenon they stand for. Thus, indicators must provide information about the main characteristics that affect the suitability of products and processes from a sustainability viewpoint (Herva et al., 2011).

Though useful to represent specific situations in industrial systems, indicators also present some limitations, mostly related to their selection, interpretation and use (Moldan et al., 2012). Therefore the purpose of the indicators in each specific case must be carefully regarded to avoid unnecessary operations and get an accurate definition for the indicator. It is assumed that indicators should be able to assess conditions and trends in relation to goals and targets, provide early warning information and anticipate future conditions and trends (Perotto et al., 2008). They should also provide both qualitative and quantitative information about the considered situation, and they must be able to compare and rank the performances of different alternatives (Lim and Park, 2009).

Material and energy flows can be considered as the basis on which all indicators are founded (Herva et al., 2011). Accordingly they have been selected to develop a new indicator which could be included in BAT Analysis methodology. This indicator is required to effectively identify the needs of a system so that its sustainability can be improved by implementing the adequate combination of techniques. It should be easily calculated and representative of the industrial system under study.

According to the material and energy flow perspective, flows have been selected as the most representative aspect of an industrial system, regarding environmental and economic aspects. They represent the consumption of raw materials and energy, the production of added-value products and the generation of secondary streams that can be regarded as waste, by-products or emissions to the environment. Flows can be easily quantified and allocated by known methodologies, as LCA or MEFA, which even allow referring flows to specific reference units, as production capacity or raw materials consumption.

A new concept has been defined, considering the material and energy flow perspective and keeping in mind the typical requirement for indicators, the Improvable Flows (IF). IF are defined as quantitatively (or qualitatively in some cases) relevant flows in an industrial system that can be improved if properly managed by applying preventive or corrective measures. They are selected considering their relevance over the whole industrial system in terms of quantity and quality. Identification tools based on process analysis are used to detect improvable material and/or energy input, output or intermediate flows. IF detection can be also supported by literature or experience available on the analysed system.

IF have already been validated as suitable indicators to select enhancement alternatives from technical inventories to get sustainable industrial systems. They have been validated in the case of an exemplary roof-tile manufacture plant (Torres et al., 2011) and in a mussel cooking plant (Bello et al., 2012). In both cases IF successfully identify the needs of the system regarding sustainability and provided useful information to identify the most appropriate corrective measures. The case of the roof-tile manufacture plant will be explained in chapter 4.

Two tools are suggested to identify the IF of industrial systems: MEFA and process simulation. Both of them allow quantifying and allocating flows within a system by quite simple methods. Though they require abundant data and deep knowledge of the system, they provide accurate information that can be easily analysed and incorporated to other methodologies as BAT Analysis. The suitability of MEFA and process simulation is analysed in chapter 3.1 and chapter 3.2 respectively.

3.1

MATERIAL AND ENERGY FLOW ANALYSIS (MEFA)

Summary

MEFA has been suggested as an adequate tool to identify IF, as it easily quantifies material and energy flows within an industrial system. This chapter presents and applies the typical methodology of MEFA to validate its suitability for IF detection.

The methodology presented includes the definition of the targets of the study, a description of the system, the acquisition of data, the modelling and scenario building using specific software, the evaluation and discussion of results, and finally the detection of the IF of the system according to the results of MEFA. The methodology provides deep knowledge about the process by qualitatively analysing all the stages and quantitatively identifying all the material and energy flows involved.

MEFA is applied to a roof-tile manufacture plant from the Galician (NW Spain) heavy ceramics manufacture sector. The specific stage considered for evaluation is the ‘transport and storage of raw materials’. The selected software is Umberto, which allows visualizing the whole process to analyse the flows involved by applying material and energy balances. The main objective of this study is to identify the IF of this stage, so that corrective measures can be proposed to improve the efficiency of the process and reduce its environmental impacts. The software allows the identification of improvement potential, by a quantitative comparison of input and output data with target values.

The application of MEFA to the case study points out transport operations as the more impactful processes. They are responsible of a great percentage of the fuel consumed and the exhaust gases released by the considered system, being lorry transport from quarry to plant the most impactful sub-stage. According to these results, fuel consumed and exhaust gases emitted have been pointed out as IF for this system, as well as particulate emissions, also from this sub-stage.

This chapter validates MEFA as a suitable tool for IF identification. It provides quantitative information about material and energy flows, and traces them over the considered industrial system. Though useful for quantitative identification, MEFA results require careful evaluation to accurately select IF. On the other hand, MEFA fails to propose corrective measures to avoid or

reduce the IF, so it requires being combined with a corrective measures proposal methodology, such as BAT Analysis.

1. Introduction

Although the mass-balance principle had been long applied to diverse fields (Brunner and Rechberger, 2004), Material Flow Analysis (MFA) emerged in the 70s as a tool for Industrial Metabolism (Fischer-Kowalski, 1998) which Ayres defined as “the whole integrated collection of physical processes that convert raw materials and energy, plus labour, into finished products and wastes…” (Ayres, 1994). The concept “metabolism”, both applied to biology and to society, appeared in the late 1860s, and it has evolved through history until the late 1960s, when it reappeared as a way to face the modern environmental concerns (Fischer-Kowalski, 2003). The publication of the book “Economics and the Environment: A Materials Balance Approach” by Kneese et al. (1970), set the basis of what would end up being MFA. It treated environmental and economic problems from a new perspective based on the utilization of mass and energy balances to evaluate the impact of the human activities over the environment. Since then, MFA has received increasing attention from the scientific community and several initiatives have been carried out to normalize the different methodological approaches developed by several working groups (SERI, 2003). The publication by the European Statistical Office of the methodological guide “Economy-wide material flow accounts and derived indicators” provided a generic harmonized standard tool (Eurostat, 2000).

MFA comprises a broad family of tools to reduce the consumption of energy, raw material, water and the discharge of effluents by pursuing systematically internal flows of mass and energy in production processes (European Commission, 2003b). Therefore, MFA can be defined the systematic assessment of the flows and stocks of materials within a system defined in space and time (Brunner and Rechberger, 2004). This definition can be further extended to include energy, the so-called MEFA.

Usually, MEFA can be classified in two wide groups: the first one relates to environmental impacts per unit of flow of substances (i.e., cadmium or carbon dioxide), materials (i.e., wooden products or plastics), or products (i.e., cars or batteries), within certain limits: plants, industrial sectors or regions. The second group relates to environmental problems connected to the throughput of industries (i.e., single plants or medium and large companies), industrial sectors (i.e., energy or chemical), or region (i.e., total throughput or mass flow balance), associated with substances, materials or products (Bringezu, 2003; OECD, 2000).

Literature review shows that authors have mainly focused the application of MEFA on large areas where general or specific flows are analysed over a period of time (Table 3.1.1). There are a wide variety of examples of MFA applied over big regions or countries (Krausmann et al. 2004, Muñoz and Hubacek, 2008; Park et al., 2011; Schwarzenbach et al., 1999), and over cities (Browne et al., 2011; Hendriks et al., 2000), but it has also been applied to evaluate specific flows, as fossil fuels in China (Dai and Chen, 2010), PET in the US (Kuczenski and Geyer, 2010) or the trends of nutrients through food consumption webs (Qiao et al., 2011) to mention some. In all these works material and energy flows are identified and quantified in socio-economic scenarios with the purpose of implementing measures that improve their management and evolution. As pointed out by Krausmann et al. (2004), MFA/MEFA results can be easily related to economic flows and social variables, so they provide a useful tool for both economical and social purposes.

As an industrial metabolism based tool, MEFA has a huge potential when applied to industrial areas, where it has been successfully used to optimise material flows and waste streams in production processes (Binder, 2007). However, the application of MEFA on industrial systems is not very extended, just a few examples of as the analysis by Sendra et al. (2007) of an industrial park by MFA combined with water and energy indicators, the characterization of recovery, re-use and recycling of residues in an industrial area in India (Bain et al., 2010), or the analysis of the steel manufacturing process (Yu et al., 2007). Though scarce, these studies have successfully applied the traditional methods of MEFA to new situations, showing up the versatility of this tool, and opening the door to new approaches.

The socio-economical focus of MEFA is complemented by other applications focussed on pollution prevention, adding an environmental approach to the concept of MEFA. This tool is known for having the potential to identify environmental or resource issues before any sign of environmental stress (Hendriks et al., 2000; Park et al., 2005). Therefore, it is a valuable tool when evaluating the potential environmental risks derived from a given process, which facilitates setting priorities and implementing effective management strategies. MEFA prioritizes prevention practices over end-of-pipe solutions (Browne et al., 2011) by evaluating all the inputs and outputs involved in a process and analyzing their coherence regarding the considered process. Inadequate flows of resources (material and energy) and pollutants can be easily detected so that corrective measures can be implemented.

The objective of this chapter is to evaluate the suitability of MEFA as a tool to identify IF in industrial systems. The traditional methods of MEFA are applied to the specific case of the Galician ceramics manufacture industry, whose relevance was analysed in chapter 2. A reference plant manufacturing roof tiles is selected. Its inputs, outputs and internal flows are qualitatively and quantitatively analysed to detect the IF and identify those stages of the process whose sustainability could be improved.

2. Case study

The selected industrial plant, *Cerámica Verea S.A.*, is an exemplary roof-tile manufacture plant located in Galicia, NW Spain, producing 111 millions of tiles per year (133200 tonnes per year) (data from 2005). This installation is an exemplary industrial plant affected by the European Directive 2003/87/EC (EU, 2003) concerning greenhouse gases emissions, and the IPPC Directive (EU, 2010). It was the first existing Galician ceramics manufacture plant adapting to the requirements of IPPC Directive (transposed in 2002 to the Spanish legal system by Law 16/2002 (Spanish Government, 2002a)). The plant got the corresponding environmental permit in 2005.

For the purposes of this chapter, just the first stage of the process will the considered, ‘transport and stage of raw materials’, as shown in Figure 2.4. This stage comprises the transport of raw materials from quarry to the plant, the reception of the raw materials and their storage after proper conditioning. All these processes also involve in site transport of the raw materials.

Table 3.1.1: Examples of MFA application in socio-economic scenarios

Author	**Approach**	**Scenario**	**Remarks**
Browne et al., (2011)	Analysis of possible dematerialization and decoupling of material consumption and waste generation from economic growth.	The city of Limerick (Ireland) for a ten-year period of time	Application of several indicators to facilitate analysis.
Dai and Chen, (2010)	Evaluation of inputs and hidden flows.	Fossil fuels in China over 2000-2007	Proposal of indexes to evaluate and compare the results.
Hendriks et al., (2000)	Evaluation of the anthropogenic metabolism.	Anthropogenic flows in the city of Vienna and an urban network of towns and villages in Switzerland	MFA as tool for policy decision-making.
Krausmann et al., (2004)	Measurement of the society-nature interaction.	Austria, 1950-2000	Assessment of the correlation between socio-economic metabolism and land use.
Kuczenski and Geyer, (2010)	Industrial metabolism network of flows linking stocks and processes.	PET flows in the US over 1996-2007	Identification of the fate of used PET to propose improvement alternatives.
Muñoz and Hubacek, (2008)	Combination of MFA and structural decomposition analysis.	Chile’s economic growth	Identification of the consequences, in terms of increasing of material consumption, of the economic growth.
Park et al., (2011)	Application of dynamic material flow analysis.	South-Korean steel resource flows within 1993-2020	Study focussed on the recycled and disposed stocks.
Qiao et al. (2011)	Nutritional practices in megacities.	Phosphorus through food consumption in two megacities in China	Identification of key problems in phosphorus metabolism and proposal of potential solutions.
Schwarzenbach et al. (1999)	Evaluation of governmental management regarding site remediation.	Contaminated site at Zürich canton	Analysis of the consequences of the ex-situ cleanup of a contaminated area.

3. Methodology

MEFA methodology consists of the use of terms and procedures to establish mass and energy balances on an industrial system. The generic methodology proposed by Hendriks et al. (2000) has been considered for purposes of this chapter. It comprises the following consecutive steps:

- Definition of the targets of the study.
- System description. The considered system is defined by spatial and temporal boundaries. The spatial boundaries normally correspond to plants, sectors, regions or national economics. A general rule for choosing a system is that the system should be as small and consistent as possible while still being broad enough to include all necessary processes, and material and energy flows. The temporal boundaries depend on the type of system and problem studied. They represent the period of time over which the system is analysed and balanced. Short time periods allow the detection of short-term anomalies and non-linear flows (Brunner and Rechberger, 2004). Furthermore the relevant processes and flows concerning the system should be defined and cross-linked. This stage requires the selection of the relevant processes, which most clearly represent and describe the complex system under study.
- Data acquisition. The flows and stocks can be determined by direct measurements, market research, expert judgment, best estimates, interviews, databases of environmental protection agencies, scientific papers, technical handbooks, and so on.
- Modelling and scenario building. Material and energy balances are performed on those processes where no data is available. The results obtained can be integrated into the model. Computer software is available to support this analysis. The structure of the model must be carefully set up to guarantee the quality of the results from the simulation.
- Evaluation of the MEFA results. The results obtained can be compared with environmental standards or even with other assessment approaches. All of them contribute to design control measures and to identify problems.
- Identification of the IF. IF are selected on the basis of the results from the MEFA. Those flows whose quantity and quality is unsustainable will be pointed out as IF for the industrial system considered. Careful evaluation of MEFA results is required, as not all the quantitatively relevant flows may be IF. Each flow should be carefully analysed to evaluate its potential to be avoided or reduced and its relevance in the industrial system regarding both quantitative and qualitative features.

4. Application of the methodology

The proposed methodology is applied, step by step, to the considered case study. The first stage of the roof-tile manufacture process performed in *Cerámica Verea, S.A.*, ‘transport and storage of raw materials’ is subdued to MEFA to identify its IF.

4.1. Definition of targets

This study refers to the environmental issues related to *Cerámica Verea, S.A.* The objectives of this analysis are:

- Describing and examining the ‘transport and storage of raw materials’ stage within the roof-tile manufacture process.
- Analysing the material streams that flow into this stage, and the processes within the system.
- Evaluating the resulting outputs from this stage: products to ‘raw materials preparation’ stage and emissions to the environment.
- Identifying the IF of the process.

4.2. System description

The main raw material in the roof-tile manufacturing process is clay. Clay is a fine grained soil of hydrous aluminium silicates with iron, magnesium, calcium, sodium and potassium. This material is characterised by being plastic when moist but hard when baked (Casares et al., 2005).

MEFA is applied to a single stage of the process, the ‘transport and storage of raw materials’ stage, which is the spatial boundary of the analysis. This system is related to other elements, such as quarries, refineries, natural resources, atmosphere and the ‘raw materials preparation’ stage.

The ‘transport and storage’ stage comprises the following sub-stages (Figure 3.1.1):

- Lorry transport (clay pit – reception). Extracted clay is transported by lorry from the quarry to the plant. The inputs are clay (coming from four different quarries) and fuel consumed by lorries. The outputs are the exhaust gases, which depend on the type of vehicle (admissible total weight and maximum useful load), the road categories (motorway, country road or local road), the distance covered, and the total weight of the transported clay.
- Reception in the plant (weighing machine). Once the lorries arrive at the plant, they are weighted to determine their load. The origin of the arriving clay is also recorded.
- Lorry transport (reception – piles). After reception, lorries transport the clay to the storage piles within the plant. The only input is the fuel consumed in transportation. The outputs are the exhaust gases and PM (Particulate Matter) generated by transportation over paved and unpaved roadways. PM from paved roads are due to direct emissions from vehicles, as exhaust gas, brake and tire wear emissions, and re-suspension of loose material on the road surface (US EPA, 2006b). When travelling over unpaved roads, the friction of the wheels over the road surface causes pulverization of surface material. Particulates are lifted and dropped from the rolling wheels, and the road surface is exposed to turbulent air flows (US EPA, 2006a).
- Clay souring (open air). Clay is stored in open stockpiles for 2 years to improve their workability. This period is known as clay souring, as clay breaks down and weathers (European Commission, 2007a). Clay with low silica content needs water to achieve the correct moisture degree. Processes involved in this sub-stage are: clay loading onto storage piles, handling of piles, pile-surface wind erosion, stockpiles water irrigation, and clay

unloading. Inputs are water and fuel used in transportation, whereas outputs are dust emissions from storage and loading and unloading operations (NPI, 2001; US EPA, 2006c).

- Lorry transport (piles – warehouse). Weathered clay is transported by lorry from open-air storage to the warehouse to further improve its conditions. The only input is the fuel consumed by the lorries. Outputs are exhaust gases from the vehicles and dust emissions due to transport over the unpaved roadway of the plant.
- Clay storage (warehouse). Clay is stored at the warehouse for a year, while its moisture is carefully controlled and corrected. This sub-stage involves clay loading into the warehouse, material handing with machinery, clay water irrigation and material unloading. Inputs are water and fuel, whereas outputs are dust emissions from handling operations.
- Shovel transport (warehouse – 'raw materials preparation' stage). Finally clay is transported to the 'preparation' stage by shovel. The only input is the fuel consumed by the shovel. Outputs are exhaust gases from the machinery and particulate emissions resulting from shovel transport over the unpaved roadway between the warehouse and the clay preparation bay.

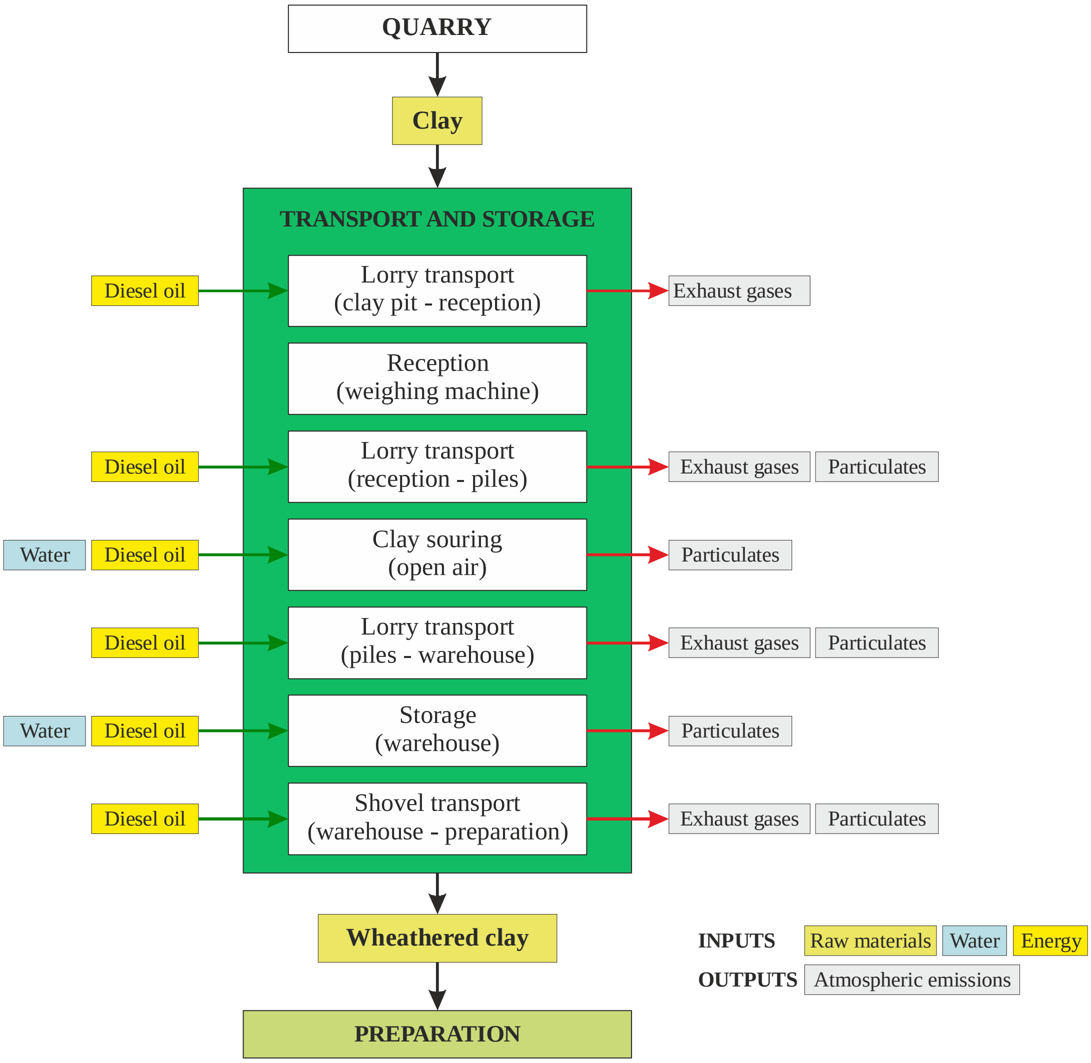


Figure 3.1.1: Flowsheet of 'transport and storage of raw materials' stage

4.3. Data acquisition

Data used in this study was directly obtained from *Cerámica Verea, S.A.*, being the time boundary the year 2005. The information has been classified regarding the sub-stages of the process:

- Lorry transport (clay pit –reception). Input data is shown in Table 3.1.2.
- Reception (weighing machine). No data is required in this sub-stage.
- Lorry transport (reception – piles). Besides data in Table 3.1.2 (lorry weight and load), it is also necessary to know the distance covered between reception and the open-air storage: 200 m on paved road and 200 m on unpaved road. Besides, in 2005 there were 101 days with at least 0.254 mm of precipitation (*MeteoGalicia*, 2006) (this data is required to calculate particulate emissions).
- Clay souring (open air). Data from Table 3.1.2 is also required, as the amount of each type of clay and their moisture content, but also the annual average wind speed. This parameter is set to 1.8 m/s for 2005 (*MeteoGalicia*, 2006). The volume of water used to irrigate the piles is 2377 m^3. It is considered that the final moisture content of the clay in this sub-stage is 30%.

Table 3.1.2: Input data for 'lorry transport (clay pit – reception)', 'lorry transport (reception – piles)' and 'clay souring (open air)' sub-stages regarding the four types of clay used as raw material (*Cerámica Verea, S.A.*, 2006)

Parameter	**Clay 1**	**Clay 2**	**Clay 3**	**Clay 4**
Total flow (wet basis) (t/y)	15668	13056	38566	5223
Covered distance per journey (km)	3.92	7.43	15.00	7.43
Lorry weight (t)	15.60	16.69	16.87	16.69
Lorry load (t)	25	15	25	15
Road categories (%)				
Highway	55	84	95	84
Secondary road	45	16	5	16
Material moisture content (%)	20	20	35	20

- Lorry transport (piles – warehouse). Input data is shown in Table 3.1.3.
- Clay storage (warehouse). The same data as in 'clay souring (open air)' sub-stage is required. Nevertheless, particulate emissions are less important as the storage area is covered. In this case, the volume of water used to irrigate the piles is 264 m^3. The final moisture content of the clay is 32.3% (wet basis) (*Cerámica Verea, S.A.*, 2006).
- Shovel transport (warehouse – 'raw materials preparation' stage). Data needed to calculate the emissions from this sub-stage is shown in Table 3.1.3.

Table 3.1.3: Input data for 'lorry transport (piles –warehouse)' and 'shovel transport (warehouse – raw materials preparation)' sub-stages (*Cerámica Verea, S.A.*, 2006)

Lorry transport (piles – warehouse)	
Covered distance per travel (m)	200
Number of lorries	2
Lorry weight (t)	16
Lorry load (t)	20
Shovel transport (warehouse – raw materials preparation)	
Covered distance per travel (m)	100
Fuel consumption (l/h)	10.8
Load (t)	6
Daily working hours	10

4.4. Modelling and scenario building

The software used build the model is Umberto (*IFU*, 2005), developed by *Ifu Institut für Umweltinformatik* Hamburg GmbH in cooperation with *Ifeu-Institut für Energie-und Umweltforschung* Heidelberg GmbH.

Umberto allows modelling, calculating and visualizing material and energy flow systems. The user can create individual projects and define several scenarios within a project. Material and energy flow networks in Umberto consist of these different types of elements:

- Transition. It is a site in the flow network where materials and energy are transformed. They are represented by squares. A transition can be defined by coefficients between input and output flows (linearly dependent) or by mathematical expressions (non-linear processes).
- Place. It is a site in the flow networks where material and energy are stored or distributed. They are represented by a circle. There are four different types of places:
  - Input. These places are the boundaries of the network or the part of the network to be examined with regard to the flows of material and energy entering the system.
  - Output. They fix the boundaries of the system regarding the flows leaving the system.
  - Storage. These elements are places where materials can be stored.
  - Connection. These places can only distribute flows and cannot act as storage.

  Furthermore, there are two special types of places:

  - Input/output. They combine the input and output place function into a single place.
  - Port. This element represents the link between two network layers: a net and its subnet.
- Arrows. They link places and transitions. They show the direction of materials and energy flows.

Figure 3.1.2 shows the main network for the 'transport and storage of raw materials' stage. The inputs are raw materials (four types of clay), secondary materials (water) and operating supplies (diesel oil). The outputs are the weathered clays to the 'raw materials preparation' stage, and atmospheric emissions (dust and exhaust gases). The materials are defined and structured in hierarchical groups according to raw materials, secondary materials, energy and emissions.

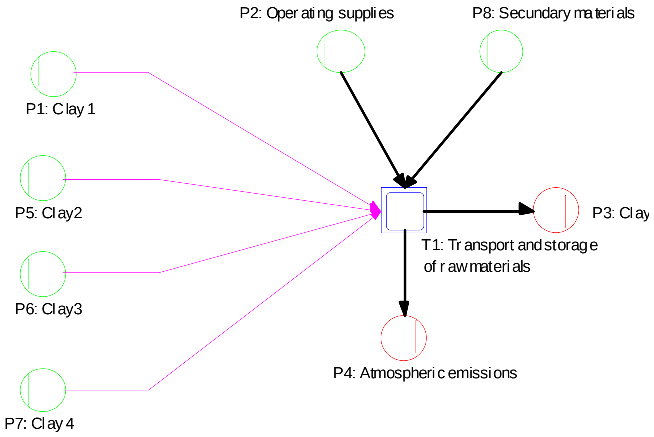


Figure 3.1.2: Main network (Torres et al., 2008)

The transition (clay storage stage) is modelled as a subnet in a separate editor window (Figure 3.1.4). In this network, the different steps of the process are represented:

- Lorry transport (clay pit – reception). The transport transition is specified by importing specification data from the module library. This module describes the transport of goods by lorry. It allows selecting between six different lorry size classes. The lorry is powered by a diesel engine and requires diesel oil as fuel. In this module the direct emissions are calculated, without considering fuel supplying. Outward and home trips are considered. Parameters such as the load factor of the outward trip, the load factor of the home trip, the vehicle type, or the distance covered (in motorway, highway and secondary roads) can be fixed.

  The default transport module has been modified to calculate the travelled distance as a function of the quarry-plant distance and amount of clay transported by lorry.

- Lorry transport (reception – piles). It involves two transitions. The first transition (lorry transport) uses the same module library as the previous transition to calculate the emissions derived from fuel combustion. The second transition (transport on paved road and unpaved road) calculates dust emissions as a result of lorry transport on the paved and unpaved roadways of the plant. In this case, the emissions are calculated using emission factors.

  Particulate emissions from re-suspension of loose material on the road surface caused by lorry transport on a paved road are estimated as:

$$E_p = \left[k_p \cdot \left(\frac{sL}{2} \right)^{0.65} \cdot \left(\frac{W}{3} \right)^{1.1} - C \right] \cdot \left(1 - \frac{P_L}{4 \cdot N} \right) \qquad \textit{Equation 3.1.1}$$

  E_p (g/VKT [1]) is the particulate emission factor for transport on a paved road. k_p (g/VKT) is the particulate size multiplier for the particulate size range and units of interest. The value used for this parameter is 4.6 g/VKT, referred to PM_{10}. sL (g/m^2) is the road surface silt loading, 70 g/m^2 for this case. W (t) is the average weight of the vehicles travelling on the road. C (g/VKT) is an emission factor for exhaust, brake wear and tire wear, 0.1317 for PM_{10} particulate size. P_L is the number of wet days with at least 0.254 mm of precipitation for the time boundary (101 for this case). N is the number of days of the time boundary.

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[1] VKT is the acronym of Vehicle Kilometer Traveled.

For transport on unpaved surfaces, emissions are estimated as (US EPA, 2006a):

$$E_{np} = 281.9 k_{np} \cdot \left(\frac{s}{12}\right)^{a} \cdot \left(\frac{W}{3}\right)^{b} \cdot \left[\frac{(365 - P_L)}{365}\right] \qquad \textit{Equation 3.1.2}$$

E_{np} (g/VKT) is the particulate emission factor for travelling on unpaved surfaces. s (%) is surface material silt content, 7.1% for this case. k_{np}, *a* and *b* are empirical constants. In this case, k_{np}=1.5 lb/VMT^3; *a*=0.9; and *b*=0.45.

- Clay souring (open air). This transition calculates PM emissions caused by clay loading and unloading, and pile handling. The following empirical expression is applied (US EPA, 2006c):

$$E_s = k_s \cdot (0.0016) \cdot \frac{\left(U/2.2\right)^{1.3}}{\left(M/2\right)^{1.4}} \qquad \textit{Equation 3.1.3}$$

E_s (kg/t) is the particulate emission factor for loading, unloading and pile handling operations. k_s is particulate size multiplier (dimensionless). The value of this parameter for PM_{10} is 0.35. U (m/s) is the average wind speed, 1.8 for this case. M (%) is the material moisture content.

The average value used to calculate dust emissions by wind erosion is 0.4 (kg/ha)/h (3504 (kg/ha)/y) (NPI, 2001). In this transition, the change in the amount of clay due to stockpiles irrigation with water is calculated internally.

- Lorry transport (open air storage –warehouse). It involves two transitions. This sub-stage is calculated the same way as the previous transitions. In this case, lorry transport only happens on unpaved roadways. As an example, Figure 3.1.3 gives the mathematical formulation of the transition ‘transport on unpaved road’.

```
; Emission factor [Other mobile sources & Machinery, EMEP-CORINAIR]
; C annual fuel consumption    VOLVO L1205 shovel
; g NOx=48.8*C           g NMVOC=7.08*C
; g CH4=0.17*C           g CO=15.8*C
; g NH3=0.007*C          g N20=1.3*C
; g PM=5.73*C            ug benzo(a)pyrene=30*C
Vv=10.8                      ; L/h
D=0.865                      ; D diesel density kg/L
Vm=Vv*D                      ; Vm consumption kg/h
R=100                        ; R distance travelled m
H=10                         ; H dialy working hours
C=Vm*H*365
X04=C
; Emissions
Y00=X00
Y01=X01
Y02=X02
Y03=X03
Y04=48.8*C/1000
Y05=7.08*C/1000
Y06=0.17*C/1000
Y07=15.8*C/1000
Y08=0.007*C/1000
Y09=1.3*C/1000
Y10=5.73*C/1000
Y11=30*C/1E+9
; ParticulatesEmission factor (Australia NPi)=0.012 kg/t
Y12=0.012*((X00+X01+X02+X03)/1000)
```

Figure 3.1.3: Mathematical formulation of ‘transport on unpaved’ road transition

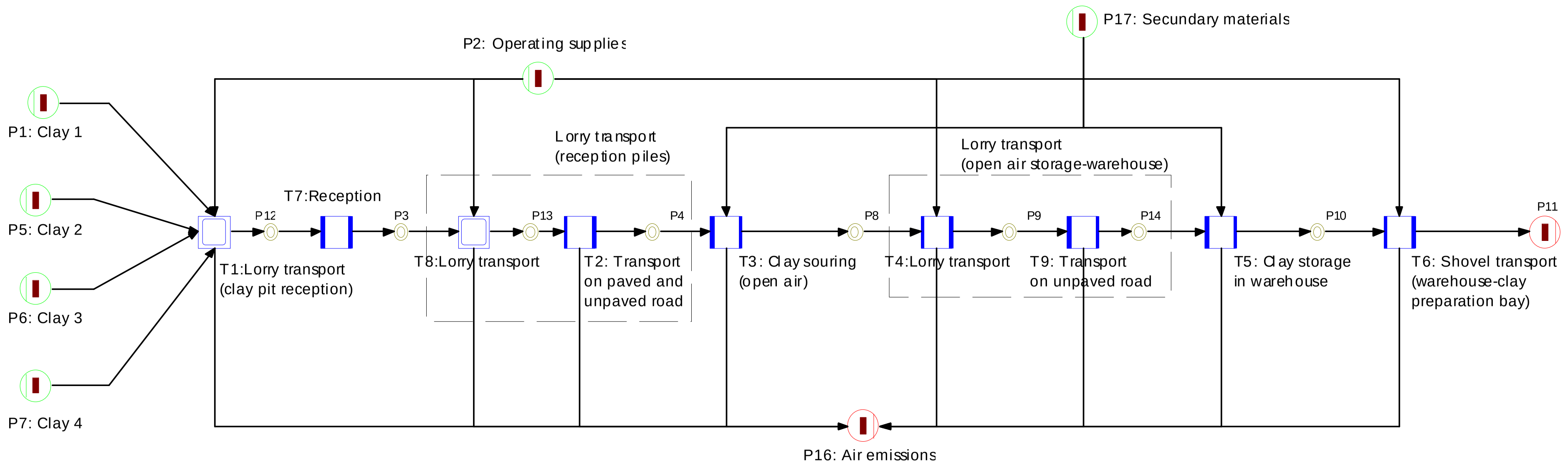

Figure 3.1.4: Subnet for the 'transport and storage of raw materials' stage (Torres et al., 2008)

- Clay storage in warehouse. The transition calculates particulate emissions from clay loading and unloading and pile handling by applying Equation 3.1.3. However, it is considered that the emission values are 20% of the original value because of the action of the warehouse walls and the prevailing wind direction. Again, the change in the amount of clay due to stockpiles irrigation with water is calculated by the program.
- Shovel transport (warehouse – clay preparation bay). It calculates the emissions due to the combustion of fuel in the engine of the shovel using the emission factors given in Table 3.1.4.

  Particulate emissions caused by the activity of the shovel are calculated using the emission factor of 0.012 kg/t (NPI, 2001).

Table 3.1.4: Emission factors for 'other mobile sources and machinery' in industry (EMEP CORINAIR, 1996b)

Diesel engines (g/kg $_{fuel}$)							
NO_x	NMVOC	CH_4	CO	NH_3	N_2O	PM	Benzo(a)pyrene
48.8	7.08	0.17	15.8	0.007	1.30	5.73	$30 \cdot 10^{-6}$

Prior to any calculation, some input parameters have to be introduced to run the model. For this case, the parameters needed are the annual amount of the four types of clay. These flows are introduced as manual values in the input arrows of clay according to the data included in Table 3.1.2. Umberto calculates the unknown flows in the network using known flows and process specifications.

4.5. Evaluation of the MEFA results

Once the network is calculated, the results can be viewed for each network element. Table 3.1.5 shows the inputs and outputs of the first transition, 'lorry transport (clay pit – reception)'. The annual amount of diesel fuel necessary to carry out this task 28250 t. Apart from the four types of clay that leave this stage as products, the main output are the emissions from fuel combustion. The main pollutant is CO_2, followed by N_2O, CO, NMVOC (Non-Methane VOC) and SO_2.

Table 3.1.6 shows the annual emissions to air due to shovel transport from warehouse to clay preparation bay. In this case, all flows are calculated with the function defined for this transition (Figure 3.1.3). PM_{10} is the main pollutant, caused by fuel combustion and, above all, as a result of vehicles travelling on unpaved roadways.

Table 3.1.5: Balance of transition T1 - lorry transport (clay pit-reception)

Place	Material	Quantity	Unit
Input			
P2	Diesel fuel	28250.03	t
P6	Clay 3	38566.06	t
P1	Clay 1	15667.46	t
P5	Clay 2	13056.22	t
P7	Clay 4	5222.49	t
Output			
Air emissions			
P16	SO_2	25425.03	kg
P16	NO_x	878809.38	kg
P16	NMVOC, unspecified	98858.20	kg
P16	Particulates (small)	46745.99	kg
P16	CO	223024.09	kg
P16	CO_2, fossil	89703180.98	kg
P16	Benzene	2144.21	kg
P16	HCl	28.25	kg
P16	Benzo(a)pyrene	0.22	kg
P16	CH_4	2709.53	kg
P16	N_2O	9367.71	kg
P16	NH_3	565.00	kg
P16	PCDD[2], PCDF[3]	$169 \cdot 10^{-6}$	kg
P16	Methylene oxide	9141.10	
Others			
P3	Clay 2	13056.22	t
P3	Clay 1	15667.46	t
P3	Clay 3	38566.06	t
P3	Clay 4	5222.49	t

Table 3.1.6: Arrow specifications A22 (output of transition T6 (shovel transport))

Material	Quantity (01/01-31/12/2005)	Unit
NMVOC, unspecified	241.42	kg
NO_x	1664.00	kg
PM_{10}	925.70	kg
NH_3	0.24	kg
Benzo(a)pyrene	$1 \cdot 10^{-3}$	kg
CO	538.75	kg
N_2O	44.33	kg
CH_4	5.80	kg
Particulates (small)	195.38	kg

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[2] PCDD: Polychlorinated dibenzodioxins

[3] PCDF: Polychlorinated dibenzofurans

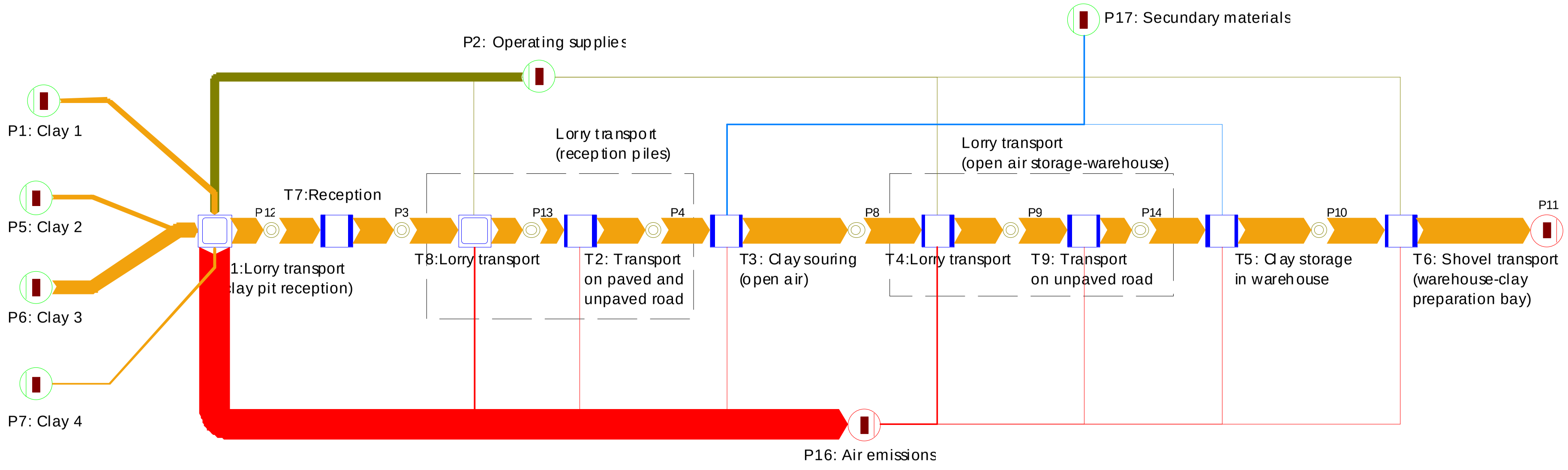

Figure 3.1.5: Sankey diagram of storage stage of clay (green: diesel fuel; yellow: raw materials; red: emissions (air); blue: water) (Torres et al., 2008)

Umberto uses Sankey diagrams to display material, energy and cost flows. Figure 3.1.5 shows the Sankey diagram for ‘transport and storage of raw materials’ stage. The selected material flows are diesel fuel, raw materials (including the four clay types), emissions to air (exhaust gases and PM), and water.

The main source of emissions to air is ‘lorry transport (clay pit – reception)’ sub-stage, and the preferred clay is number 3. This quarry is located further than the other clay pits, so emissions related to transporting this clay are larger if compared with the others.

Water is used in ‘clay souring (open air)’ and ‘clay storage in warehouse’ stages. The largest consumption takes place during clay weathering. In this case, water consumption is not a problem because this resource comes from the rainwater collected in a lagoon inside the plant.

Umberto allows editing the balances according to materials, transitions, places and arrows. Table 3.1.7 shows the global balance sorting the streams by material order. Inputs are classified as raw materials, energy and secondary materials. Outputs are emissions to air and clay. Apart from the exhaust gases, the most significant pollutant is the PM emitted as a result of lorry and machinery operating, as well as clay loading, handling and unloading.

Table 3.1.7: Total balance of materials

	Item							**Quantity**	**Unit**
Inputs [a]	Raw materials (wet basis)				Clay 1	Moisture content (%)	20	15667.46	t
					Clay 2		20	13056.22	t
					Clay 3		35	38566.06	t
					Clay 4		20	5222.49	t
	Secondary materials				Water			2641.00	t
	Energy				Diesel fuel			30381.10	t
Outputs [b]	Emissions to air	Inorganic compounds			NH_3			607.18	kg
					CO_2			96361.71	t
					CO			245580.76	kg
					N_2O			10107.39	kg
					HCl			30.35	kg
					NO_x			648289.90	kg
					SO_2			27312.29	kg
		Particulates (small)						51410.36	kg
		PM_{10}						1331.91	t
		VOC	Methane					3107.19	kg
			NMVOC	Halogenated	Aromatic	PCDD, PCDF		$1.82\cdot10^{-6}$	kg
				Aldehydes		Methylene oxide		10463.11	kg
				Aromatic	HC	Benzene		2454.31	kg
				PAH[c]		Benzo(a)pyrene		0.24	kg
				Unspecified				113396.78	kg
	Raw materials (wet basis)				Clay 1	Moisture content (%)	32.3	18513.99	t
					Clay 2			15428.33	t
					Clay 3			37027.98	t
					Clay 4			6171.33	t

[a] Combustion air is not included.

[b] Water from souring which is not retained in the clay is not included.

[c] PAH: Polycyclic Aromatic Hydrocarbons

4.6. Identification of the IF

After evaluating the results of MEFA and after carefully considering the quantitative and qualitative conditions of each flow involved in the industrial process, three IF have been detected for the ‘transport and storage of raw materials’ stage:

- Inputs: the only input identified as IF is diesel fuel, specially the consumed in the ‘lorry transport (clay pit – reception)’ sub-stage. This IF is highly influenced by the quite bigger consumption of clay 3 over the rest of raw materials. However, due to the availability and quality of clay 3 regarding the other clays available, it is not easy for the plant to reduce the consumption of this type of clay, and so it has not been identified as an IF.
- Outputs: two IF have been detected among the outputs of the stage.
  - Exhaust gases: mainly from the ‘lorry transport (clay pit – reception)’ sub-stage. They are also generated in all the other stages, though at a smaller scale. The main pollutant in this flow is CO_2, followed by N_2O, CO, NMVOC and S_2O.
  - Particulate emissions: also from the ‘lorry transport (clay pit – reception)’ sub-stage.

5. Results and discussion

This chapter has evaluated the suitability of MEFA as an IF identification tool, regarding the principles of IE and industrial metabolism philosophies. A typical methodology for MEFA has been applied, including target definition, a thorough qualitative description of the system, data acquisition, modelling and scenario building using Umberto software, evaluation of the results from MEFA, and finally identification of the IF of the considered industrial system.

The application of MEFA to the case study has provided important information about the ‘transport and storage of raw materials’ stage of the roof-tile manufacturing process. It has also led to the identification of three IF for this system.

Transport-related operations have the highest negative impact over the environment, being ‘lorry transport (clay-pit reception)’ the most impactful sub-stage. Almost 93% of total fuel used in the whole stage, is consumed here, and accordingly its diesel fuel input has been pointed out as an IF.

Another consequence of this high fuel consumption is the exhaust gas emissions, also greater than for the rest of the stage, and also identified as IF. The main pollutants is CO_2. These emissions depend on several factors, as the distance from the quarry to the plant, the load of the lorry and the type of road.

Other sources of pollution are the diffuse emissions of particulate matter. This type of pollution is generated as a result of the vehicle activity over the paved and unpaved roadways of the plant. Again, they are especially relevant in the ‘lorry transport (clay-pit reception)’ sub-stage, and so they are also defined as IF for this stage.

Clay 3 has also been pointed out as a conflictive flow, as it has a great impact over the total exhaust gases emissions. It is the main raw material and comes from the furthest quarry. However, owing to their specific characteristics which make it the best raw material for roof-tile production, it has not been selected as an IF. As a more equitable distribution of the four types of clay is not an available option, the proper planning of clay transport could be suitable for reducing the atmospheric emissions associated to this material.

In spite of being intensively consumed, water for moistening is a sustainable flow, as only rain water is consumed. This is a BEP used in this plant, as it avoids consuming water from any other source. Hence this flow is not regarded as an IF.

These results show how MEFA provides early recognition of environmental problems and how this information can be used to establish priorities for improving an existing plant. It has effectively led to the identification of the IF of the industrial system considered, which makes it a suitable tool for IF identification.

6. Conclusions

This chapter has validated MEFA as a suitable tool to identify IF in an industrial system. It applies the principles of industrial metabolism about analyzing flows of materials and energy to identify and assess all possible emission sources and other effects related to these flows. As an industrial metabolism derived tool, MEFA was a potential tool for IF identification. Its application to an industrial system has validated this theory, as it has efficiently led to the identification of the flows likely to be improved, the IF.

MEFA methodology has been proved to be a valuable tool when quantitatively identifying the material and energy flows related to an industrial system. It qualitatively analyses all the individual processes involved and quantitatively identifies all the material and energy flows. The results obtained are of significance for the plant as they can be used to modify the operating conditions of the plant in terms of materials usage, diesel fuel consumed, water and clay usage.

This methodology requires deep knowledge of the analysed process, as the quality of the model highly depends on the ability of the modeller, but also on the information available about the process. Direct contact with the industrial systems under study is recommended, aiming to get rigorous information about the process but also enough data to run the model. Otherwise the models will not faithfully reflect reality, providing inaccurate results. The success of MEFA highly depends on the system description and data acquisition stages of the methodology, as they strongly influence the quality of the models.

Applying MEFA by means of software such as Umberto facilitates IF detection. This software graphically displays material and energy flows in Sankey diagrams, allowing their allocation and quantification. Sankey diagrams provide a useful and visual source of information. All the material and energy flows are qualitatively displayed, so that the sources of inputs, outputs and internal flows are identified. Decision-makers can base their improvement proposals on these diagrams, focussing their solutions on the specific processes or stages were consumptions are demanded, emissions are released, or any material or energy stream is unsustainably managed.

Though quite useful as an IF identification tool, MEFA has some limitations. Not all the quantitatively relevant flows could be considered as IF, whereas some flows whose amount may not be disturbing should be avoided or reduced (due to their economic cost or their impact over the environment) and pointed out as IF. MEFA simply quantifies and traces flows, providing valuable information to decision-makers, which are the ones who must evaluate which flows should be classified as IF, owing to their specific features.

Its application in an industrial plant has corroborated the theory that, though typically applied in socio-economic environments, MEFA can be quite useful when applied in industrial contexts, considering not only industrial parks but also individual plants. It is a powerful tool on process-optimisation oriented strategies, as it can easily quantify and trace all the flows involved in a given process. Accordingly, once the major unsustainable flows have been properly identified, they can be defined as IF so that specific corrective measures could be proposed to avoid, reduce or take advantage from them.

As an IF identification tool, MEFA could be complemented by any methodology that proposes corrective measures. That is the case of the methodology for technical inventories, BAT Analysis, proposed in chapter 2. The combination of IF detection and corrective measures implementation, by means of identification tools and technical inventories, into a single methodology is meant to get sustainable industrial systems.

3.2

PROCESS SIMULATION AND WASTE MANAGEMENT HIERARCHY

Summary

Process simulation has been proposed as a suitable tool to identify IF, as it is able to simulate and quantify material and energy flows within an industrial system. This tool predicts the behaviour of processes after modifying one or more variables. It is widely used with multiple purposes, as evaluating modifications on processes, predicting emissions, or analysing integration potentials, to mention some. This chapter presents and applies a methodology for identifying the IF of treatments selected from an inventory.

The methodology establishes some criteria based on the European WMH and on the IPPC philosophy to select suitable alternatives for waste management in an industrial system. It includes three well differentiated modules, starting with a description of the system under study.

Then qualitative analysis is applied to define the waste stream concerned and to elaborate a technical inventory, representing the available management options classified in accordance with the WMH. The most appropriate technique or set of techniques is selected regarding the pollution prevention principles established by the IPPC philosophy but also respecting the hierarchical classification of the WMH.

The final module involves the quantitative analysis of the technique selected. It includes the selection of appropriate simulation software, data acquisition, modelling and scenario building, and simulation to quantitatively define all the material and energy streams of the process, but also the specific quantitative requirements of the units involved. This quantitative analysis leads to the identification of the IF of the system.

The suitability of the methodology is validated in a case study, which considers the waste management sector, represented by a waste treatment plant treating different residues. The specific waste considered is used lubricating oil. The application of the methodology results in the selection of a recycling treatment, ‘regeneration of oils by extraction with solvents’, which is qualitatively validated by process simulation. The simulation software selected to validate the methodology is Aspen HYSYS V7.1. After simulation, four IF are detected for the system.

The application of process simulation validates it as a suitable tool for IF identification. However, the implementation of the methodology also points out that the biggest potential of process simulation is predicting the behaviour of a system.

1. Introduction

Process simulation is implemented by process simulators, which are software programs designed to model industrial systems (Casavant and Côté, 2004). They are useful tools to predict process behaviour in response to changes in one or more variables (Halim and Srinivasan, 2011), both steady and unsteady state. Models used in steady-state simulation base their predictions on physical mechanisms (Palmer and Realff, 2002), being the most popular software packages ASPEN Plus, CADSIM Plus, CHEMCAD, PRO/II and HYSYS. When used for dynamic modelling, process simulation is particularly powerful to design control systems and verify their effectiveness (Bezzo et al., 2004). In any case, authors agree that modelling is highly dependent on the expertise of individual modellers, the organizational procedures and support, and also on the modelling and simulation tools (Cameron and Ingram, 2008).

Focussing on steady-state simulation, the mentioned software packages are well known and widely applied, though they are not the only options available. Other authors develop their own tools or improve the existing ones, normally adapting them to specific situations. That is the case of SyPProT (Symbolic Pre Processing Tool) (Köhler et al. 2001), which improves mathematical formulation; the WAR algorithm (Cabezas et al., 1997), used to calculate the potential environmental impact of a process (Barrett Jr. et al., 2011); or GAMEDE, an accurate model for simulation in farms and dairy industry (Vayssières et al., 2009). In other cases the simulator is integrated in a methodology with different purposes. Sammons Jr. et al. (2008) based a decision support tool to optimise biorefining plants on process simulation; González Alriols et al. (2009) used Aspen Plus to optimise recovery and recycling conditions in a process; and more recently Lutze et al. (2012) developed a simulation supported methodology to improve existing processes. In all cases the methodologies have been validated, confirming their suitability for the specific situations for which they were designed. This tendency of adapting simulation tools to concrete needs is facilitating process modelling in sectors with specific needs and particularities which may not be considered in the traditional simulators.

Besides the variety of contexts in which it can be applied, process simulation can also be used in sustainability based strategies. All the above mentioned tools can be applied and adapted in such a way that sustainability criteria are analysed or evaluated in a model. There are some contributions in the literature that illustrate this type of approaches, being most of them new methodologies that include process simulation. One approach on sustainable process design is the one given by Cabezas et al. (2005), who applied simulation to explore the relation between sustainable ecosystems and industry; or Halim and Srinivasan (2008), who use intelligent simulation-optimisation to identify potential minimisation alternatives, strongly focussing on waste prevention and management. Another example is SustainPro, an indicator-based approach proposed by Carvalho et al. (2008) to identify, select and evaluate sustainable alternatives of chemical processes.

As the knowledge and expertise of individuals strongly influences modelling, some of the sustainability based methodologies include elements driven by the criteria of the modeller. That is the case of ENVOPExpert, by Halim and Srinivasan (2011), a knowledge-based design support system on a simulation-optimisation framework for sustainable design of chemical process plants. One step further is the heuristic based methodology that integrates two software tools, ENVOPExpert and SustainPro, recently developed by Halim et al. (2011). These knowledge-based methodologies are quite subjective, as they are highly dependent on the criteria of the modeller. Though valuable, these criteria should be supported by solid information about the benefits and drawbacks of the decisions made or the alternatives chosen.

The objective of this chapter is to propose a methodology for selecting accurate waste treatment alternatives from a technical inventory whose potential IF are detected by process simulation. The WMH set by the EU and the IPPC philosophy have been selected as driving forces for selecting the optimal alternative to manage waste. The methodology combines them as decision tools, while process simulation is used as a quantitative evaluator that leads to the identification of the IF of the industrial system. The suitability of the methodology is validated in a case study, the waste management sector represented by a generic plant.

2. Case study

The case study considered is the waste management sector, which is directly affected by the WMH and by the directive setting it, Directive 2008/98/EC (EU, 2008b). A waste treatment plant interested on implementing new processes for in-situ waste recovery has been selected to validate the methodology proposed.

3. Methodology

Waste management is defined by the European waste Directive as “the collection, transport, recovery and disposal of waste, including the supervision of such operations and the after-care of disposal sites, and including actions taken as a dealer or broker” (EU, 2008b). It is a complex issue implicating several different aspects as social responsibility, global economics, production processes, material technology or environmental impact (Galante et al., 2010).

In recent years many authors have discussed about different waste management strategies, being the general trend designing MSW (Municipal Solid Waste) management systems that operate at regional or even local level. They mainly consider the selection of the most appropriate treatment and disposal installations, the distribution of waste from the production centres to these installations, and the design of suitable transport routes. Most of these works consist of multi-objective models combining economical and environmental aspects, which facilitate decision-making while designing the waste management system (Abou Najm and El-Fadel, 2004; Fiorucci et al., 2003; Galante et al., 2010; Salvia et al., 2002; Shmelev and Powel, 2006). Other similar works focus on management systems for hazardous waste (Sheu, 2007). In these cases other factors, such as the inherent risk of the management activities (Nema and Gupta, 1999) or a more exhaustive waste characterization (Misra and Pandey, 2005), have to be taken into account.

The WMH provides a robust framework to set waste management goals and to establish targets (Lazarevic et al., 2012).It has legal status and it is required to be applied by Member States in waste management plants and in waste prevention programs. Besides, the IPPC Directive also provides a binding legal framework for proper waste management. It aims, among others, to prevent the generation of waste, in order to achieve a high level of protection of the environment taken as a whole. Accordingly, waste shall be managed respecting these principles, guaranteeing that no pollution is generated and, when unavoidable, it is properly managed.

The methodology proposed combines the WMH and the IPPC philosophy as decision criteria for selecting the optimal waste treatment alternative for a given residue. The chosen alternative is qualitatively evaluated by process simulation to detect the IF of the process. The procedure proposed includes the following elements:

1. System description: definition of the specific industrial system under study.
2. Qualitative analysis:
    - Definition of the waste stream. The waste to be treated is defined in qualitative terms, identifying the possible pollutants and the main components.
    - Technical inventory. It gathers the available management options and classifies them according to the WMH. The available management options are classified as preventive, preparing for re-use, recycling or recovering treatments. Disposal is not considered as an alternative, as it is the last option of the hierarchy.
    - Selection of the most appropriate technique on the basis of the WMH and the IPPC philosophy. Among the available alternatives, one technique or a set of them is selected for implementation regarding its classification in the WMH and its potential to prevent pollution achieving a high level of protection of the environment taken as a whole.
    - Detailed description of the proposed process. The selected process is qualitatively defined, describing the processes performed and the stages involved. This step also involves the identification of the inputs and outputs to the process.
3. Quantitative analysis
    - Software selection. It involves selecting appropriate software for process simulation.
    - Data acquisition. Compilation of specific quantitative information about the waste concerned and the treatment proposed.
    - Modelling and scenario building. The proposed process is modelled for simulation. Material and energy balances, as well as operating conditions are specified for those stages where no data is available. Computer software is used for modelling and simulation. The structure of the model must be carefully set up to guarantee the quality of the results from the simulation.
    - Simulation and results evaluation. The scenario is simulated, and the results are assessed to identify the potential benefits of implementing the proposed process.
    - Identification the IF of the process. IF are selected regarding the results from process simulation. Quantitative and qualitative data should be carefully evaluated to detect those flows which should really be defined as improvable.

4. Application of the methodology

The proposed methodology is applied, step by step, to the considered case study, the waste management sector, represented by a generic plant. The methodology is intended to propose a suitable waste management option for a specific waste, regarding the WMH and the IPPC philosophy, and to accurately identify the IF of the resulting process.

4.1. System description

The system considered is a specific waste stream, used lubricating oil, which is generated by a waste producer (derived from maintenance operations) and is delivered to a waste treatment plant, where it has to be further processed.

Besides the hierarchical categories, the Framework Directive on waste defines the specific case of the ‘regeneration of waste oils’, as any recycling operation whereby base oils can be produced by refining waste oils, in particular by removing the contaminants, the oxidation products and the additives contained (EU, 2008b). This policy also establishes that Member States shall ensure that waste oils are collected separately (where feasible), are treated according to the WMH and without risk to the human health and the environment and, where feasible, waste oils of different characteristics are not mixed between them or with other waste or substances. These requirements involve additional and specific requirements for the waste oils, which not only should apply the WMH, but do it under certain conditions.

As defined by the Framework Directive on waste, used lubricating oils are waste oils[4]. Mineral-based oils used as lubricants are a mixture of hundreds to thousands of hydrocarbons (mainly straight and branched chain hydrocarbons (alkanes), cycloalkanes, and aromatic hydrocarbons), including some fractions of nitrogen and sulphur containing compounds (ATSDR, 1999). Used lubricating oils are the by-products derived from the application of lubricants in any kind of machinery. They must be periodically replaced due to the contamination from dirt, water, salt, metals, spent additives, or other materials (Hamad et al., 2005). They are a complex mixture of low and high (C_{15}-C_{50}) molecular weight aliphatic and aromatic hydrocarbons, heavy metals and various organic and inorganic compounds (Kanokkantapong et al., 2009; Ramasamy and T-Raissi, 2007).

Used oils suppose a great hazard for both the environment and the human health if not disposed of correctly (Guerin, 2008; Hamad et al., 2005). Only in Europe, more than $4.9 \cdot 10^6$ tonnes of base oils were consumed in 2000, roughly 65% as automotive oil and up to 35% as industrial oil (European Commission, 2001a), meaning about $2.1 \cdot 10^6$ t/y of used lubricating oils (Sotelo et al., 2001). Normally, these waste oils are recycled to produce heavy oil or lower-graded fuels (Singhabhandhu and Tezuka, 2010), though other energy-intensive processes such as vacuum flashes, solvent extractions, distillation or de-metallization (Ramasamy and T-Raissi, 2007) are also used. In spite of the availability of options, about 50% of the waste oil in the EU is used as fuel, 35% in cement kilns (European Commission, 2006c). Besides, even the most advanced technologies only recover a part of the used lubricating oil, and produce in turn an important amount of wastes that have to be dealt with.

Though it seems that the best solution for the management of used lubricating oils is to employ the lubricating oil more efficiently (Kanokkantapong et al., 2009), waste minimization by proper recovery processes is a valuable option, given the fact that waste oils cannot be avoided. However, there is a lack of proper methods to adapt typical waste management strategies to the progressive European targets (Pires et al., 2011), and so some methods or strategies are needed to facilitate accurate used lubricating oil management.

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[4] Waste oils means any mineral or synthetic lubrication or industrial oils which have become unfit for the use for which they were originally intended, such as used combustion engine oils and gearbox oils, lubricating oils, oils for turbines and hydraulic oils (EU, 2008b).

4.2. Qualitative analysis

This stage of the methodology involves the definition of the waste stream, the development of an inventory of available techniques for used lubricating oil management, the selection of the most appropriate treatment regarding the WMH and the IPPC philosophy, and finally a detailed description of the proposed process.

4.2.1. Definition of the waste stream

Used lubricating oils from industrial machinery and the automotive sector are considered. They are weekly received at the waste treatment plant, mixed and stored until delivery. These used lubricating oils have a rather heterogeneous composition and contain quite a variety of pollutants.

Lubricating oils contain a large number of hydrocarbons and between 1-25% of additives (Sotelo et al., 2001) whose formulae in most cases is a trade secret (European Commission, 2006c). Therefore the composition of the used lubricating oils is quite difficult to generalize. It is quite dependent on the original crude oil and its additives, the combustion products, and the time the oil has remained in the engine (Ramasamy and T-Raissi, 2007).

As the considered used lubricating oils come from small industrial plants and minor garages, they will be mostly polluted with water, ashes, PCB (polychlorinated biphenyl), chlorine and heavy metals, mainly lead and copper.

4.2.2. Available management options according to the WMH

Available management options are firstly collected and described, and then they are classified according to the WMH.

INVENTORY OF TREATMENT ALTERNATIVES

Traditionally, the main alternatives for used lubricating oil management are re-refining and direct burning for energy recovery, each accounting for about 30% of the total oil recovered in the EU (European Commission, 2006c). Each of these general alternatives includes a variety of options which are shortly described.

- Re-Refining: It involves all the techniques meant to reconvert used lubricating oils into base oils that can be used to produce new lubricants. Normally re-refining is a multi-step, complex and energy intensive process involving lightweight impurities removal, heaviest impurities removal, hydrogenation and finally re-additivation (Starkey Ott et al., 2010). In general terms, re-refining techniques include acid/clay processes, distillation, chemical and clay treatments and solvent extraction (Gourgouillon et al., 2000; Kanokkantapong et al., 2009).
    - Acid/clay process. It involves treating the residual oil with sulphuric acid, which is then neutralized with clay. Though traditional (Hamad et al., 2005), this method is in disuse due to economic and environmental issues, mostly derived from residual clay treatment.
    - Vacuum distillation and hydrogenation. It involves atmospheric distillation (to remove light hydrocarbons and water), followed by vacuum distillation to separate hydrocarbon fractions, and hydrogenation to remove S and N compounds. 60% of base oil and 8% of light oil is obtained. Residues contain additives, asphaltenes, oxidation and polymerization compounds, metals and other impurities, which are destroyed by combustion.

  - Vacuum distillation and clay treatment. It involves vacuum distillation (to remove water and light compounds and fractionate hydrocarbons) followed by a thermal clay treatment, to remove impurities and improve the quality of the resulting oils. The final product is filtered. This technology involves low investment costs and high-quality oils, though environmentally it has the disadvantage of generating residual clays that must be properly managed. Instead of filtration, natural polymers can be used before vacuum distillation to remove carbon sludge (Hamad et al., 2005).
  - Solvent extraction. This process is a good alternative to acid clay treatments, as instead of toxic acidic sludge, useful organic sludge is produced (Elbashir et al., 2002). It involves extracting, by means of a proper solvent, the heavier fractions of hydrocarbons, the additives and other impurities found in used lubricating oils.
- Energy recovery: it can be mainly performed by two means:
  - Heat production, mainly by combustion in boilers or by direct burning in cement kilns (Kanokkantapong et al., 2009).
  - Fuel production by cleaning waste oils, thermal cracking and gasification (European Commission, 2006c). Other options are mild cleaning methods, as settling, heating, filtration or centrifugation (Rincón et al., 2003).
  - Co-generation to produce energy in engines coupled to generators.
- Other options: Depending on the degree of pollution of the waste stream and on the purpose of the final product, softer alternatives as filtering or re-additivation may be available.

Besides these traditional options, some authors are developing some new management options for used lubricating oils management. Sotelo et al. (2001) propose transforming used oils with zeolitic catalysts into mixtures of useful hydrocarbons that can be used as fuels or raw petrochemical materials. Other option is the proposal of Ramasamy and T-Raissi (2007) about converting used lubricating oils into hydrogen and other valuable low molecular weight hydrocarbons, owing to the high content (13-14 wt%) of H_2 in the residual oils.

CLASSIFICATION ACCORDING TO THE WMH

WMH establishes the priority order to manage used lubricating oils. Accordingly, the inventoried alternatives are classified as preparing for re-use, recycling and recovery techniques. As management at a waste treatment plant is considered, not prevention techniques are taken into account. Disposal is neither considered, as it is the last option of the hierarchy, and should be only applied when no other option is practicable. Initially, it is assumed that used lubricating oils can be benefited from any of the other priority management alternatives.

Figure 3.2.1 shows the classification of the available treatment alternatives according to the priorities of the WMH. Filtering and re-additivation have been classified as preparing for re-use techniques. They are only practicable when the residual oil is not too polluted and the quality required for the recovered product in not too strict. All the re-refining techniques (acid/clay treatment, vacuum distillation and hydrogenation, vacuum distillation and clay treatment and solvent extraction), have been classified as recycling treatments, as all of them re-process used lubricating oils into products for both the original or other purposes. Finally, energy cogeneration, fuel processing treatments, and heat production have been classified as recovery options, as in all cases residual oils are serving a useful purpose by replacing other materials which would have been otherwise used (EU, 2008b).

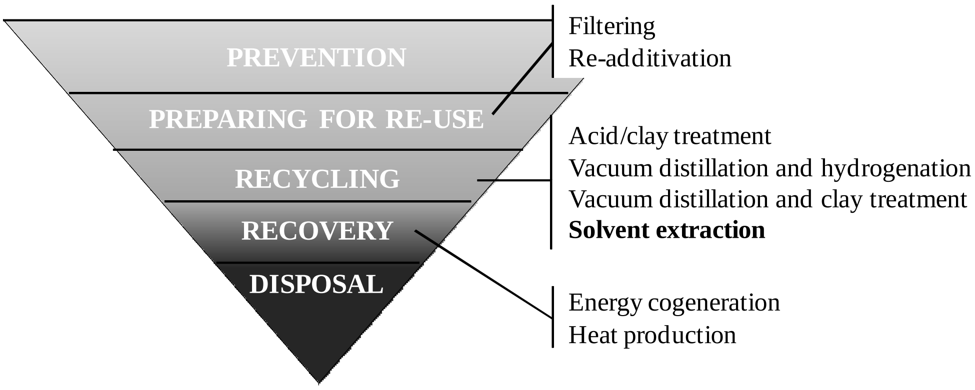


Figure 3.2.1: WMH and waste treatment options

4.2.3. Selection of the most appropriate technique on the basis of the IPPC philosophy

The criteria for selecting the most appropriate technique are the WMH and the IPPC philosophy. Accordingly, the first options of the WMH will be prioritized, considering those treatments which prevent or reduce emissions and prevent the generation of further waste.

Owing to the quite high degree of pollution of the considered used lubricating oil, no preparing for re-use option is really applicable. Therefore, only recycling and recovery options are considered. Regarding recycling options, acid/clay treatments are directly rejected, as they are not practicable due to the great amount of hazardous waste they generate. As vacuum distillation with clay treatment present the same disadvantage, this option is also rejected.

Vacuum distillation and hydrogenation is quite appropriate when the used lubricating oils present high concentrations of chlorine and sulphur, as they are effectively removed by this treatment. Chlorine and sulphur are removed at high temperatures and hydrogen atmospheres by contacting with specific catalysts that convert them into HCl and H_2S. The process is also suitable for removing phosphorus, lead, zinc and PAH (European Commission, 2006c). However, as the fractions of these pollutants are not expected to be very high, this treatment is not really appropriate, so solvent extraction has to be considered.

Solvent extraction is a recycling treatment that allows removing about 10-14% of the used lubricating oil as contaminants, which corresponds to the normal amount of additives and pollutants found in residual oils (Elbashir et al., 2002). It pre-cleans the used oil before feeding it to the vacuum distillation column, avoiding cracking reaction and further hydrogenation processes (Rincón et al., 2003), and does not need any clay treatment, as pollutants are previously removed, so no additional residue is generated.

Used lubricating oil recycling by applying solvent extraction provides high-quality bases at low plant capacities (Rincón et al., 2007). According to the IPPC philosophy, this treatment alternative seems a suitable management option, as it is one of the most innovative technologies for used lubricating oil management and avoids further waste generation.

A satisfactory recycling alternative has been found, so none recovery alternatives are considered, as they are in a lower degree of priority in the WMH. Therefore, solvent extraction is selected as the most appropriate technique for used lubricating oil management. The whole process required to apply this treatment is described in the next step of the methodology.

4.2.4. Detailed description of the process

The configuration considered for the proposed process was firstly developed by SENER and INTERLINE, two companies devoted to oil refinery (SENER, 2012). This original process involves liquid-liquid propane extraction combined with atmospheric and vacuum distillation. Propane selectively extracts all base oil components from the waste oil (Rincón et al., 2003), separating asphaltenes and pollutants. However, some pollutants are not removed by propane extraction, and hydro-finishing treatments are sometimes required. To avoid this, Rincón et al. (2007) have proposed and validated ethane as a solvent for regenerating used lubricating oils. It properly eliminates all the pollutants of the used oil, improving the quality of the extracted base oil, avoiding further treatments after distillation.

The process suggested for the proper management of used lubricating oils is shown in Figure 3.2.2. It is divided in three stages:

- Pre-treatment: waste oil is firstly decanted to remove water and solid particulates. The stream is then subdued to filtration to eliminate the rest of the solid particulates. The resulting oil is water and particulate free, so it is ready for ethane extraction. This stage consumes electricity, and releases wastewater, solid particulates and sludge.
- Ethane extraction: asphalts and pollutants are extracted by ethane, which is then recovered in a flash unit. The inputs to this stage are ethane, fuel, and electricity. Outputs are exhaust gases and heat from fuel combustion, as well as residual ethane, asphalts and other heavy pollutants.
- Distillations: waste oil is flashed at atmospheric pressure to remove the light hydrocarbons (naphtha) (Hamad et al., 2005). The rest of the hydrocarbon fractions are stripped in a vacuum distillation column producing diesel, lubricants and asphalts. This stage consumes energy as fuel and electricity. It also produces the final recovered products, namely naphtha, diesel, lubricants and asphalts. It also generates exhaust gases from fuel combustion.

4.3. Quantitative analysis

This stage involves selecting appropriate software for process simulation, data acquisition about the proposed process, modelling and scenario building, simulation and evaluation of results, and finally identification of the IF of the system.

4.3.1. Software selection

The process is modelled using Aspen HYSYS V7.1 (AspenTech, 2009) steady state simulation software, which allows modelling chemical processes by solving material and energy balances.

4.3.2. Data acquisition

15000 tones of used lubricating oil are yearly treated (1893.94 kg/h). They are polluted with 5% of water and 5% of metal particulates, mainly lead, copper and zinc. The rest of the stream (90%) is the mixture of lubricating hydrocarbons. Its composition is defined on the basis of a distillation curve, as it is the only practical way to assess the vapour-liquid equilibrium in complex fluids. The generic distillation curve for used automotive oil determined by Starkey Ott et al. (2010) has been considered. This curve represents the Normal Boiling Point (NBP) of the oil.

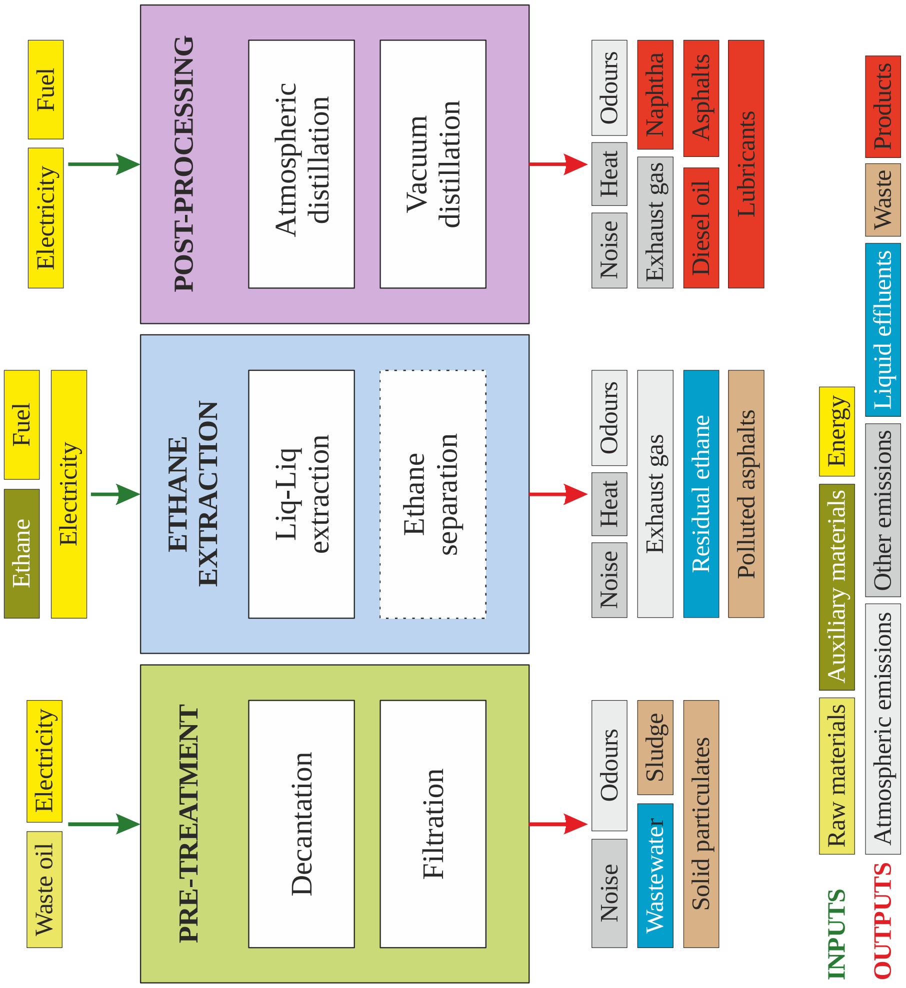


Figure 3.2.2: Flowsheet of the solvent extraction process for used lubricating oil recycling

4.3.3. Modelling and scenario building

The Peng-Robinson equation of state (Equation 3.2.1) (Peng and Robinson, 1976) is used to model the process, owing to its suitability to evaluate the properties of pure substances and equilibrium ratios of mixtures:

$$P = \frac{R \cdot T}{V_m - b} - \frac{a \cdot \alpha}{V_m^2 + 2b \cdot V_m + b^2}$$

Equation 3.2.1

where:

$$a = \frac{0.45724 \cdot R^2 \cdot T_c^2}{P_c}$$

$$b = \frac{0.07780 \cdot R \cdot T_c}{P_c}$$

$$\alpha = \left(1 + \left(0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2\right) \cdot \left(1 - T_r^{0.5}\right)\right)^2$$

The equation of state is related with the rest of thermodynamic properties by means of the fundamental equations of thermodynamic.

The composition of the lubricating oil hydrocarbon mixture is defined on the basis of their NBP. The percentage of water polluting the oil is also considered. It is assumed that, due to the particularities of the process selected, the metals are removed by solvent extraction as part of the asphaltenes.

The model includes all the elements qualitatively described except the filter, as it is assumed that the solid particulates are removed in the decanter and the traces of other metals are extracted by ethane with the asphaltenes (Figure 3.2.3). The decanter has been selected as a three-phase separator, where no vapour is released, and where more than 99.9% of the aqueous fraction is removed. The flow of ethane is regulated using the HYSYS function SET, so that the ethane/used lubricating oil ratio is 3.

Solvent extraction is modelled as a liquid-liquid extractor, where the solvent is the ethane. It extracts asphalts and other pollutants from the base oils. 9802 kPa of pressure and 40 ºC of temperature are considered; as they are the optimum conditions defined by Rincón et al. (2007). At these conditions the extraction yield is 72%.

After solvent extraction the resulting base oil/ethane mixture is flashed to recover the ethane, which is fed back to the liquid-liquid extractor. The temperature of the mixture is adjusted, using the ADJUST function of HYSYS, so that it is 20 ºC. To model the flash a separator is selected and configured so that more than 99.9% of the ethane is recovered.

The base oils are then subdued to atmospheric distillation at 300 ºC, so that the lightest fraction of the hydrocarbon mixture is separated. This process is modelled as a distillation column, where 98.5% of the naphtha is recovered, and the remaining ethane is separated. A partial condenser has been considered, so that ethane and naphtha are recovered.

The mixture of heavy hydrocarbons is vacuum distilled. A distillation column working at 10 kPa and 327.2 ºC has been modelled. It has been considered a total condenser where diesel is recovered and a side-draw for recovering lubricants. The remaining asphalts are also separated.

The ethane recovered in both the flash and the atmospheric distillation column is fed back to the liquid-liquid extractor by the HYSYS function RECYCLE.

Besides the elements described, the model includes heaters and coolers to adjust the temperature of the streams concerned, and valves, compressors and pumps to regulate pressure.

4.3.4. Simulation and results evaluation

The model has been run in steady state, calculating the stationary material and energy flows for each case and the operating conditions of each unit. The application selected process could lead to the recovery of used lubricating oils as different products (Table 3.2.1). Lubricating bases are, by far, the most abundant product, followed by asphalts and diesel. Naphtha only represents 3.72% of the final product, as the considered lubricating oils contained quite heavy hydrocarbons.

Table 3.2.1: Distribution of the final products

Fraction	**%**
Naphtha	3.72
Diesel	7.21
Lubricating bases	78.29
Asphalts	10.82

More than 99.9% of the water is taken out by decantation and the rest is removed in the flash unit. It also recovers 99.95% of the ethane, which is recycled to the liquid-liquid extractor.

Using ethane instead of propane allows high recovery rates; in fact more than 62% of the asphalts are removed in the extraction stage, whereas the rest is removed by vacuum distillation. The products obtained, naphtha, diesel, and lubricating bases, are ready for consumption, as they not contain any pollutant.

The process is quite energy-consuming, as $6.56 \cdot 10^3$ kJ of thermal energy are consumed per kg of used lubricating oil treated. Atmospheric distillation is the process consuming more energy. Indirectly, liquid-liquid extraction also highly contributes to the total energetic demand of the process, due to the high pressures required to get the optimal working conditions.

The implementation of this management alternative is justified by the recovery of a product that otherwise would be disposed of as a waste. Furthermore the other recycling alternatives available also imply great energy consumptions, as they involve distillation processes as well. The implementation of the simulated alternative is justified by its recovery rate, its effectiveness and by the fact that it does not generate any further residue.

All the results generated by modelling and simulation can be used in the designing, calculating and dimensioning of all the units needed for implementation.

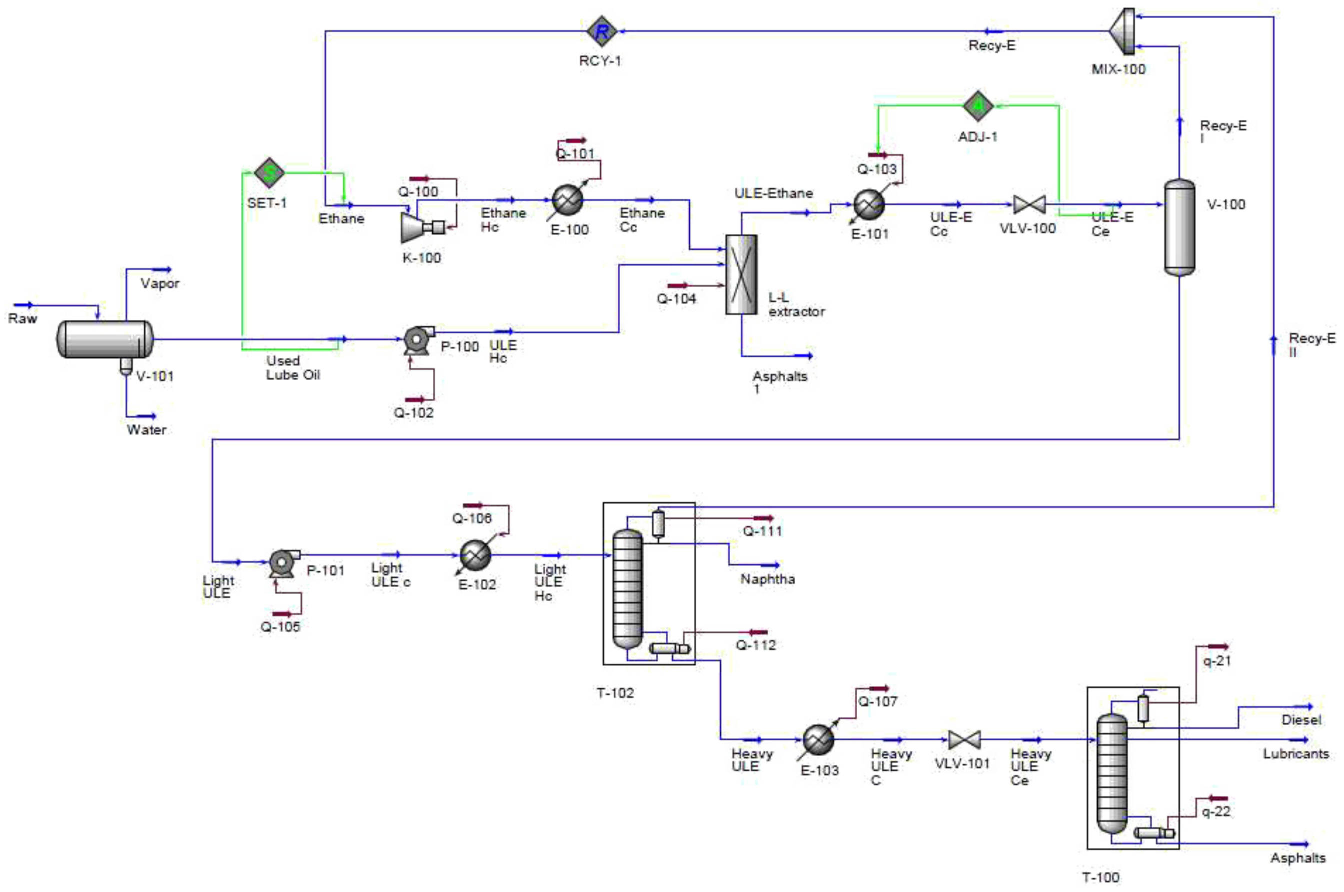


Figure 3.2.3: HYSYS model for the used lubricating oil recycling process

4.3.5. Identification of the IF of the process

According to the results from simulation, three input and one output flows have been identified as IF for the analysed process:

- Inputs: all the inputs pointed out as IF are energy flows, two from the 'ethane extraction' stage and one from the 'post-processing' stage. These flows are the most quantitatively relevant energy flows in the process, and they are directly reflected on the exhaust gas emissions derived from the process.
    - Fuel input to 'liq-liq extraction', mostly used in ethane compression.
    - Fuel input to 'ethane separation', used to adjust the temperature and pressure conditions of the mixture of ethane and base oil before flash separation.
    - Fuel input to 'atmospheric distillation', consumed in the distillation column.
- Outputs: polluted asphalts from 'liq-liq extraction' are also an IF, not due to their amount but because to their pollution potential. Though this flow is not likely to be reduced, as it corresponds to the pollutants contained in the used lubricating oil, it is likely to be treated to reduce its impact over the environment.

5. Results and discussion

This chapter has evaluated the suitability of process simulation as an IF identification tool. Process simulation has been included in a methodology to identify the best waste management technique from an inventory, and detect the potential IF of the selected alternative. The methodology begins with the description of the system. Then performs a qualitative analysis, resulting in a technical inventory (classified according to the WMH) and in the selection of a management alternative (regarding the IPPC philosophy). Finally quantitative analysis is applied by process simulation to identify IF.

The application of the methodology to the case study has provided a technical inventory for used lubricating oil management, classified according to the WMH. A management alternative has been selected, supported by the IPPC principles and respectful with the WMH. The alternative proposed is a recycling treatment, as no previous alternative from the WMH is applicable owing to the degree of contamination of the used lubricating oils. The treatment, 'regeneration of oils by extraction with solvents', combines liquid-liquid extraction with atmospheric and vacuum distillation, as proposed by Rincón et al. (2003). The original process has been modified by changing the conventional propane solvent by ethane. This change allows achieving better quality products, as vacuum distillation products pre-treated with liquid-liquid ethane extraction are directly suitable for commercialization or for preparing new formulations (Rincón et al., 2007). Using ethane instead of propane meets the objectives of both the IPPC philosophy and the WMH.

After the qualitative selection, analysis, and description of the most appropriate management alternative, process simulation was applied to quantify the selected option and to identify its IF. Besides providing quantitative information about the consequences of implementing solvent extraction for used lubricating oil regeneration, process simulation allows predicting the behaviour of the system and testing any modification intended to optimise the process. The simulation results can be further used in the designing and dimensioning of the system.

Four IF have been selected for the analysed process. Three IF concern fuel consumption in the ‘ethane extraction’ and ‘atmospheric distillation’ stages. The other IF refers to the polluted asphalts released in ‘liq-liq extraction’.

Though the model built is a preliminary approximation to the final system, it provides quite valuable information that supports the decision taken on the qualitative module of the methodology. Solvent extraction by ethane allows removing asphalts before atmospheric and vacuum distillation processes, so that the global energetic demand of the process is highly reduced regarding other options. Respecting the more traditional processes involving clay treatments, the advantages are quite obvious. The selected process avoids the generation of any residual stream (except the pollutants on the used lubricating oils), as practically all the ethane is recovered and fed back to the process. The sustainability of used lubricating oils management could be quite improved by the application of the proposed technique. Besides respecting the WMH, it avoids waste generation, reduces energy consumption, and provides a suitable alternative to recover a product that otherwise will be disposed of or burnt for energy recovery.

6. Conclusions

This chapter has validated process simulation as a suitable tool to predict the behaviour of an industrial system and to identify its IF. The positive results derived from the validation of the methodology confirm its suitability to identify the most appropriate management alternative for wastes. The case study considered for validation is the waste management sector. The methodology has been specifically applied to the used lubricating oils to get the most suitable treatment option regarding the IPPC philosophy and the WMH, and to identify the potential IF of the process.

Process simulation, included in a more complex methodology, has been proved to be a valuable tool to quantitatively identify material and energy flows within a system, and to predict its behaviour. It allows flow allocation and quantitative estimation of the material and energy flows of a process. Besides identifying IF, process simulation can be used to evaluate the implementation potential of a technique or to analyse the effects of modifications within the industrial system.

The methodology could be applied to other sectors where any type of waste, as defined by Directive 2008/98/EC, is generated. The application of this type of methodologies could highly improve the sustainability of systems where waste is simply disposed of, and not used as a valuable by-product. The WMH has set an important basis to encourage responsible and sustainable material resources consumption. Now stakeholders are forced to implement preventive and recycling measures over the typical energy recovery or disposal ones.

Not all the alternatives available are applicable in any given situation, the same as not all the candidate techniques are always BAT, as commented in chapter 2. In fact the technique selected as more suitable for the system considered was a recycling technique, while preparing for re-use alternatives were available. It is important to get a deep knowledge of the specific waste stream under study, its composition, physical and chemical properties, its amount, and any other relevant features. Then the qualitative analysis module of the methodology can be accurately applied, as the success of this module highly depends on the information available about the waste stream. All the alternatives, classified according to the hierarchical management options settled by the

WMH have to be deeply analysed one by one, considering the specific system. This type of oriented analysis is meant to avoid selecting alternatives just because they meet the requisites of the WMH, which is not enough. The pros and cons of each alternative should be carefully analysed and evaluated to guarantee a solid election.

As the selection of the waste management option highly relies on qualitative analysis, process simulation is used as an evaluation tool that quantitatively supports or rejects the decision on a specific treatment. The selected treatments are simulated in a model that reflects the future situation after implementation. In case the model validates the suitability of the technique, process simulation allows improving the model to get an optimised sustainable system by firstly identifying the IF of the system. Process simulation enables decision-makers to introduce any modification and evaluate their impact over the process. On the other hand, process simulation can also highlight the disadvantages of a technique or treatment that may look appropriate after qualitative analysis. In that case, the WMH and the IPPC principles will be recovered to qualitatively analyse again the available options.

Process simulation can be used as an IF identification tool, though it is a more valuable tool to evaluate the suitability of options intended to improve any given process. It allows modifying all the variables involved, process stages and equipment, or even whole sections of the process to analyse the impacts. It requires abundant and rigorous information about the simulated system to guarantee faithful models as similar to the reality as possible. Economic investments derived from process optimisation will be more justified and will be better supported if they are derived from the application of a methodology as the proposed, where improvement alternatives are validated by process simulation.

The methodology proposed, or process simulation as an IF identification tool, could be enhanced if combined with a corrective measures proposal tool, as BAT Analysis. Thus, techniques could be proposed to optimise the IF identified and get a sustainable industrial system.

CHAPTER 4

COMBINING BAT ANALYSIS AND MEFA: APPLICATION TO A CERAMICS MANUFACTURE PLANT

Summary

BAT Analysis was presented in chapter 2 as a methodology to develop technical inventories, though it did not provide any method to select the techniques needed in every specific situation. It was suggested identifying the IF of the system by MEFA or process simulation. Chapter 3.1 concluded that MEFA was a suitable tool for IF identification, though it did not propose any measure to reduce the impact of the IF.

This chapter proposes a methodology that combines BAT Analysis (a methodology to develop technical inventories based on the IPPC philosophy) with MEFA (a tool to identify IF derived from the industrial metabolism) to get sustainable industrial systems. This methodology, applied to an industrial system, seeks to identify the IF by MEFA, so that the appropriate candidate BAT can be selected by BAT analysis. Material and energy inputs, outputs and internal flows are allocated and quantified, and sustainable solutions are provided on the basis of industrial metabolism.

This combined methodology involves a thorough qualitative analysis of the system, defining its limits, identifying the stages involved, and determining and allocating the associated consumptions and emissions. Then MEFA methodology (as defined in chapter 3.1) is applied to the system to identify the IF. Finally BAT Analysis methodology (as defined chapter 2) is applied to the system to select the techniques available to prevent, reduce or enhance the IF identified. As a result, a complete strategy focussed on improving the unsustainable flows of the industrial system will be proposed.

The methodology is validated in the roof-tile manufacture plant considered in chapter 3.1. The application of this methodology to this exemplary plant leads to the identification of 14 IF, most of them corresponding to the ‘thermal treatments’ stage. 4 BAT were already implemented in the analysed plant, and 7 candidate BAT have been proposed to reduce the IF.

The proposed methodology provides a way to detect IF in a process and selects the most sustainable options to enhance them. Solutions are proposed for the detected IF, taking into account their effectiveness on improving such flows.

1. Introduction

Chapter 2 introduced and defined BAT Analysis as a methodology for examining, evaluating and selecting the techniques candidate to be BAT for a given industrial system. The application of the methodology results in an inventory of techniques candidate to be BAT, specifically selected for the considered case study, each of them provided of a technical data sheet. This methodology was validated in the Galician heavy ceramics manufacture sector, confirming its suitability for getting accurate technical inventories.

However it was also concluded that, as not all the techniques from the inventory are likely to be implemented, a method for selecting the techniques required in every specific situation was needed. The suitability of material and energy flows to represent an industrial system led to the definition of the IF and pointed out the necessity of getting IF identification tools. Chapter 3.1 validated MEFA as a suitable tool for IF identification. It provides material and energy flow allocation and quantification, which facilitates IF detection. But MEFA just identifies the flows, without providing any improvement measures.

It seems that the advantages of the technical inventories methodology (BAT Analysis) and of the IF identification tool (MEFA) can be combined, and their limitations overcome in an integrated methodology. The objective of this chapter is to develop and validate a methodology to get sustainable industrial systems. This methodology is based on the combination into a single method of two known tools: MEFA and BAT Analysis. The first tool, MEFA, provides both qualitative and quantitative information about the IF of the system, from environmental and economic (indirectly) points of view. The second one, BAT Analysis, uses technology to prevent and reduce the IF by applying BAT, defined by economic, environmental and social criteria. The method is applied to an industrial system for validation, an exemplary roof-tile manufacture plant.

1.1. BAT Analysis

After defining and evaluating the advantages and limitations of BAT Analysis in chapter 2, the next challenge is the appropriate selection of the techniques needed to improve the sustainability of processes. Literature provides several approaches, each considering different criteria for the selection of the best combination of candidate techniques for a given situation. Bréchet and Tulkens (2009) propose maximizing the economic profit by a selected combination of techniques, regarding private investment and social costs; Mavrotas et al. (2007) suggest a multi-objective optimisation method that considers a great variety of social, economic and environmental parameters to get the optimal combination of BAT to achieve a given objective; Nicholas et al. (2000) use the LCA concept to select those candidate techniques with the lower environmental impact; whereas Schramm (1998) used the cleaner production philosophy and criteria to determine whether a candidate technique could be considered as best available. These methods illustrate the general trend of this type of methodologies, which focus on the effect of the selected techniques over environmental parameters, mostly focussing on reducing emissions. Though quite effective, these methods fail to identify which elements of the considered process should be improved, so that the unsustainable elements of the process are not effectively corrected.

These limitations when selecting BAT compromise the efficiency of the techniques implemented. Besides knowledge about the candidate techniques, knowledge about the process concerned is also needed. The disturbing elements of the process should be clearly identified, as well as the potential impacts they may cause over the specific environment. It seems that an element integrating these considerations is missing in the traditional BAT selection methodologies. BAT selection methodologies, as BAT Analysis, should be preceded by an accurate procedure of identification of the drawbacks of the process, so that the selection of techniques could be properly oriented.

1.2. MEFA

MEFA was defined in chapter 3.1 as the systematic assessment of the flows and stocks of materials and energy within a system defined in space and time (Brunner and Rechberger, 2004), and a methodology was defined and validated in a real system. The method allowed the quantitative definition of material and energy flows on the considered system, clearly identifying unsustainable or inefficiently managed flows, defined as IF.

The flow perspective has been proved to be very useful when integrating society, technological change, and environmental effects (Anderberg, 1998) and, as Bringezu (2003) stated, it can be used to derive indicators for sustainability and analyse if sustainable industrial metabolism conditions are being met. In spite of its origins, MEFA is typically used in accounting studies using accounting methodology and data (Finnveden and Moberg, 2005), being the objective analyzing the social metabolism of countries and regions (Gregory et al., 2009). Some examples were presented in chapter 3.1, and there are some more (Bringezu et al., 2004; Hashimoto and Moriguchi, 2004; Raugei and Ulgiati, 2009; Schwarzenbach et al., 1999). Other works complement this social approach with some economic analysis, aiming to understand socio-economic interactions (Bouman et al., 2000; Haberl et al., 2004). Some examples are Kytzia et al. (2004), who fed MFA with economic data to study causal relationships between economically motivated behaviour and resource consumption; Hawkins et al. (2007), who combined MFA and economic input-output modelling to track economic transactions and material flows throughout the economy; or Krausmann et al. (2009), who applied economy-wide MFA to quantify global materials extraction. There is a lack of works that use MFA or MEFA to improve or evaluate industrial metabolism. The original purpose of MEFA should be recovered to establish and improve symbiotic relationships in industrial systems or processes, combining it with other tools to consider, in an integrated manner, the three dimensions of sustainability.

As illustrated, literature provides some examples of how to combine MEFA with other tools so that the three dimensions of sustainability are taken into account. However these tools only provide information about the system, but no solutions to improve it. A different option to complement MEFA is BAT Analysis, which provides novel technical concepts to improve the sustainability of the process. MEFA allows the identification of the IF of the considered industrial system, so that the techniques collected in an inventory by BAT Analysis can be selected. Such a methodology facilitates the selection of techniques, which are intended to mitigate the impact of the IF over the system. In this chapter IF obtained by MEFA are used as starting point for the BAT Analysis, obtaining solutions for a sustainable industrial system.

2. Case study

The reference plant selected in this chapter is the same as in chapter 3.1, an exemplary roof-tile manufacture plant, *Cerámica Verea, S.A.*, located in Galicia (NW Spain). In this case the whole plant will be considered to validate the proposed methodology.

As MEFA has already been applied in chapter 3.1 to the ‘transport and storage of raw materials’ stage (Torres et al., 2008), it will not be applied again to this stage. Just the most relevant results will be shown in this chapter. Either way, it will be clearly indicated whether the stage is being subdued to the methodology or if the needed data is just being recalled from chapter 3.1.

3. Methodology

The methods used in this chapter include the proposal of a new methodology and its validation in a real exemplary plant. The possibilities and applicability of the results obtained are discussed.

The proposed methodology integrates two tools: MEFA, applied to an industrial system to identify its IF; and BAT Analysis to select of the most appropriate candidate techniques to enhance the process based on the identified IF. MEFA adapts the methodology proposed in chapter 3.1, whereas BAT Analysis uses the method adopted from the EIPPCB in chapter 2.

The proposed methodology includes the following steps:

1. Definition of the system under study.
    - Identification of the industrial plant.
    - Qualitative analysis of the selected process: identification of its limits, definition and description of its stages, and analysis of inputs, outputs and internal flows. This analysis must be based on technical visits to the plant and on bibliographic review.
2. MEFA.
    - Data recompilation. Identification of the data needed to fill the model. The material and energy flows and stocks of the process can be determined by direct measurements (supported by technical visits to the industrial plant), best estimates, interviews, databases of environment protection agencies, scientific papers and so on.
    - Scenario modelling.
        - Software selection.
        - System modelling using the selected software. Scenario building creating networks and subnets. The model is fed with the data recompiled. Material and energy balances are performed on those processes where no data is available.
        - Model running and results of the MEFA. When it is complete, the model is run to obtain the results of the MEFA of the selected system.
3. Selection of the IF. The results obtained from the MEFA are analysed to identify the IF, meaning those inputs, outputs or internal flows that are remarkable in comparison with the other flows of the process.

4. BAT Analysis.
    - Recompilation and inventory of techniques candidate to be BAT for the selected industrial system.
    - Identification of the already implemented BAT. It gives an idea of the environmental performance of the plant and of the efficiency of the implemented techniques.
    - BAT selection according to IF. Candidate techniques from the inventory are selected for each of the identified IF.

4. Application of the methodology to an exemplary plant

The proposed methodology is applied, step by step, to the selected exemplary industrial plant to detect its IF and propose measures to enhance them.

4.1. Definition of the system under study

The considered industrial system is defined in space and time. Qualitative analysis is applied to identify the stages involved in the process.

4.1.1. Identification of the industrial plant

The selected industrial plant, *Cerámica Verea S.A.*, was defined in chapter 2. It is a roof-tile manufacture plant producing 111 millions of tiles per year (133200 tonnes per year) (data from 2005). The plant performs a complete process regarding industrial metabolism. It includes physical, chemical and thermal processes requiring several raw materials and generating a variety of different waste streams.

4.1.2. Qualitative analysis of the selected industrial system

The productive process consists of five consecutive stages (Figure 4.1) whose objective is producing roof-tiles from clay, which is the raw material of the process.

- Transport and storage of raw materials: Four types of clay from different sources are used. Clays 1, 2 and 4 are extracted from three different quarries next to the installation (no further than 7.5 km). Clay 3 is the clay mud resulting from quartz washing in the industrial and mineral rocks exploitation process carried out by a nearby installation. After extraction, clay is transported and stored in the plant. These activities mainly generate particulates and exhaust gases associated to transport.
- Raw materials preparation: Clay is loaded into the shredders and then into one of the four available dossing hoppers, which dose the appropriate combination of clays.

  The four types of clay are mixed in the belt weigher, and the resulting mixture is preliminary milled in the roller mill. The clay mixture is finely grinded in the lamination and refining units, where the clay particulates get the adequate size before storage.

  The dust and particulate released to the floor, mostly by the lamination equipment, is weekly collected and fed to the storage stage (Figure 4.2).

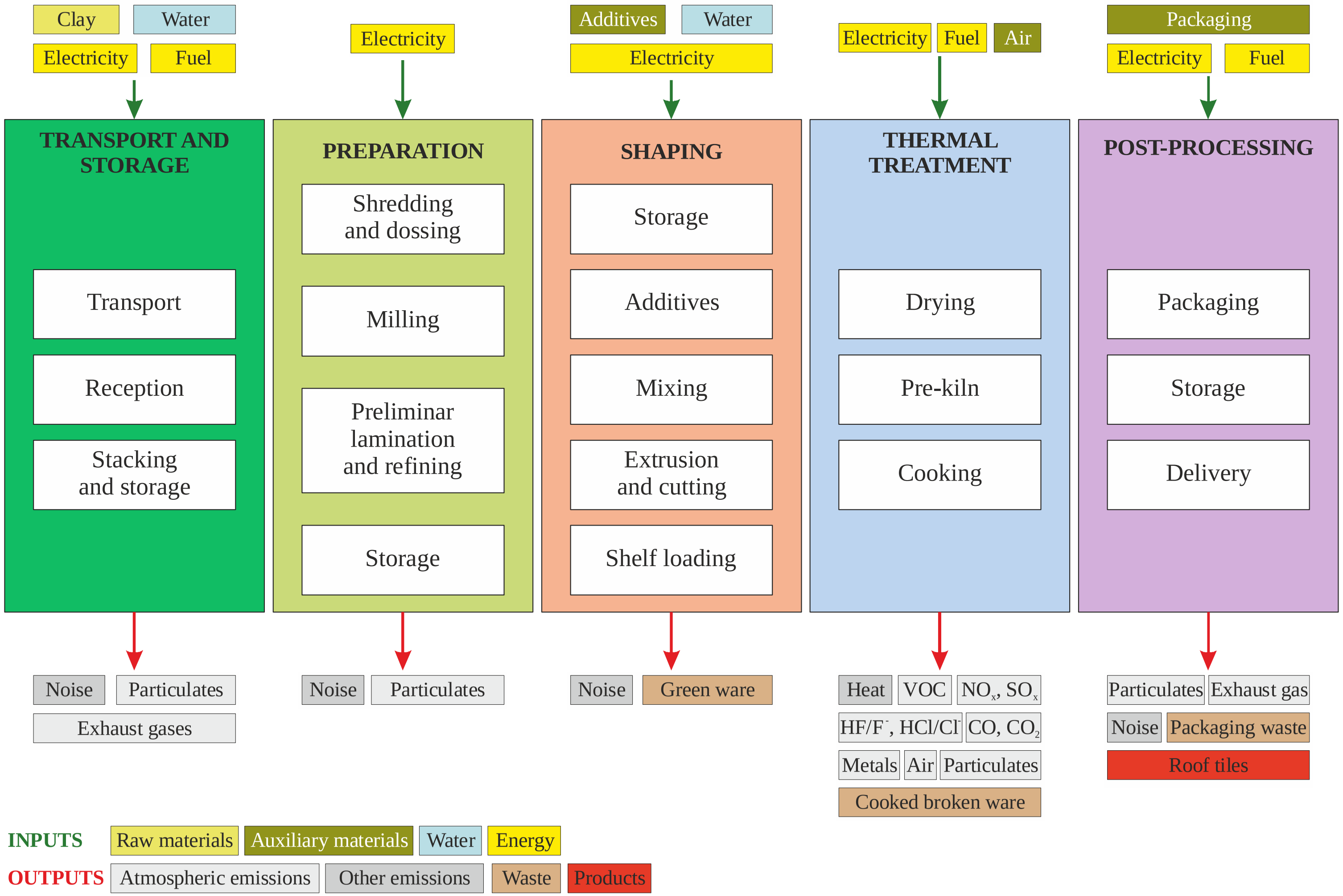


Figure 4.1: Flowsheet and environmental aspects of the *Cerámica Verea S.A.* process (Torres Rodríguez et al., 2011)

- Shaping: It involves all the processes turning the milled clay mixture into raw tiles ready for thermal treatment.

  The clay, previously loaded into a feed hopper, is added a CO_3Ba solution, which insolubilizes the SO_4Ca that clay may contain, avoiding possible efflorescence. Some clay is added a Mn_3O_4 solution to obtain graphite coloured tiles. After chemicals additions, the clay and its additives are mixed and added some water if necessary. The mixture is extruded through a mould, so the clay is shaped into a continuous piece of material which is cut. The resulting raw tiles are loaded into shelves that are conducted to the "thermal treatment" equipments. The green ware cuttings are fed back to the mixer so that no clay is wasted (Figure 4.2).

- Thermal treatment: The raw tiles are subjected to a thermal treatment integrated by three processes, namely drying, previous storage at the pre-kiln, and cooking (Figure 4.3).

  - Drying: The plant uses a counter current tunnel dryer divided into two sections, Dryer 1 and Dryer 2, where the raw tiles are set in wagons to be dried with pre-heated air from the kiln.

    In Dryer 1 humidity is reduced. This dryer has two distinct zones with different air inputs. In zone 1 air is a mixture of fresh air and used air fed back from zone 1 itself. Zone 2 uses a mixture of air from zone 3 and fresh air.

    Once tiles have gone across Dryer 2, their humidity is reduced. The counter current input air in Dryer 2 is a mixture of fresh air together with air from the cooling zone of the kiln. This dryer has a burner used to heat the air entering the dryer.

    Tiles leaving the dryer go through an artificial vision system where their dimensions, weigh and structure are verified. The out-of-specifications tiles are removed and fed back to the milling stage so that they can be re-used in the production process.

  - Pre-kiln: the dried tiles are temporary kept in the pre-kiln to avoid humidifying from the ambient air. Pre-kiln uses air from the cooling zone of the kiln, which has been previously heated in a burner.

  - Cooking: in the continuous tunnel kiln, tiles are cooked to get the appropriate properties by complex chemical reactions governed by the mineralogical, chemical and granulometric composition of the material (Casares et al., 2005). At first tiles are slowly pre-heated. Then the temperature quickly rises, and the tiles get properly cooked. Finally they are cooled by cooling air that is later used in the dryer. The heat source is natural gas combusted in a burner. Broken cooked tiles are used as filler in the quarries.

    Emissions are inorganic compounds, metals and VOC associated to chemical reactions and natural gas combustion. Besides, particulates and air are released.

- Post-processing: The final product is palletized before expedition. The stage involves activities as packaging, palletizing and storage, which consume auxiliary materials (mainly packaging) and energy (both electricity and fuel) and release solid waste and exhaust gases (Figure 4.2).

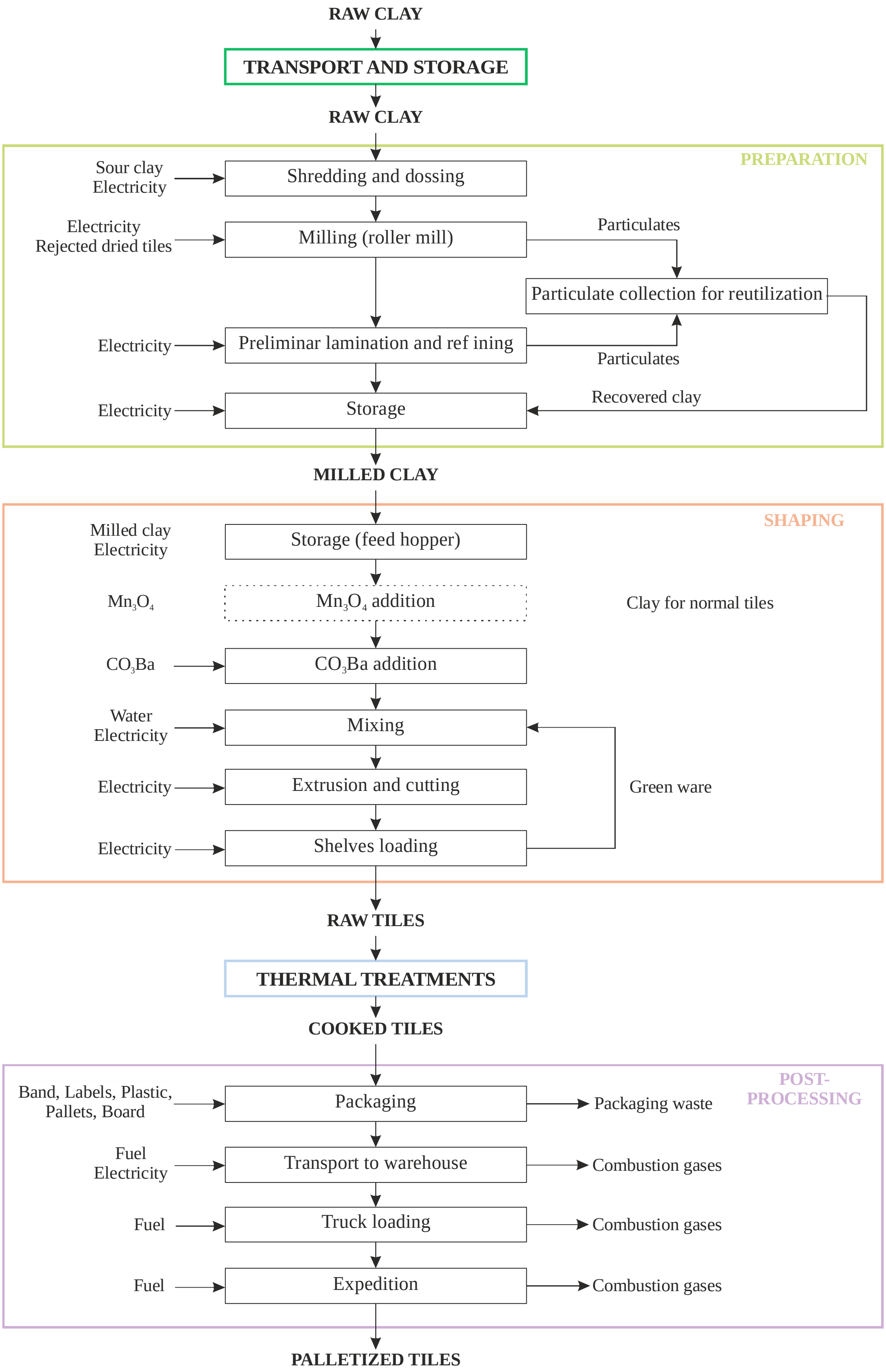


Figure 4.2: Qualitative analysis and flow allocation of the process (Torres Rodríguez et al., 2011)

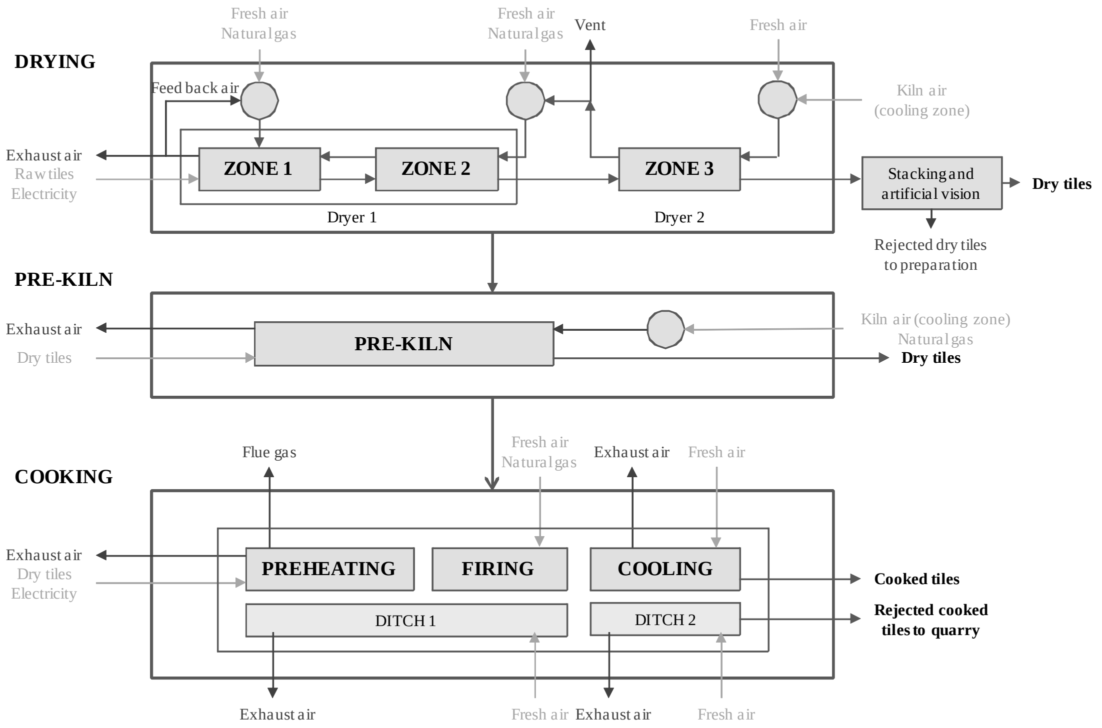


Figure 4.3: Qualitative analysis and flow allocation of the “thermal treatment” stage (Torres Rodríguez et al., 2011)

4.2. MEFA

The MEFA corresponding to the “Transport and storage of raw materials” stage has already been presented and evaluated in chapter 3.1, so only the important results needed for the purposes of this chapter are presented here.

4.2.1. Data recompilation

All data used in this study was provided by *Cerámica Verea S.A.*, being 2005 the time boundary (*Cerámica Verea, S.A.*, 2006). Some data was measured in-situ, other was obtained from tests at the laboratory and other was directly gotten from the on-line monitoring of the process. The data has been classified according to the process division shown in Figure 4.1.

Table 4.1 and Table 4.2 show the data recompiled concerning, respectively, electricity consumption and material flows. Though these tables show most of the information needed to feed the model, it is necessary to include some particularities about some stages:

- Shaping: some of cuttings from other stages of the process are fed back to this stage.
- Thermal treatment: the specifications for all the flows involved in this stage are displayed in Figure 4.4. On the other hand, in the cooking process, tiles are at first slowly pre-heated to 650 ºC. Then the temperature is quickly risen to 1054 ºC, so that tiles get properly cooked.
- Post-processing: Table 4.3 and Table 4.4 include the specific requirements of this stage.

Table 4.1: Electrical consumption of the stages of the process

Stage	**Process**	**Electricity[2] (kJ/kg)**
Raw materials preparation[1]	Shredding and dossing	5.25
	Milling	6.51
	Primary lamination and refining	19.57
	Storage (transportation)	3.22
Shaping	Storage of clay in the hoppers	1.33
	Mixing	21.83
	Extrusion and cutting	67.63
	Shelves loading	1.02
Thermal treatment	Drying	107.45
	Pre-kiln	40.50
	Cooking	759.29
Post-processing	Storage (transportation)	3.5

[1] The electricity to operate the conveyor belts is included in the electrical consumption of each engine.

[2] All the electrical consumptions are referred to 1 kg of clay.

Table 4.2: Material flows and specifications of the process

Stage	**Material**	**Flow specifications**		**Rejects (%)**	
Raw materials preparation[1]	Clay 1	24%	50 t/h	-	
	Clay 2	20%			
	Clay 3	48%			
	Clay 4	8%			
Shaping	Clay mixture	8.38 t/h		-	
	Mn_3O_4	3%[1]		-	
	$BaCO_3$	3‰[1]		-	
	Water	27.5%[1]		-	
Thermal treatment	Tiles	-		Drying	0.89[2]
				Cooking	0.32[3]
Post-processing	Pallets	14976 pallets		-	
	Band (11.6 mm)	0.360 kg/pallet		4.0	
	Carton	0.323 kg/pallet		0.0	
	Band (14.6 mm)	0.062 kg/pallet		2.6	
	Retractable plastic	0.500 kg/pallet		4.0	
	Wooden pallets[4]	9.825 kg/pallet		-	
	Labels	0.0015 kg/pallet		-	

[1] Weight content regarding clay flow

[2] To *Raw material preparation.*

[3] To quarries as filler material.

[4] 16% of the pallets are re-used in the plant.

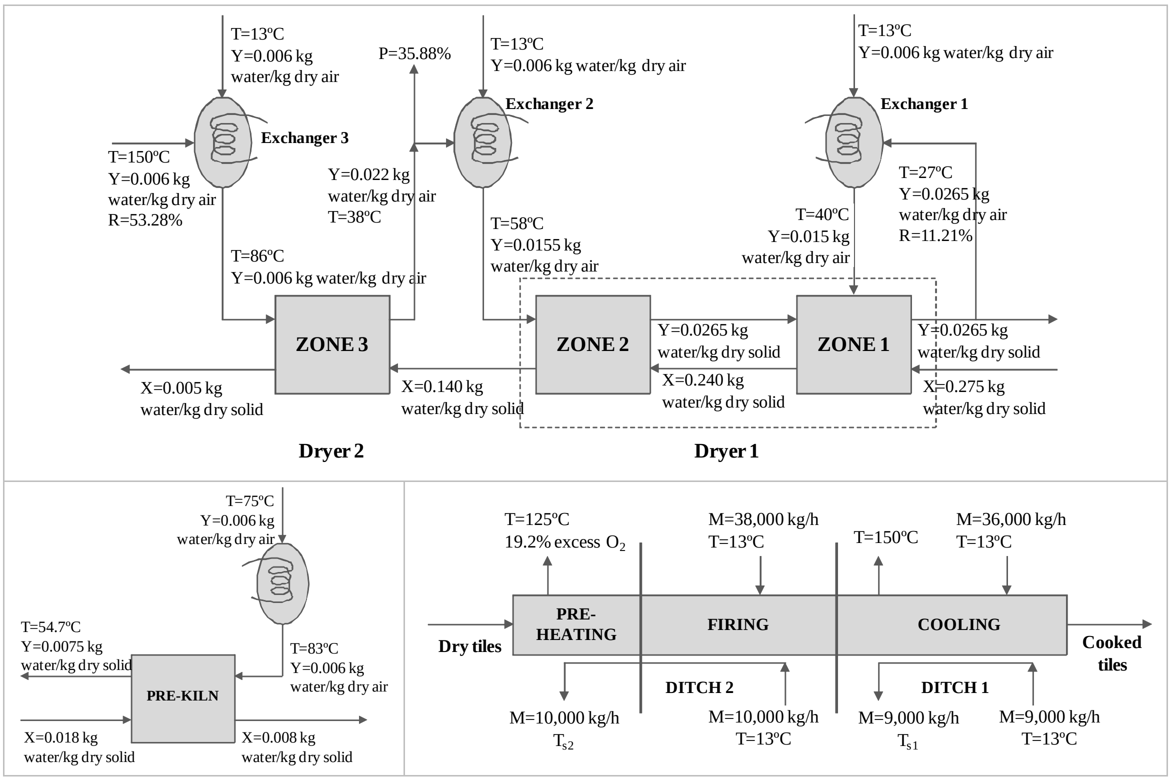


Figure 4.4: Input data to model "thermal treatments" (Torres Rodríguez et al., 2011)

Table 4.3: Pallet transportation (inside the plant)

	Transportation to storage area	Lorries loading
Diesel (l/h)	4.2	4.2
Load (t)	1.8	1.8
Worked hours (h/day)	5	4

Table 4.4: Expedition data for the finished product

Parameter		Unit	Value
Average covered distance		km	200
Lorry weigh		t	15
Lorry load		t	25
Road categories	Highway	%	25
	Secondary road	%	55
	Urban road	%	20

4.2.2. Scenario modelling

This step of the methodology involves the selection of appropriate software, system modelling using the selected software and model running to get MEFA results.

SOFTWARE SELECTION

The software selected for this work is Umberto (*IFU*, 2005), developed by *Ifu Institut für Umweltinformatik* Hamburg GmbH in cooperation with *Ifeu-Institut für Energie-und Umweltforschung* Heidelberg GmbH. A thorough description of Umberto is included in chapter 3.1, where all the elements available to build a model were defined.

SYSTEM MODELLING

The main network (Figure 4.5), or 1st level network, of the model includes five different transitions, each corresponding to one of the five stages of the process (as shown in Figure 4.1), connected by connection places. Each of these transitions includes a subnet (2nd level network), where all the corresponding sub-stages identified in the qualitative analysis (Figure 4.2) are modelled as transitions. Due to its complexity, the transitions included in “thermal treatments” are modelled as subnets (3rd level network), corresponding to the qualitative analysis in Figure 4.3.

Inputs, outputs and internal flows are places. Places representing inputs are raw materials (namely the four types of clay), secondary materials (water, $BaCO_3$, Mn_3O_4), operating supplies (electricity, diesel, natural gas, air) and auxiliary materials (packaging). Places representing outputs are atmospheric emissions, waste and rejected materials. Finally, input/output places are the recycling flows of clay and air.

The transitions involved in “raw materials preparation” and “shaping” subnets are linear. Therefore, coefficients have been determined for each input and output flow in all the transitions. These coefficients are calculated by simple material balances on the basis of 1 kg of clay mixture, using the data on Table 4.1 and Table 4.2. The coefficients corresponding to each flow involved in these transitions are all displayed in Figure 4.6. Flows are classified as inputs or outputs, indicating the materials involved, the places they come from or go to, and the variables assigned by Umberto for calculation.

The transitions of the 3rd level network are non-linear. Most of them represent thermal treatments that have been manually programmed considering mass balances on the basis of 1 kg of clay mixture. Data collected in Figure 4.4 is also used, as well as information in Table 4.1 and Table 4.2. Figure 4.7 represents the allocation of input and output flows and the programmed mathematical expressions for some representative transitions.

For the drying subnet, transitions T1 (dryer – zone 1), T3 (dryer – zone 3), T4 (exchanger 1) and T6 (exchanger 3) are presented (Figure 4.7). Some of the variables regarding air and clay humidity and temperatures are fixed on the basis of the data showed in Figure 4.4. Others are calculated considering mass and enthalpy balances. T2 (dryer – zone 2) and T5 (exchanger 2) have been modelled as T1 and T4 respectively, adapting the humidity and temperature parameters to the special requirements of these equipments, according to Figure 4.4. The total electrical consumption of the dryer is programmed in T3. In this transition there have also been programmed the atmospheric emissions associated to the drying process, using the corresponding emission factors (Table 4.5). The rejected tiles factor (Table 4.2) is considered in T7 (stacking and artificial vision) to determine the amount of tiles rejected after drying.

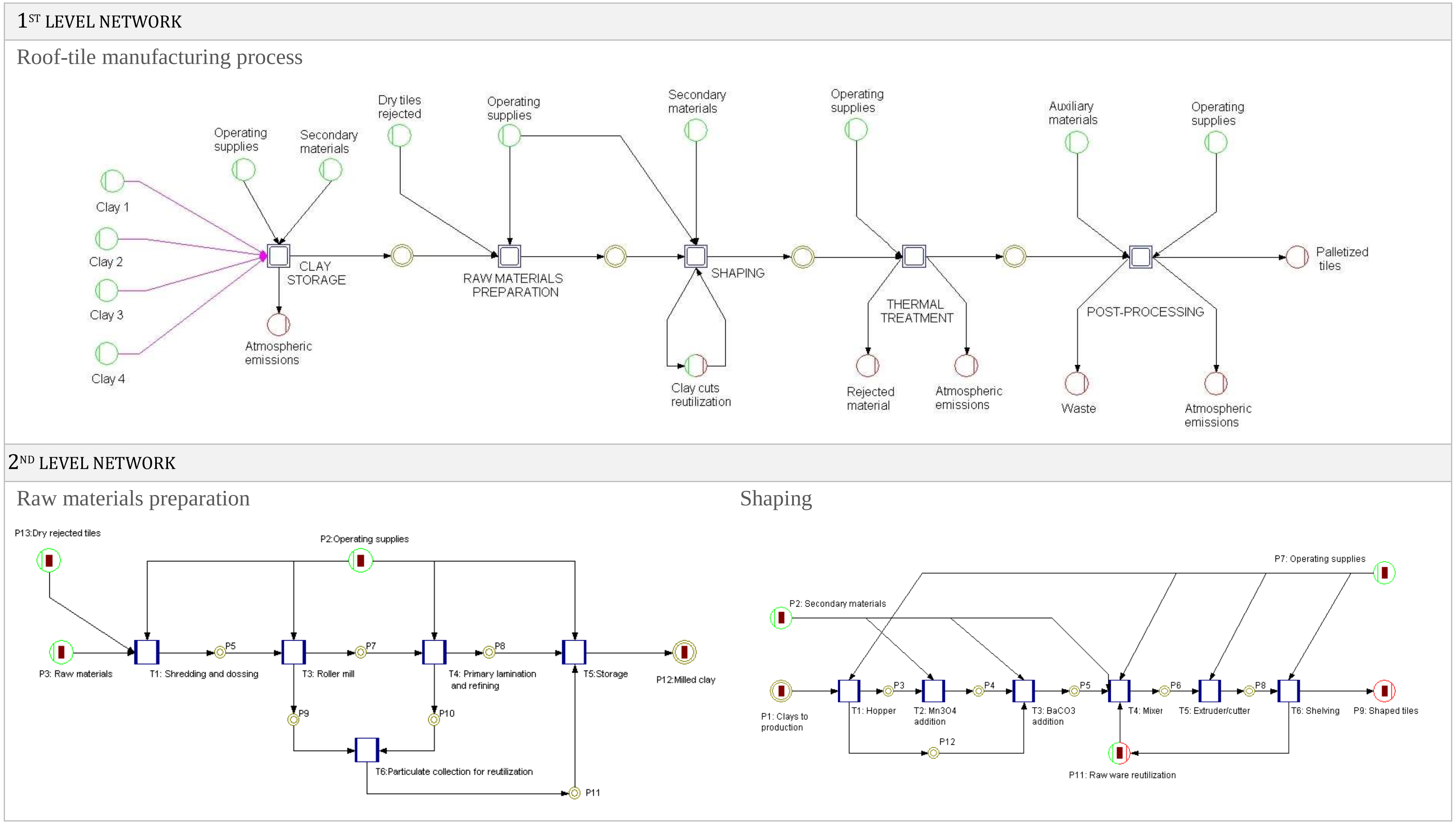


Figure 4.5: Process networks (1^{st} level, 2^{nd} level, 3^{rd} level) (part I) (Torres Rodríguez et al., 2011)

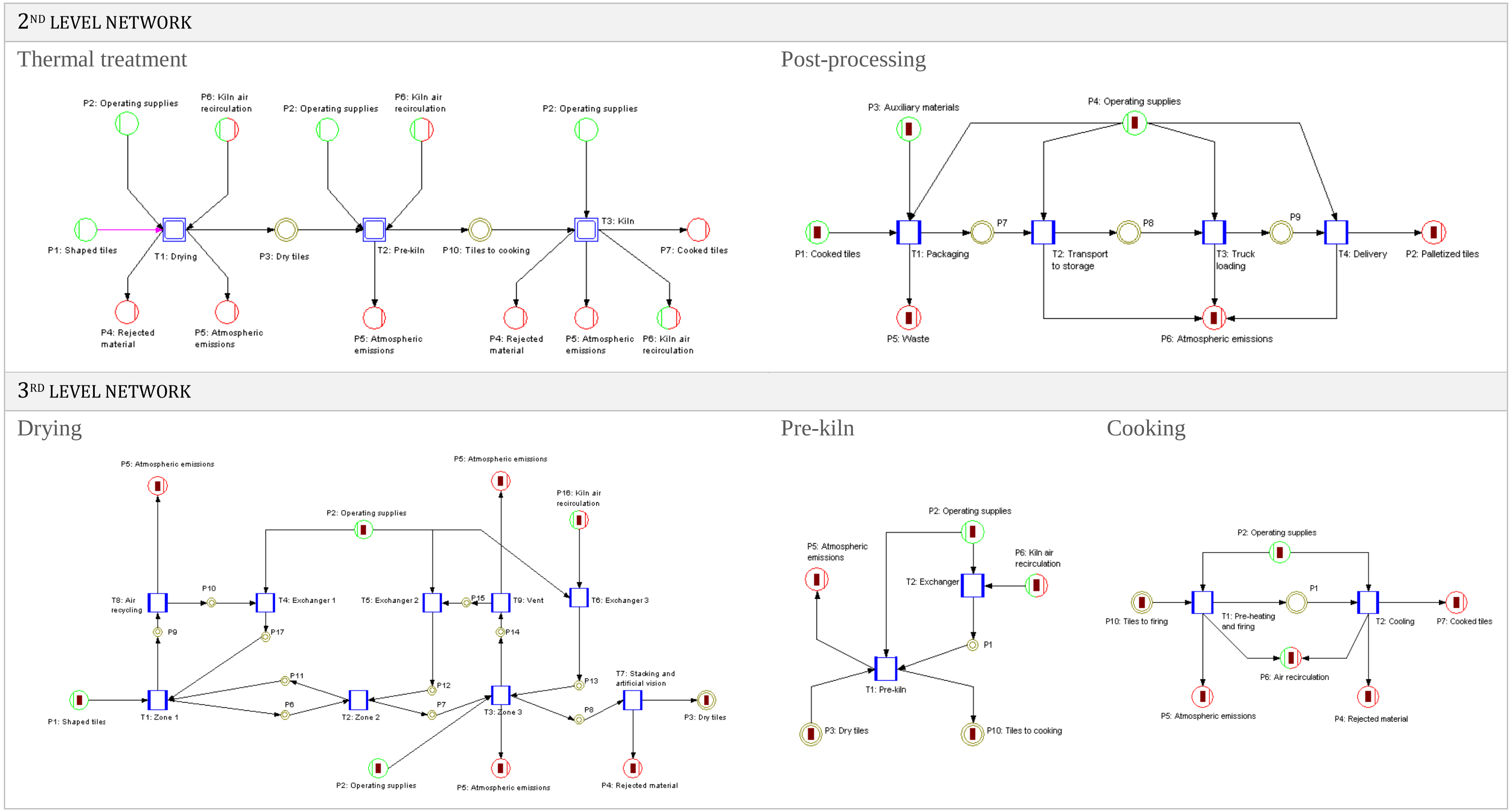
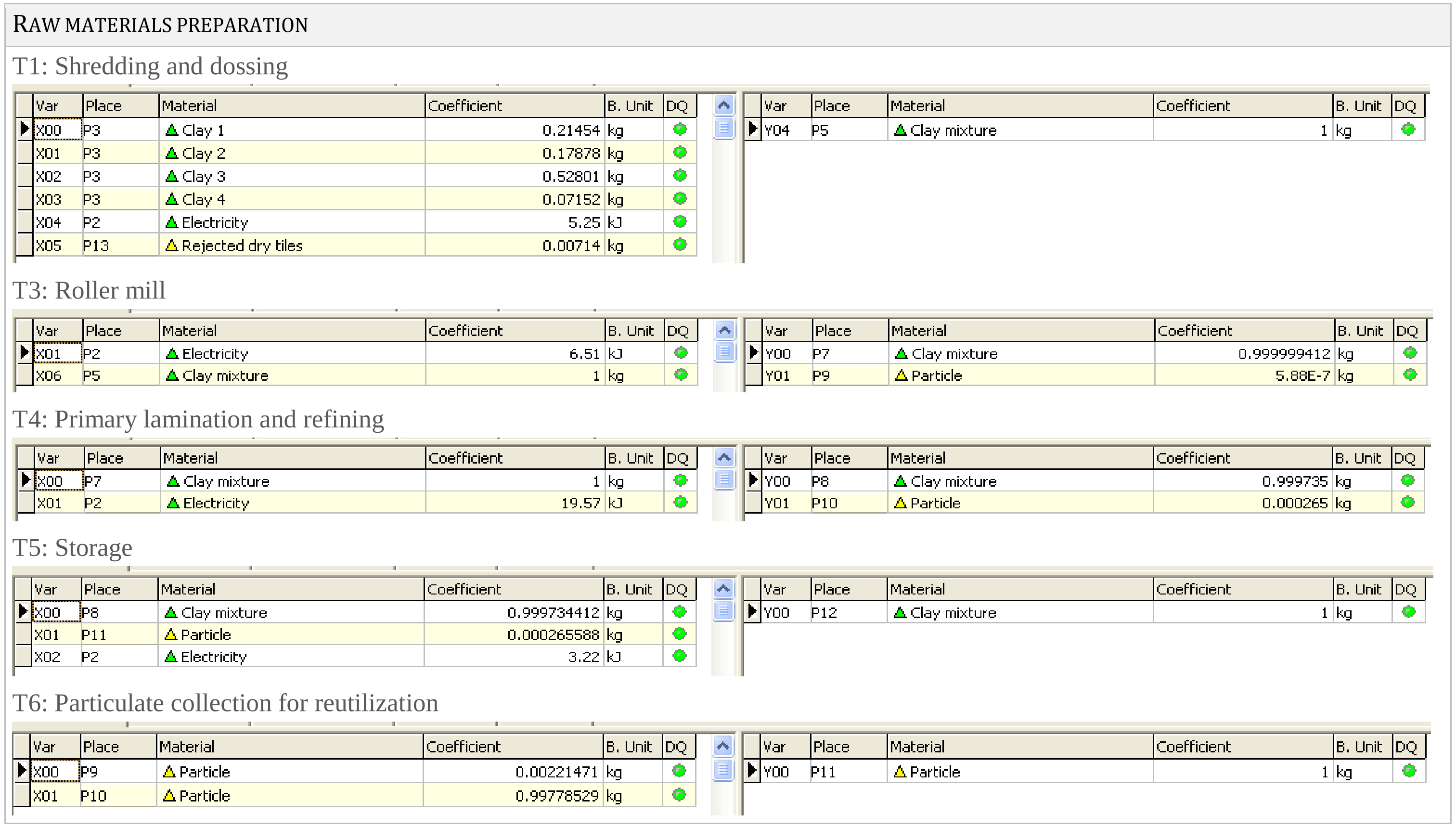


Figure 4.5: Process networks (1st level, 2nd level, 3rd level) (part II) (Torres Rodríguez et al., 2011)



RAW MATERIALS PREPARATION

T1: Shredding and dossing

Var	Place	Material	Coefficient	B. Unit	DQ
X00	P3	△ Clay 1	0.21454	kg	●
X01	P3	△ Clay 2	0.17878	kg	●
X02	P3	△ Clay 3	0.52801	kg	●
X03	P3	△ Clay 4	0.07152	kg	●
X04	P2	△ Electricity	5.25	kJ	●
X05	P13	△ Rejected dry tiles	0.00714	kg	●

Var	Place	Material	Coefficient	B. Unit	DQ
Y04	P5	△ Clay mixture	1	kg	●

T3: Roller mill

Var	Place	Material	Coefficient	B. Unit	DQ
X01	P2	△ Electricity	6.51	kJ	●
X06	P5	△ Clay mixture	1	kg	●

Var	Place	Material	Coefficient	B. Unit	DQ
Y00	P7	△ Clay mixture	0.999999412	kg	●
Y01	P9	△ Particle	5.88E-7	kg	●

T4: Primary lamination and refining

Var	Place	Material	Coefficient	B. Unit	DQ
X00	P7	△ Clay mixture	1	kg	●
X01	P2	△ Electricity	19.57	kJ	●

Var	Place	Material	Coefficient	B. Unit	DQ
Y00	P8	△ Clay mixture	0.999735	kg	●
Y01	P10	△ Particle	0.000265	kg	●

T5: Storage

Var	Place	Material	Coefficient	B. Unit	DQ
X00	P8	△ Clay mixture	0.999734412	kg	●
X01	P11	△ Particle	0.000265588	kg	●
X02	P2	△ Electricity	3.22	kJ	●

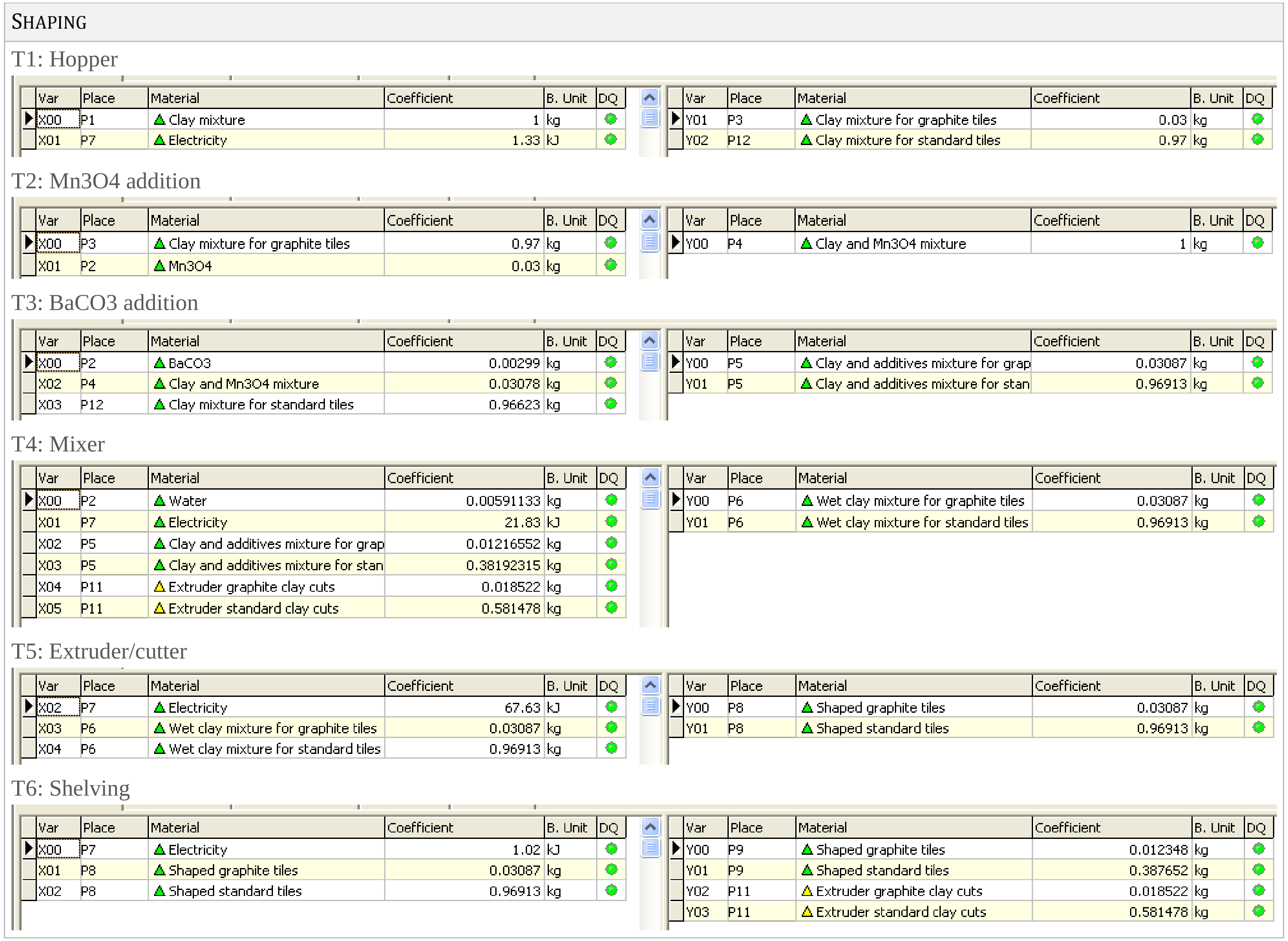
Var	Place	Material	Coefficient	B. Unit	DQ
Y00	P12	△ Clay mixture	1	kg	●

T6: Particulate collection for reutilization

Var	Place	Material	Coefficient	B. Unit	DQ
X00	P9	△ Particle	0.00221471	kg	●
X01	P10	△ Particle	0.99778529	kg	●

Var	Place	Material	Coefficient	B. Unit	DQ
Y00	P11	△ Particle	1	kg	●

Figure 4.6: Transition specifications for “raw materials preparation” and “shaping” stages (part I) (Torres Rodríguez et al., 2011)



SHAPING

T1: Hopper

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	X00	P1	▲ Clay mixture	1	kg	●
	X01	P7	▲ Electricity	1.33	kJ	●

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	Y01	P3	▲ Clay mixture for graphite tiles	0.03	kg	●
	Y02	P12	▲ Clay mixture for standard tiles	0.97	kg	●

T2: Mn3O4 addition

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	X00	P3	▲ Clay mixture for graphite tiles	0.97	kg	●
	X01	P2	▲ Mn3O4	0.03	kg	●

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	Y00	P4	▲ Clay and Mn3O4 mixture	1	kg	●

T3: BaCO3 addition

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	X00	P2	▲ BaCO3	0.00299	kg	●
	X02	P4	▲ Clay and Mn3O4 mixture	0.03078	kg	●
	X03	P12	▲ Clay mixture for standard tiles	0.96623	kg	●

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	Y00	P5	▲ Clay and additives mixture for grap	0.03087	kg	●
	Y01	P5	▲ Clay and additives mixture for stan	0.96913	kg	●

T4: Mixer

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	X00	P2	▲ Water	0.00591133	kg	●
	X01	P7	▲ Electricity	21.83	kJ	●
	X02	P5	▲ Clay and additives mixture for grap	0.01216552	kg	●
	X03	P5	▲ Clay and additives mixture for stan	0.38192315	kg	●
	X04	P11	△ Extruder graphite clay cuts	0.018522	kg	●
	X05	P11	△ Extruder standard clay cuts	0.581478	kg	●

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	Y00	P6	▲ Wet clay mixture for graphite tiles	0.03087	kg	●
	Y01	P6	▲ Wet clay mixture for standard tiles	0.96913	kg	●

T5: Extruder/cutter

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	X02	P7	▲ Electricity	67.63	kJ	●
	X03	P6	▲ Wet clay mixture for graphite tiles	0.03087	kg	●
	X04	P6	▲ Wet clay mixture for standard tiles	0.96913	kg	●

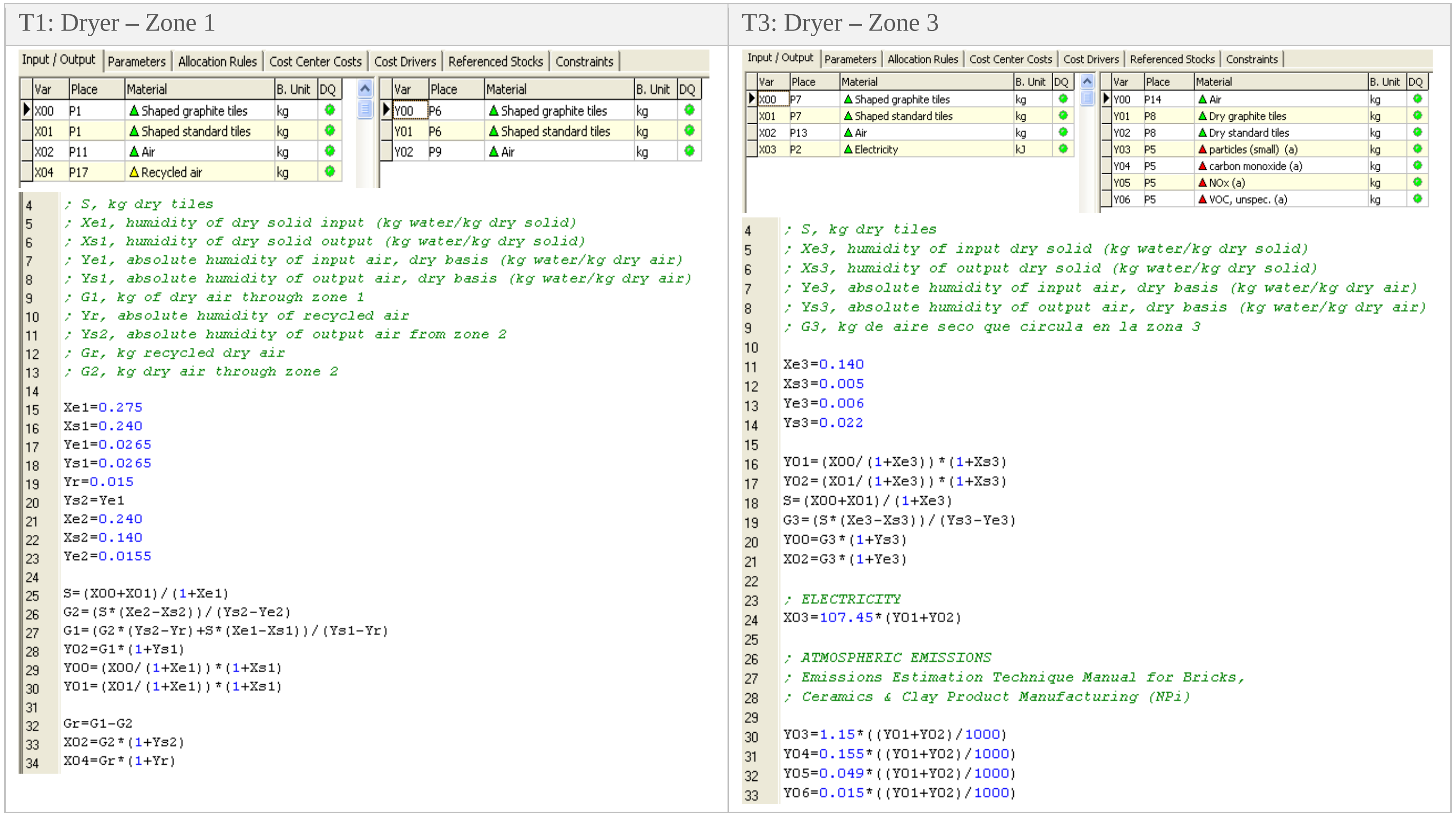
	Var	Place	Material	Coefficient	B. Unit	DQ
▶	Y00	P8	▲ Shaped graphite tiles	0.03087	kg	●
	Y01	P8	▲ Shaped standard tiles	0.96913	kg	●

T6: Shelving

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	X00	P7	▲ Electricity	1.02	kJ	●
	X01	P8	▲ Shaped graphite tiles	0.03087	kg	●
	X02	P8	▲ Shaped standard tiles	0.96913	kg	●

	Var	Place	Material	Coefficient	B. Unit	DQ
▶	Y00	P9	▲ Shaped graphite tiles	0.012348	kg	●
	Y01	P9	▲ Shaped standard tiles	0.387652	kg	●
	Y02	P11	△ Extruder graphite clay cuts	0.018522	kg	●
	Y03	P11	△ Extruder standard clay cuts	0.581478	kg	●

Figure 4.6: Transition specifications for “raw materials preparation” and “shaping” stages (part II) (Torres Rodríguez et al., 2011)



T1: Dryer – Zone 1

Var	Place	Material	B. Unit	DQ
X00	P1	Shaped graphite tiles	kg	●
X01	P1	Shaped standard tiles	kg	●
X02	P11	Air	kg	●
X04	P17	Recycled air	kg	●

Var	Place	Material	B. Unit	DQ
Y00	P6	Shaped graphite tiles	kg	●
Y01	P6	Shaped standard tiles	kg	●
Y02	P9	Air	kg	●

```
; S, kg dry tiles
; Xe1, humidity of dry solid input (kg water/kg dry solid)
; Xs1, humidity of dry solid output (kg water/kg dry solid)
; Ye1, absolute humidity of input air, dry basis (kg water/kg dry air)
; Ys1, absolute humidity of output air, dry basis (kg water/kg dry air)
; G1, kg of dry air through zone 1
; Yr, absolute humidity of recycled air
; Ys2, absolute humidity of output air from zone 2
; Gr, kg recycled dry air
; G2, kg dry air through zone 2

Xe1=0.275
Xs1=0.240
Ye1=0.0265
Ys1=0.0265
Yr=0.015
Ys2=Ye1
Xe2=0.240
Xs2=0.140
Ye2=0.0155

S=(X00+X01)/(1+Xe1)
G2=(S*(Xe2-Xs2))/(Ys2-Ye2)
G1=(G2*(Ys2-Yr)+S*(Xe1-Xs1))/(Ys1-Yr)
Y02=G1*(1+Ys1)
Y00=(X00/(1+Xe1))*(1+Xs1)
Y01=(X01/(1+Xe1))*(1+Xs1)

Gr=G1-G2
X02=G2*(1+Ys2)
X04=Gr*(1+Yr)
```

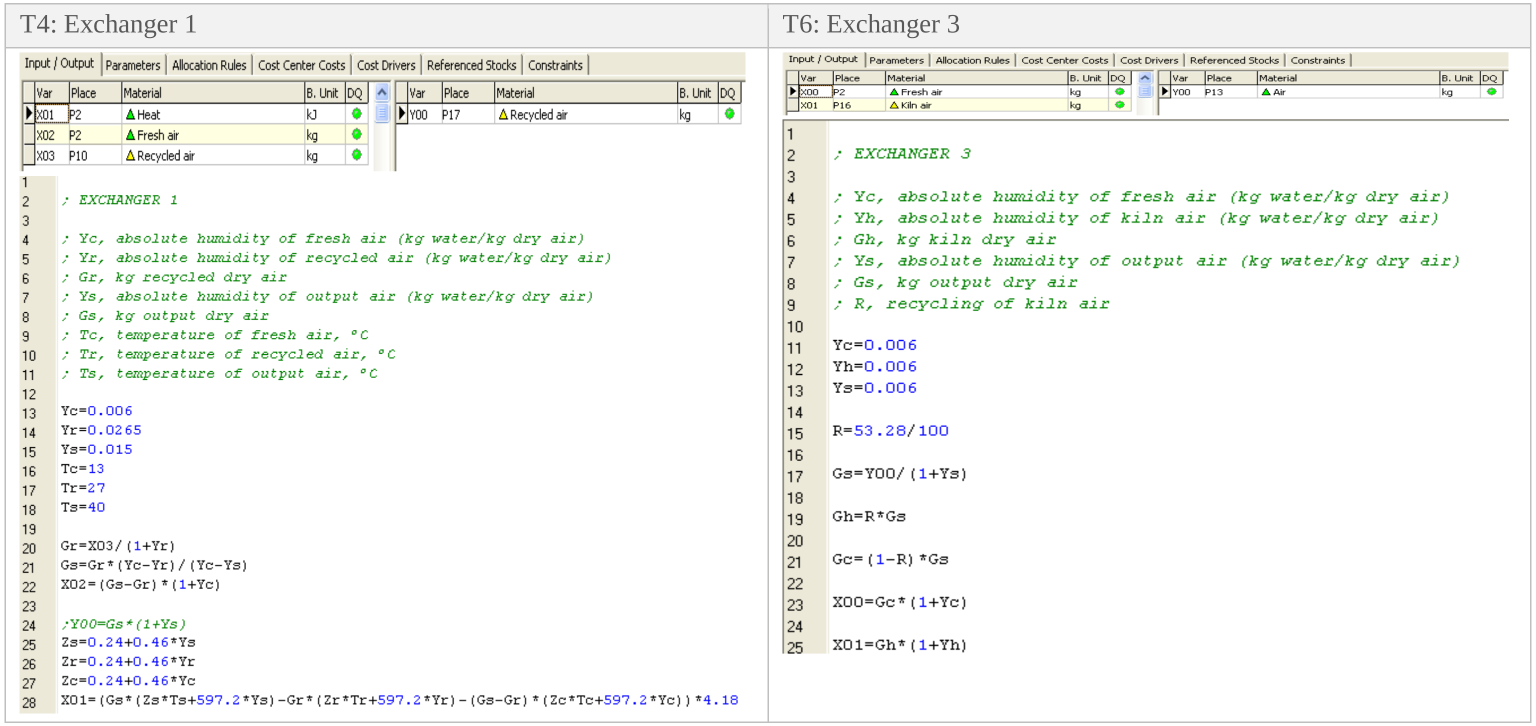
T3: Dryer – Zone 3

Var	Place	Material	B. Unit	DQ
X00	P7	Shaped graphite tiles	kg	●
X01	P7	Shaped standard tiles	kg	●
X02	P13	Air	kg	●
X03	P2	Electricity	kJ	●

Var	Place	Material	B. Unit	DQ
Y00	P14	Air	kg	●
Y01	P8	Dry graphite tiles	kg	●
Y02	P8	Dry standard tiles	kg	●
Y03	P5	particles (small) (a)	kg	●
Y04	P5	carbon monoxide (a)	kg	●
Y05	P5	NOx (a)	kg	●
Y06	P5	VOC, unspec. (a)	kg	●

```
; S, kg dry tiles
; Xe3, humidity of input dry solid (kg water/kg dry solid)
; Xs3, humidity of output dry solid (kg water/kg dry solid)
; Ye3, absolute humidity of input air, dry basis (kg water/kg dry air)
; Ys3, absolute humidity of output air, dry basis (kg water/kg dry air)
; G3, kg de aire seco que circula en la zona 3

Xe3=0.140
Xs3=0.005
Ye3=0.006
Ys3=0.022

Y01=(X00/(1+Xe3))*(1+Xs3)
Y02=(X01/(1+Xe3))*(1+Xs3)
S=(X00+X01)/(1+Xe3)
G3=(S*(Xe3-Xs3))/(Ys3-Ye3)
Y00=G3*(1+Ys3)
X02=G3*(1+Ye3)

; ELECTRICITY
X03=107.45*(Y01+Y02)

; ATMOSPHERIC EMISSIONS
; Emissions Estimation Technique Manual for Bricks,
; Ceramics & Clay Product Manufacturing (NPi)

Y03=1.15*((Y01+Y02)/1000)
Y04=0.155*((Y01+Y02)/1000)
Y05=0.049*((Y01+Y02)/1000)
Y06=0.015*((Y01+Y02)/1000)
```

Figure 4.7: Programmed mathematical expressions for some transitions in the 3rd level network (part I) (Torres Rodríguez et al., 2011)



Var	Place	Material	B. Unit	DQ
X01	P2	▲ Heat	kJ	●
X02	P2	▲ Fresh air	kg	●
X03	P10	△ Recycled air	kg	●

Var	Place	Material	B. Unit	DQ
Y00	P17	△ Recycled air	kg	●

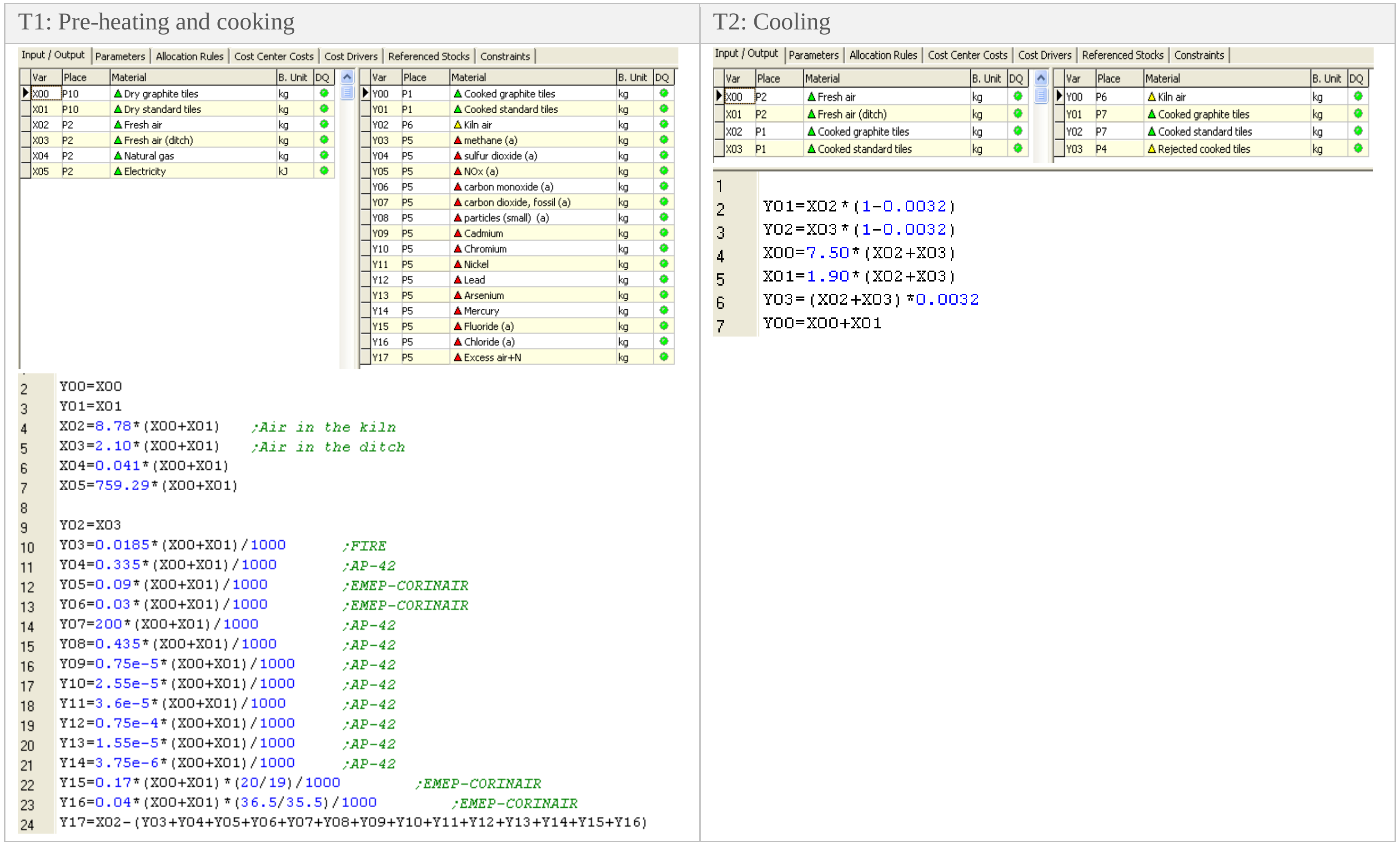
```

; EXCHANGER 1

; Yc, absolute humidity of fresh air (kg water/kg dry air)
; Yr, absolute humidity of recycled air (kg water/kg dry air)
; Gr, kg recycled dry air
; Ys, absolute humidity of output air (kg water/kg dry air)
; Gs, kg output dry air
; Tc, temperature of fresh air, °C
; Tr, temperature of recycled air, °C
; Ts, temperature of output air, °C

Yc=0.006
Yr=0.0265
Ys=0.015
Tc=13
Tr=27
Ts=40

Gr=X03/(1+Yr)
Gs=Gr*(Yc-Yr)/(Yc-Ys)
X02=(Gs-Gr)*(1+Yc)

;Y00=Gs*(1+Ys)
Zs=0.24+0.46*Ys
Zr=0.24+0.46*Yr
Zc=0.24+0.46*Yc
X01=(Gs*(Zs*Ts+597.2*Ys)-Gr*(Zr*Tr+597.2*Yr)-(Gs-Gr)*(Zc*Tc+597.2*Yc))*4.18
```

Var	Place	Material	B. Unit	DQ
X00	P2	▲ Fresh air	kg	●
X01	P16	△ Kiln air	kg	●

Var	Place	Material	B. Unit	DQ
Y00	P13	▲ Air	kg	●

```

; EXCHANGER 3

; Yc, absolute humidity of fresh air (kg water/kg dry air)
; Yh, absolute humidity of kiln air (kg water/kg dry air)
; Gh, kg kiln dry air
; Ys, absolute humidity of output air (kg water/kg dry air)
; Gs, kg output dry air
; R, recycling of kiln air

Yc=0.006
Yh=0.006
Ys=0.006

R=53.28/100

Gs=Y00/(1+Ys)

Gh=R*Gs

Gc=(1-R)*Gs

X00=Gc*(1+Yc)

X01=Gh*(1+Yh)
```

Figure 4.7: Programmed mathematical expressions for some transitions in the 3rd level network (part II) (Torres Rodríguez et al., 2011)



Var	Place	Material	B. Unit	DQ
X00	P10	▲ Dry graphite tiles	kg	●
X01	P10	▲ Dry standard tiles	kg	●
X02	P2	▲ Fresh air	kg	●
X03	P2	▲ Fresh air (ditch)	kg	●
X04	P2	▲ Natural gas	kg	●
X05	P2	▲ Electricity	kJ	●

Var	Place	Material	B. Unit	DQ
Y00	P1	▲ Cooked graphite tiles	kg	●
Y01	P1	▲ Cooked standard tiles	kg	●
Y02	P6	▲ Kiln air	kg	●
Y03	P5	▲ methane (a)	kg	●
Y04	P5	▲ sulfur dioxide (a)	kg	●
Y05	P5	▲ NOx (a)	kg	●
Y06	P5	▲ carbon monoxide (a)	kg	●
Y07	P5	▲ carbon dioxide, fossil (a)	kg	●
Y08	P5	▲ particles (small) (a)	kg	●
Y09	P5	▲ Cadmium	kg	●
Y10	P5	▲ Chromium	kg	●
Y11	P5	▲ Nickel	kg	●
Y12	P5	▲ Lead	kg	●
Y13	P5	▲ Arsenium	kg	●
Y14	P5	▲ Mercury	kg	●
Y15	P5	▲ Fluoride (a)	kg	●
Y16	P5	▲ Chloride (a)	kg	●
Y17	P5	▲ Excess air+N	kg	●

```
Y00=X00
Y01=X01
X02=8.78*(X00+X01)    ;Air in the kiln
X03=2.10*(X00+X01)    ;Air in the ditch
X04=0.041*(X00+X01)
X05=759.29*(X00+X01)

Y02=X03
Y03=0.0185*(X00+X01)/1000       ;FIRE
Y04=0.335*(X00+X01)/1000        ;AP-42
Y05=0.09*(X00+X01)/1000         ;EMEP-CORINAIR
Y06=0.03*(X00+X01)/1000         ;EMEP-CORINAIR
Y07=200*(X00+X01)/1000          ;AP-42
Y08=0.435*(X00+X01)/1000        ;AP-42
Y09=0.75e-5*(X00+X01)/1000      ;AP-42
Y10=2.55e-5*(X00+X01)/1000      ;AP-42
Y11=3.6e-5*(X00+X01)/1000       ;AP-42
Y12=0.75e-4*(X00+X01)/1000      ;AP-42
Y13=1.55e-5*(X00+X01)/1000      ;AP-42
Y14=3.75e-6*(X00+X01)/1000      ;AP-42
Y15=0.17*(X00+X01)*(20/19)/1000         ;EMEP-CORINAIR
Y16=0.04*(X00+X01)*(36.5/35.5)/1000         ;EMEP-CORINAIR
Y17=X02-(Y03+Y04+Y05+Y06+Y07+Y08+Y09+Y10+Y11+Y12+Y13+Y14+Y15+Y16)
```

Var	Place	Material	B. Unit	DQ
X00	P2	▲ Fresh air	kg	●
X01	P2	▲ Fresh air (ditch)	kg	●
X02	P1	▲ Cooked graphite tiles	kg	●
X03	P1	▲ Cooked standard tiles	kg	●

Var	Place	Material	B. Unit	DQ
Y00	P6	▲ Kiln air	kg	●
Y01	P7	▲ Cooked graphite tiles	kg	●
Y02	P7	▲ Cooked standard tiles	kg	●
Y03	P4	▲ Rejected cooked tiles	kg	●

```

Y01=X02*(1-0.0032)
Y02=X03*(1-0.0032)
X00=7.50*(X02+X03)
X01=1.90*(X02+X03)
Y03=(X02+X03)*0.0032
Y00=X00+X01
```

Figure 4.7: Programmed mathematical expressions for some transitions in the 3rd level network (part III) (Torres Rodríguez et al., 2011)

Table 4.5: Emission factors for combustion in the process

Pollutant	**Units**	**Dryer – zone 3**	**Kiln**	**Machinery**
Inorganic compounds				
NH_3	g/kg fuel	-	-	0.007
CO_2	kg/t tiles	35.500	61.00(4)	-
CO	kg/t tiles	0.155	$3.00\cdot10^{-2}$	15.80(5)
N_2O	g/kg fuel	-	-	1.30
Chlorides (as Cl)	kg/t tiles	-	$4.00\cdot10^{-2}$	-
Fluorides (as F)	kg/t tiles	-	$1.70\cdot10^{-1}$	-
NO_x	kg/t tiles	0.049	$9.00\cdot10^{-2}$	48.80(5)
SO_2	kg/t tiles	-	$3.35\cdot10^{-1}$	-
Particulates				
PM_{10}	kg/t tiles	1.150	$4.35\cdot10^{-1}$	5.73(5)
VOC				
CH_4	kg/t tiles	-	$1.85\cdot10^{-2}$	0.17(5)
VOC	kg/t tiles	0.015	-	-
NMVOC	g/kg fuel	-	-	7.08
Benzo(a)pirene	g/kg fuel	-	-	$30\cdot10^{-6}$
Metals				
Arsenic (As)	kg/t tiles	-	$1.55\cdot10^{-5}$	-
Cadmium (Cd)	kg/t tiles	-	$0.75\cdot10^{-5}$	-
Chromium (Cr)	kg/t tiles	-	$2.55\cdot10^{-5}$	-
Mercury (Hg)	kg/t tiles	-	$3.75\cdot10^{-6}$	-
Nickel (Ni)	kg/t tiles	-	$3.60\cdot10^{-5}$	-
Lead (Pb)	kg/t tiles	-	$0.75\cdot10^{-4}$	-

(1) (NPI, 1998)
(2) (EMEP CORINAIR, 1996a; US EPA, 1996)
(3) (EMEP CORINAIR, 1996b)
(4) as kg/GJ
(5) as g/kg fuel

The modelling for the pre-kiln subnet is similar the one presented for transitions T1 and T4 in the drying subnet, including also the calculation for the electrical consumption.

In the cooking subnet mass balances for air and clay are considered. The atmospheric emissions derived from chemical reactions are also calculated in T1 (pre-heating and cooking), using emission factors (Table 4.5).

Finally post-processing subnet also includes non-linear transitions. T1 (packaging) considers simple mass balances to estimate the amount of packaging material used and rejected. T2 (transport to storage) calculates electrical consumption for the pallets electrically transported and the atmospheric emissions derived from transporting tiles using diesel vehicles. These emissions are calculated on the basis of annual diesel consumption, using data from Table 4.3, and considering the corresponding emission factors (Table 4.5). These calculations are the same for T3 (truck loading). T4 (delivery) uses a specific module library included in Umberto, which describes transport of goods by truck and considers travel distance, load, vehicle type and road type to calculate emissions corresponding to fuel combustion.

MODEL RUNNING AND RESULTS OF THE MEFA

The model has been executed considering the raw clay input during 2005. Table 4.6 shows the results of the global material and energy balance for the whole process. Materials and energy have been classified as inputs and outputs. Figure 4.8 represents the most relevant Sankey diagrams obtained for the process. Umberto uses them to display materials, energy and costs flows.

Results obtained for the storage stage (chapter 3.1) concluded that transport was the most important source of pollution, regarding atmospheric emissions. This stage is a great fuel consumer and consequently a great exhaust gases releaser, being CO_2 the main pollutant. Another important environmental impact linked with transport is particulate matter.

The most remarkable point about “raw material preparation” is the electricity consumption. The processes involved in this stage require approximately $2.40 \cdot 10^9$ kJ of electrical energy, most of it consumed by the primary lamination and refining processes, though this consumption is not that relevant if compared with other stages.

The electrical consumption in “shaping” is $16.14 \cdot 10^9$ kJ, mostly demanded by the mixer and the extruder/cutter engines. However, the most relevant issue about “shaping” is not its electrical demand but clay cuts. Clay cuts from shelving are totally fed back to the mixer, so that they are re-used in the process. As a result, no material is rejected and therefore no waste is generated.

Thermal treatments differ from the already mentioned stages as they not only demand electricity but also fuel, natural gas in this case. Natural gas consumption affects both the inputs and the outputs, as its combustion, besides heat, generates emissions. Most of these emissions are CO_2, as 11627.12 tonnes are released, mainly from the cooking sub-stage. However not only CO_2 is released because of natural gas combustion but also other pollutants such as CO, NO_x, PM_{10} or VOC. Non-CO_2 atmospheric pollutants become especially relevant on the cooking subnet, as pollutants resulting from the natural gas combustion get mixed with other compounds, such as metals, CH_4, chlorides and fluorides released as a consequence of the chemical reactions that take place during cooking (European Commission, 2007a).

Thermal treatments are typically the most polluting stage in the ceramics manufacture processing. However, as the considered plant uses a low-carbon fuel, natural gas, atmospheric emissions (mainly CO_2) are much lower than expected.

The other relevant mass flows associated to the thermal treatments are the two rejected tiles flows, one corresponding to the defective dry tiles from the dryer and other to the broken cooked tiles from the kiln. Almost all the dry tiles are fed back to the “raw materials preparation” stage, in order to be milled and re-used, whereas the cooked tiles are a residual flow which has to be conveniently managed.

Thermal treatments are highly energy demanding processes; in fact they consume 72.41% of the total amount of electricity required by the plant. Among thermal treatments, cooking is the one requiring more energy, as it demands 83.50% of the electricity provided to the stage and 84.96% of the total natural gas fed to heat the air streams. The cooking kiln needs an important fuel supply, natural gas in this case, in order to heat air to the high temperatures required to cook the tiles. Air inputs come both from the outside and from the cooling pits, whereas air outputs are air from the cooling zone which is used as pre-heating air in the dryer and the pre-kiln, as well as excess air that is released.

Table 4.6: Global balance for the roof-tile manufacturing process

	Item							**Quantity**	**Unit**
Inputs	Raw materials (wet basis)				Clay 1		20	14921.00	t
					Clay 2	Moisture content (%)	20	12434.00	t
					Clay 3		35	36729.00	t
					Clay 4		20	4974.00	t
	Secondary materials				Water			3689.43	t
					CO_3Ba			208987.91	kg
					Mn_3O_4			64541.62	kg
					Air			1638092.58	t
	Auxiliary materials				Carton			17457.27	kg
					Labels			810.71	kg
					Band (11.6 mm)			19457.02	kg
					Band (14.6 mm)			3350.93	kg
					Wooden pallets			446052.21	kg
					Re-usable pallets			84962.33	kg
					Retractable plastic			27023.64	kg
	Energy				Fuel oil			26781.80	t
					Natural gas			3036.00	t
					Electricity			$68.95 \cdot 10^9$	kJ
Outputs	Emissions to air	Inorganic compounds			NH_3			535.07	kg
					CO_2			99849.36	t
					CO			176348.98	kg
					N_2O			8922.85	kg
					Chlorides			2283.71	kg
					Fluorides			9820.36	kg
					NO_x			936141.92	kg
					SO_2			42448.86	kg
		PM_{10}						1938.83	t
		VOC	Methane					3061.28	kg
			NMVOC	Halogenated	Aromatic	PCDD, PCDF		$1.60 \cdot 10^{-6}$	kg
				Aldehydes		Methylene oxide		6877.77	kg
				Aromatic	HC	Benzene		1613.30	kg
				PAH		Benzo(a)pyrene		0.21	kg
				Unspecified				76350.16	kg
		Metals			Arsenic (As)			0.85	kg
					Cadmium (Cd)			0.41	kg
					Chromium (Cr)			1.40	kg
					Mercury (Hg)			0.21	kg
					Nickel (Ni)			1.98	kg
					Lead (Pb)			4.12	kg
		Air			Purge from drier			172156.31	t
					Air from drier and pre-kiln			981059.78	t
					Air from kiln			473045.48	t
	Waste	Band (11.6 mm)						778.28	kg
		Band (14.6 mm)						87.12	kg
		Retractable plastic						1080.95	kg
		Rejected cooked tiles						175611.15	kg
	Products				Graphite tiles pallets			1706.65	t
					Normal tiles pallets			53595.34	t

Regarding “post-processing”, its most relevant fact is the fuel consumption, though irrelevant if compared with the one obtained for the “transport and storage of raw materials” stage (chapter 3.1). Consequently CO_2 is emitted.

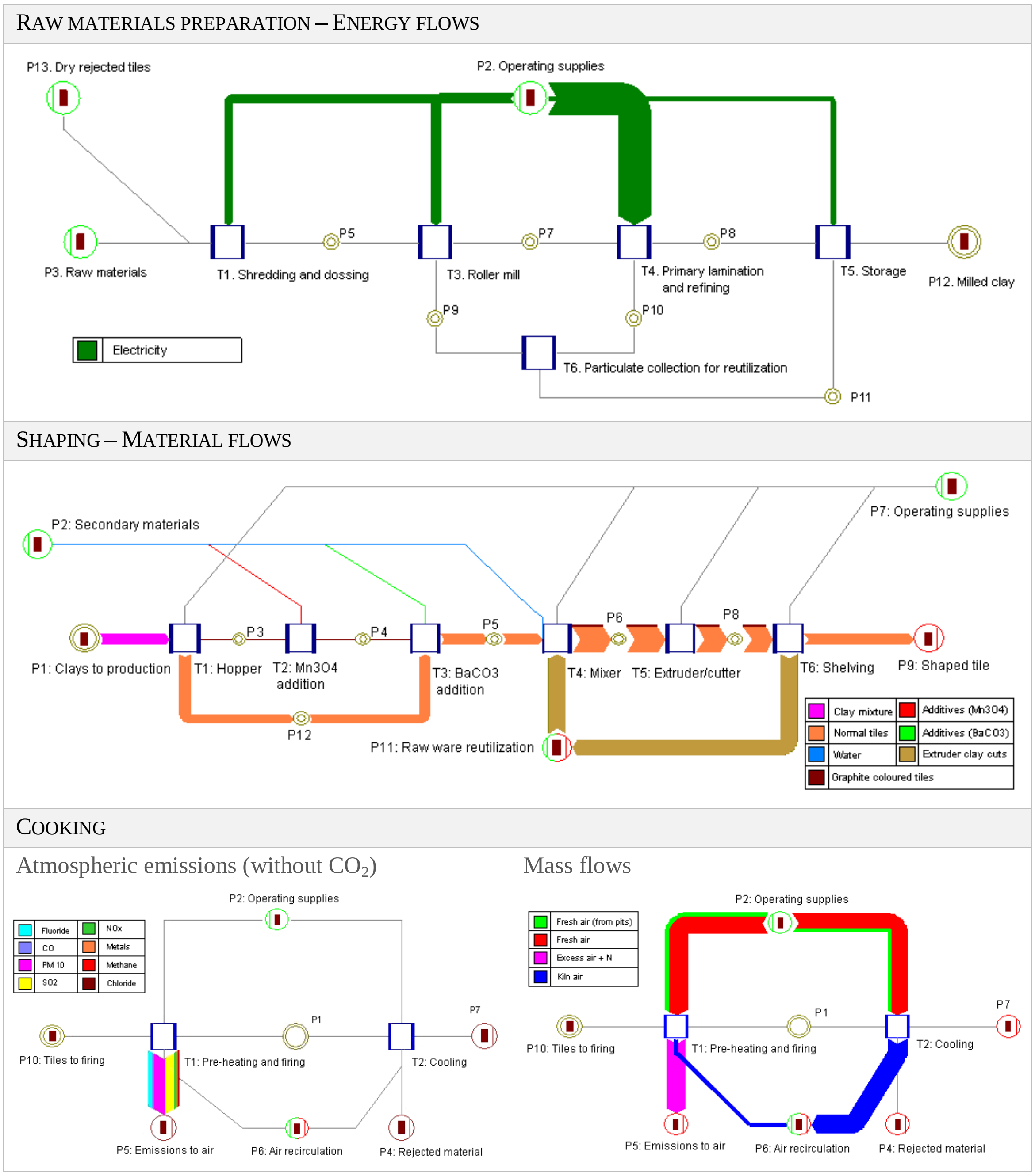


Figure 4.8: Sankey diagrams (Torres Rodríguez et al., 2011)

4.3. Selection of IF

MEFA results have proved that “transport and storage of raw materials” and “thermal treatments” are the most likely to be improved stages, because of their high resources consumptions and pollutants emissions. Both stages demand important amounts of combustible, meaning fuel and natural gas, depending on the stage considered. Furthermore they release relatively high amounts of atmospheric pollutants, mainly exhaust gases that, though they do not exceed the ELV fixed in the environmental permit (Cristóbal Andrade et al., 2009), they are improvable.

Table 4.7 shows the IF identified after evaluating the results of the MEFA. For each stage, the quantitatively relevant flows (Figure 4.8) have been selected as improvable. Therefore, 3 IF have been selected for both “transport and storage of raw materials” and “post-processing” stages. Only 1 IF has been identified for stages “raw materials preparation” and “shaping”. Finally, 6 IF have been identified for “thermal treatments”.

Concerning their type, there have been identified seven inputs, all of them associated with energy, and seven outputs, all of them concerning waste streams.

Table 4.7: Improvable flows identified for the process

Stage	**Improvable Flows**	
	Inputs	**Outputs**
Transport and storage	Diesel fuel	Exhaust gases Particulate emissions
Preparation	Electricity	
Shaping	Electricity	
Thermal treatment	Natural gas Electricity	Rejected cooked tiles Particulate emissions CO_2 Fluorine and other atmospheric emissions
Post-processing	Fuel Electricity	Exhaust gases

4.4. BAT Analysis

The last step of the methodology is BAT Analysis, which includes a recompilation of an inventory of techniques candidate to be BAT for the considered system, the identification of the already implemented techniques, and the selection of the suitable techniques to enhance the IF.

4.4.1. Recompilation and inventory of techniques candidate to be BAT

The inventory of candidate techniques for the heavy ceramics manufacture industry was developed in chapter 2 by applying BAT Analysis to the Galician heavy ceramics manufacture sector. That chapter presented a deep analysis of the sector in the region, as well as a detailed description of the generic typical process, which can be adapted to any of the integrating plants. Regarding the process, associated consumptions and emissions were identified, highlighting the special relevance of atmospheric emissions, mostly particulates and exhaust gases from thermal treatments. Finally, a technical inventory for the heavy ceramics industry was developed, resulting in 46 techniques, classified attending to the process stage where they should be applied, were gathered together and complemented by a series of best environmental practices, both generic and specific.

4.4.2. Identification of the already implemented BAT

Cerámica Verea S.A. has already implemented four BAT, which has directly affected the results obtained for the MEFA. The already implemented techniques are:

- *Installation of bulk storage areas for dusty materials enclosed with walling*. It affects to “transport and storage of raw materials”, “raw materials preparation” and “shaping” stages, reducing particulate and dust emissions. The effectiveness of this technique is quite good as not dust neither particulates have been quantified in “raw materials preparation” and “shaping” stages (Figure 4.8).
- *Reprocessing of green and unfired wares.* This technique (implemented in “raw materials preparation” and “shaping”) aims to benefit the residual usable ceramic. In the case of “raw materials preparation”, rejected dry tiles are fed back to the process from the drying stage, whereas in “shaping” green ware, as extruder clay cuts, is fed back to the mixer (Figure 4.8).
- *Optimizing cooking and drying processes*. Thermal treatments have been optimised by recovering heat from flue gases from the kiln and feeding it back to the dryer. It is the best option for minimizing energy consumption in such an energy demanding process.
- *Utilization of low ash fuels such as natural gas*. Due to the typical relatively high emissions rate from cooking, natural gas is used as fuel in the thermal treatments stage. In spite of being the most energy consuming stage, it is not the one releasing more atmospheric pollutants.

4.4.3. BAT selection according to IF

Candidate techniques to be BAT are proposed for those IF likely to be enhanced, as indicated in Table 4.7.

TRANSPORT AND STORAGE OF RAW MATERIALS

- To enhance the IF “diesel fuel” *limiting vehicles speed* and *minimising transport distances* is proposed. Both measures affect diesel fuel consumption and exhaust gases emissions as well.
- The IF “exhaust gases” can be reduced by *limiting vehicles speed* and *minimising transport distances.* The last measure effectively reduces exhaust gases emissions as fuel consumption, and thereby combustion gases, directly depends on the travelled distance. Furthermore, the most consumed clay is Clay 3 (Table 4.2), the one collected from the furthest quarry, which is 15 km away from the plant, so proper planning of travels to the quarry could contribute to reduce two IF, namely “diesel fuel” and “exhaust gases”.
- The techniques proposed to reduce the IF “particulate” are *limiting vehicles speed*, *minimising transport distances* and *circulating through paved roads*, which have been reported to reduce dust and particulate emissions (European Commission, 2006b).

RAW MATERIALS PREPARATION

- To enhance the IF “electricity”, *energetic optimisation* is proposed. This technique involves programming and using equipment only when necessary and in the appropriate conditions.

SHAPING

- The IF “electricity” can also be reduced by *energetic optimisation,* the same technique as described for “raw materials preparation”.

THERMAL TREATMENT

- The IF “natural gas” cannot be reduced, as it is itself a BAT, and it is also affected by another implemented BAT, *optimizing cooking and drying processes*. In fact, energy consumption could have been even greater in case of not re-using hot air in the process.
- As in the case of “natural gas”, the IF “electricity” cannot be improved as energy consumption has already been optimised for this stage.
- The IF “rejected cooked tiles” is another IF that cannot be further improved. After cooking, tiles cannot be fed back to the process, so there is no chance to recover them. Besides there are no techniques that can effectively reduce the amount of tiles broken while cooking.
- The IF “particulate” can be highly reduced by the implementation of either *bag filters with injection of* $NaHCO_3$ or *electrostatic precipitators with injection of* $NaHCO_3$. Both techniques are able to reduce even more than 99% dust and acid gases emissions (Casares et al., 2005). Other advantages are that, besides requiring some extra energy supply, they do not consume many raw materials and they barely release any waste. Moreover investment and operational costs are not too high (Casares et al., 2005), so the installation of such equipments can be easily afforded by the company.
- The IF “CO_2” cannot be further improved, as it is quite lower than the value expected for such a process. CO_2 emissions have been highly reduced, regarding typical ceramics manufacturing process, thanks to the already implemented technique *utilization of low ash fuels such as natural gas*.
- The IF “fluorine and other atmospheric emissions” also benefit from the techniques *bag filters with injection of* $NaHCO_3$ and *electrostatic precipitators with injection of* $NaHCO_3$, as they not only reduce particulate emissions but also sulphur oxides, fluorine and chlorine components (European Commission, 2007a).

  Among the atmospheric pollutants included in this IF, fluorine is a special case. Though fluorine emissions do not exceed the ELV fixed by the competent authority (Cristóbal Andrade et al., 2009) (and they are not even mentioned in the environmental permit), they exceed the BAT-AEL proposed by the European Commission (European Commission, 2007a). Besides the already mentioned techniques, this IF could be also reduced by implementing one of the multiple *techniques for reducing inorganic compounds*. However these techniques, although effective, are not really applicable, as they demand chemical compounds and great amounts of water that has to be treated as wastewater. Besides, economical investments are considerably greater than in the case of bag filters of electrostatic precipitators.

POST-PROCESSING

- The IF “diesel fuel” can be enhanced by *limiting vehicles speed* and/or *minimising transport distances*.
- There are no candidate techniques that can effectively reduce the IF “electricity” in the “post-processing” stage.
- The IF “exhaust gases” can be reduced by the techniques *limiting vehicles speed* and *minimising transport distances.*

5. Results and discussion

This chapter has presented a methodology combining a technical inventories method, BAT Analysis, and an IF identification tool, MEFA, to get sustainable industrial systems. The methodology includes a thorough description of the system, MEFA (adapting the methodology presented in chapter 3.1), the identification of the IF of the system, and BAT Analysis (as presented in chapter 2).

The methodology has been applied to an industrial system, a roof-tile manufacture plant, to make it more sustainable. As a result, its IF have been identified and the most appropriate candidate BAT have been selected to mitigate the effect of those IF.

Modelling the process and applying MEFA has enabled to the identification of the IF. 14 IF (7 inputs and 7 outputs, concerning both materials and energy) were identified. Six IF concern “thermal treatments” stage, which has been proved to be the most likely to be improved stage, whereas the stages involving transport, namely “transport and storage of raw materials” and “post-processing”, have 3 IF each. The other 2 IF correspond to “raw materials preparation” and “shaping”. All the input IF are related to energy, as they correspond to electricity or fuel flows. On the other hand, almost all output IF are atmospheric emissions except one, which corresponds to rejected cooked tiles.

The application of BAT Analysis has led to the identification of 4 techniques that have already been successfully implemented. According to the identified IF, 7 candidate BAT directly affecting 9 IF have been proposed.

The already implemented techniques highly contribute to the exemplary environmental performance of the plant. In fact, for two of the stages of the process there have not been detected particulate flows or rejected clay flows. In addition, a low ash fuel, natural gas, is used in thermal treatments. The optimised configuration of this stage is also a BAT. Consequently both fuel consumption and CO_2 emissions are much lower than those expected for a typical process.

On the other hand, among the proposed techniques *circulating through paved roads*, *limiting vehicles speed* or *minimizing transport distances,* are really easy to implement and do not involve any additional cost for the plant. They can considerably reduce the IF particulates, exhaust gases and diesel fuel involved in “transport and storage of raw materials” and “post-processing”. *Energetic optimisation* of the equipments involved in “raw materials preparation” and “shaping” is also quite easy and cheap to implement. It includes good practices such as minimising pumping distances, adjusting the operating conditions to the needs of the process, controlling electricity consumption, or automating the process, among others. All these practices could mean an important reduction of the IF electricity.

Techniques proposed to reduce atmospheric emissions, namely *bag filters with injection of* $NaHCO_3$ or *electrostatic precipitators with injection of* $NaHCO_3$, and *techniques for reducing inorganic compounds*, are more difficult to implement. They involve economical costs, as equipment has to be acquired, chemicals are required and waste streams are generated. However, the good performance data reported for these techniques justifies their application, as IF regarding PM and atmospheric emissions (especially HF) can be highly enhanced. The best option will be selecting either *bag filters with injection of* $NaHCO_3$ or *electrostatic precipitators with injection* *of $NaHCO_3$*. Besides reducing particulate emissions, these techniques are very effective to reduce acid gases emissions, such as HF, making it possible to meet the BAT-AEL 10 mg HF/Nm^3.

Even when applied to such an exemplary plant as the considered, the methodology provides important information about the IF and a list of candidate BAT with a technical data sheet for each technique. These results could be used by decision-makers to select and implement the appropriate modifications to enhance the process under study, based on industrial metabolism and sustainability criteria.

6. Conclusions

The proposed methodology has been validated as a suitable method to get sustainable industrial systems. The method combines two known tools to identify the IF of the process and to propose the most appropriate techniques (concerning sustainability) to improve its industrial metabolism. The method has been validated in an exemplary ceramics manufacture plant. 14 improvable flows have been identified for the process, six of them related to the “thermal treatments” stage. Consequently 7 candidate BAT have been proposed aiming to reduce these flows.

The combination of MEFA and BAT Analysis has turned out to be a good option for process evaluation considering sustainability criteria. The application of the methodology to an exemplary process shows that MEFA gives deep information about the environmental aspects of the process to identify the IF, while BAT Analysis helps taking into account not only environmental factors, but also economic aspects that may affect the selection of techniques. It is shown that even a plant with such an exemplary environmental performance as the analysed one can be improved by the implementation of the selected modifications.

The proposed methodology provides a way to detect improvable material or energy flows in a process, whether they are inputs, outputs or internal flows, and selects the most sustainable options to enhance them. Solutions are proposed for the detected IF, and their effectiveness on improving them is roughly considered, though not specific and quantitative data about these improvements is provided.

These results are very useful to enhance the process regarding resources consumption, environmental performance and, at lower level, economical aspects related to the habitual operation of the analysed process.

An interesting continuation for this work will be the implementation of the proposed techniques in the selected plant. This task is not easy to accomplish with, as it will require a strong implication of the plant, with important inversion and long period of time to fully implant and implement the techniques, and to analyse their effectiveness. For this reason, this methodology could be further improved by including a final step to evaluate the consequences of implementing the selected techniques in the system. Process simulation could be a suitable tool, as it predicts the behaviour of processes after modifying one or more variables. Decision-makers will have now complete information about the effect of the proposed techniques over the IF.

CHAPTER 5

COMBINING BAT ANALYSIS AND PROCESS SIMULATION: APPLICATION TO HYDROGEN SYNTHESIS

Summary

As concluded in chapter 3.2, process simulation is a suitable tool for IF detection, so it can effectively complement BAT Analysis in an integrated methodology to get sustainable industrial systems. Furthermore, process simulation effectively predicts the behaviour of processes after implementing modifications.

This chapter proposes a methodology to improve the sustainability of industrial systems combining two tools: BAT Analysis and process simulation. Both tools are jointly applied to identify the IF of the analysed process, so that the most appropriate candidate techniques from an inventory can be selected. The selected alternatives are evaluated in different scenarios by process simulation to determine the configuration that best improves the sustainability of the industrial process.

The first module of the methodology involves a deep analysis of the process concerned, followed by a rigorous evaluation of the main environmental aspects. Then BAT Analysis (as defined in chapter 2) is applied to get an inventory of candidate techniques. Process simulation software is applied to the base case to analyse the process, quantifying all the material and energy flows. The simulation results are used to identify the IF of the process, so that candidate techniques from the inventory can be selected to improve the process.

In the second module of the methodology alternative scenarios implementing one or a set of candidate techniques are proposed. Each scenario is qualitatively analysed to clearly define the implementation conditions of the candidate techniques. Then process simulation software is applied to each scenario and the simulation results are compared to evaluate which one is the most appropriate to enhance the IF detected in the base case.

The methodology is validated in a case study: a hydrogen production plant applying the natural gas steam reforming process. The first module of the methodology reveals three IF for the

process, which have been summarised to ‘CO_2 emissions from’ and ‘energy consumption in’, associated to some stages of the process. Accordingly, three alternative scenarios are proposed and evaluated, pointing out two candidate techniques as the more suitable to improve the process.

The combination of these tools in an integrated methodology will help decision-makers to select the most sustainable configuration for a given process.

1. Introduction

In the actual scenario of continuous technological advances, authors agree that a sustainable industry requires innovative approaches (Bakshi, 2011; Dijkema et al., 2003) with an increased emphasis on decisions over process selection (Clift, 2006). As discussed in previous chapters (chapter 2 and chapter 4), BAT Analysis is a tool that can provide such a support in the decision-making elements of a methodology. This tool not only supplies a list of candidate techniques, but a set of contrasted information about each technique. Accordingly, modellers can base their decisions on experiences from other plants, on results obtained after applying the techniques, or even be aware of the secondary effects of such techniques.

However BAT Analysis is not properly implemented if the candidate techniques are not accurately selected and evaluated, which compromises their efficiency. Besides knowledge about the candidate techniques, knowledge about the process concerned is also needed. The disturbing elements of the process should be clearly identified, as well as the potential impacts they may cause over the specific environment. It seems that an element integrating these considerations is missing in the traditional BAT selection methodologies. BAT selection methodologies, as BAT Analysis, should be preceded by an accurate procedure to identify the drawbacks of the process, so that the selection of techniques could be properly oriented. The previous chapter suggested MEFA as a tool to determine the IF of the process and have an oriented selection of candidate techniques. This chapter proposes another tool, process simulation, not only to detect IF but also to evaluate the suitability of the proposed candidate techniques.

Modelling as a decision-making tool has a long history in the process industries (Cameron and Ingram, 2008), by means, for example, of process simulators. As discussed in chapter 3.2, process simulation provides deep knowledge about processes and their behaviour under different operating conditions (Alves Santos et al., 2008), allowing designing and retrofitting processes (Casavant and Côte, 2004) before implanting the changes in situ. Accordingly, it seems a good option to identify the IF of a given process, but also to test the impact of implementing candidate techniques.

As discussed in chapter 4, quantitative identification of IF provides valuable information about the process, as well as specific information about the elements that could be improved. In this chapter not only a different tool for IF identification is applied, but also it is evaluated the suitability of that tool to predict the future situation after implementing the candidate techniques proposed to improve the process.

The objective of this chapter is to propose a methodology to improve the sustainability of industrial systems combining two tools: BAT Analysis and process simulation. Both tools are jointly applied to identify the IF of the analysed process, so that the most appropriate candidate techniques from an inventory can be selected. The selected alternatives are tested in different scenarios that are evaluated by process simulation, which would determine the configuration that best improves the sustainability of the system. The combination of both tools in an integrated methodology will help decision-makers to select the most sustainable configuration for a given process. The methodology has been validated in a hydrogen production plant.

2. Case study

The case study is a real plant producing hydrogen (H_2) by the conventional steam reforming process using natural gas as raw material. The resulting H_2 is due to produce NH_3. The plant produces 1360 tonnes of NH_3 per day, with an energetic demand of 39.77 GJ/t NH_3. For the purpose of this work, it will only be considered the production of hydrogen, excluding the ammonia synthesis.

H_2 has multiple industrial applications in the chemical and refinery industries, where it accounts for nearly 50% of the world's consumption (Elam et al., 2003). It is also an energy carrier that can be used for power generation and in transport (IEA, 2007). Although hydrogen can be produced from a variety of sources including biomass, water and some industrial waste chemicals (McLellan et al., 2005), fossil fuels are clearly the main precursor. They currently account for 96% of the world's production (Dufour et al., 2009) (some 65 million tonnes per year (IEA, 2007)), being natural gas the most used hydrocarbon (Dufour et al., 2009; McLellan et al., 2005), as it is the cleanest option and has the highest hydrogen/carbon ratio (McLellan et al., 2005). Concerning processing, there are a wide variety of processes available, as partial oxidation of hydrocarbons, coal and biomass gasification, or differently powered electrolysis (Cetinkaya et al., 2011), to mention some. However, it is the steam reforming of natural gas the major hydrogen production technique (Dufour et al., 2009; Marbán and Valdés-Solís, 2007; Muradov and Veziroğlu, 2005; Ozalp, 2008), as it is the most practical and economic known process to meet the world market demand for hydrogen (Ozalp, 2008), though it is highly sensitive to the cost of natural gas (Bartels et al., 2010). Steam reforming is far from being sustainable due to the high GHG (Green-House Gases) emissions (Dufour et al., 2009). In fact, its global warming potential is around 13.7 kg CO_2 equivalent per kilogram of net H_2 (Muradov and Veziroğlu, 2005).

3. Methodology

This work proposes a new methodology which is validated in the case study. The results obtained after validation are used to evaluate and discuss the suitability, possibilities and applicability of the methodology.

Two known tools, BAT Analysis and process simulation, are combined into a methodology that prevents and controls emissions by reducing the IF detected in the analysed processes. BAT Analysis is applied to select the most appropriate candidate techniques to optimise the IF identified by process simulation. Individual techniques or a combination of some can be potential process improvers. Process simulation is then applied to quantitatively evaluate the evolution of the identified IF after the implementation of each selected technique or set of techniques in different alternative scenarios.

As discussed, there are a wide variety of methodologies for determining which techniques must be considered as BAT (Dijkmans, 2000; Geldermann and Rentz, 2004) and for selecting the most appropriate techniques for a given process (Barros et al., 2007; Bréchet and Tulkens, 2009; Georgopoulou et al., 2008; Mavrotas et al., 2007; Nicholas et al., 2000; Samarakoon and Gudmestad, 2011). However, these methods fail to determine to what extent the selected techniques may be beneficial to the situation where they are applied. Techniques are mostly selected according to environmental, safety and economic criteria, as suggested by the IPPC Directive (EU, 2010). The afterwards effects are hardly considered, though some methods, as the one proposed in chapter 2, take into account the secondary effects that may arise from the implementation of a technique. Process simulation is suggested as an effective tool for analysing the effects of implementing a technique or a set of techniques. The original and final situations can be individually simulated, and the results can be compared to evaluate the benefits of the implemented candidate technique over the whole process.

The proposed methodology is structured as it follows:

1. Base case analysis.

- Detailed qualitative analysis of the process. The productive process is divided into stages to facilitate its understanding and analysis. Material and energy inputs and outputs are defined.
- Evaluation of the main generic environmental impacts. Evaluation of the consumptions (materials and energy) and emissions (atmospheric emissions, liquid effluents and solid waste) derived from the process.
- BAT Analysis. Identification and compilation in an inventory of the techniques candidate to be BAT for the analysed process, based on the methods proposed in chapter 2.
- Process simulation to identify the IF of the process. It includes:
  - Software selection. Selection of appropriate software for process simulation.
  - Data acquisition. Compilation of information concerning the process to be analysed.
  - Modelling and scenario building. Each stage of the process is modelled according to the flows, reactions and working conditions involved.
  - Simulation. The model is executed to calculate the material and energy flows involved in the process.
  - Identification of the IF. The most impactful flows of the process, owing to their quantity and environmental impact, are identified and categorized as IF.
- Selection of the techniques to be evaluated by simulation. The most appropriate techniques from the inventory are selected for application, considering those that directly impact over the identified IF. The methodology allows the possibility of proposing several alternative scenarios where different techniques or combinations of techniques are implemented.

2. Alternative scenarios analysis.

- Qualitative description of the proposed scenarios. The scenarios may represent the application of a single technique or of a set of techniques.
- Process simulation to evaluate each scenario:
  - Software selection.
  - Modelling and scenario building. An individual scenario is built for each scenario.
  - Simulation. Each scenario is individually simulated.
- Evaluation of the alternatives. The results of the simulation are compared to analyse and identify the best option to optimise the process by reducing the IF detected.

The methodology is applied, step by step, to the case study proposed in this chapter. In the ‘base case’ stage of the methodology the current situation of the plant will be analysed, and then the alternative scenarios will be proposed and evaluated.

4. Application of the methodology: base case analysis

The first module of the methodology is applied step by step to the base case, represented by the original situation of the H_2 production plant.

4.1. Detailed description of the process

Figure 5.1 shows a flowsheet of the conventional hydrogen production process by steam reforming of natural gas. The process can be divided in three stages, as defined below.

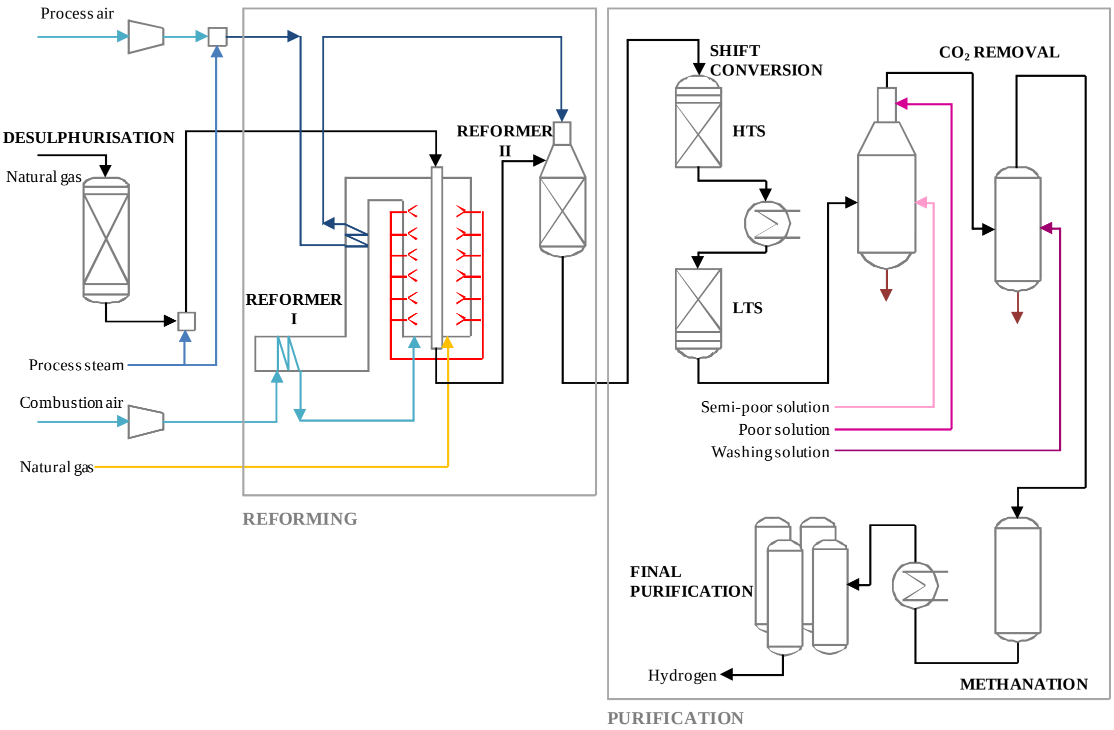


Figure 5.1: Conventional hydrogen production process by steam reforming of natural gas (base case)

DESULPHURATION

It avoids catalyst poisoning in the downstream reactors. Sulphur compounds must be reduced to 0.15 mg/Nm^3 in the natural gas stream. To get such low concentrations natural gas is heated to 350-400 ºC and hydrogenated over Co-Mo catalyst, to get H_2S, which is absorbed in ZnO pellets.

$R\text{-}SH + H_2 \rightarrow H_2S + RH$

$H_2S + ZnO \rightarrow ZnS + H_2O$

H_2 needed for desulphuration is fed back from the process itself.

REFORMING

H_2 is produced in this stage by reacting natural gas with steam over a specific catalyst. Reformers include a radiant section, where H_2 is produced, and a convection section for waste heat recovery from the exhaust gases and cooling before releasing them by the stack (Fleshman, 2001).

Reforming stage includes two reformers: the primary reformer (reformer I) and the secondary reformer (reformer II).

- Primary reformer. In reformer I highly endothermic reactions take place over a Ni-based catalyst to produce CO and H_2. Gas from desulphuration is mixed with steam and pre-heated before entering reformer I. In this stage the mixture is subdued to catalytic reforming, which causes the cracking of the hydrocarbon molecules (Table 5.1). As CH_4 is the main hydrocarbon in the natural gas stream, the reactions predominating in reformer I are R1 (endothermic) and R2 (exothermic). The global reaction is highly endothermic, with 60% of conversion, and takes place inside the reformer tubes, full of catalyst. Outside the tubes, the combustion of part of the natural gas (Table 5.1) provides the heat needed for the catalytic reaction (R4, R5, R6).

  Half of the heat generated in the reformer is directly used, and the rest is used in the convection section of the reformer, to heat other streams of the process. The processed gas leaving reformer I is straight fed to reformer II.

- Secondary reformer. Reformer II completes the reactions started in reformer I by adding O_2 (air). Compressed air pre-heated in the convection section of reformer I is added to the reacting gas in reformer II. Gas from the primary reformer still contains CH_4 enough to consume all the O_2 added with the air, by means of reactions R4 and R7 (Table 5.1).

  The reformate gas leaves reformer II at really high temperatures, so it needs to be cooled down before purification. Cooling can be used to produce high pressure steam.

PURIFICATION

In this stage CO and CO_2 are eliminated from the reformate gas. It includes shift conversion (to convert CO into CO_2), CO_2 absorption, methanation to get CH_4, and final purification.

- Shift conversion (CO-CO_2 converter). The reformate gas from reformer II still contains some CO, which can be turned into CO_2 and H_2 by reacting with steam by means of reaction R2 (Table 5.1). The reaction takes place in two stages with an intermediate phase for heat dissipation. Initially reformate gas goes through a Fe_3O_4/Cr_2O_3 catalytic bed at high temperature in the HTS (High Temperature Shift), reaching high conversion rates. Then the reformate gas goes through a $Cu/ZnO/Al_2O_3$ catalytic bed at lower temperatures in the LTS (Low Temperature Shift) where conversion is almost completed. The final CO content is highly reduced. The gas is cooled before entering in the CO_2 removal unit to condense and separate the exceeding water vapour.
- CO_2 removal. CO_2 is removed by chemical absorption. This stage involves a two-stage process. Firstly CO_2 from the reformate gas is absorbed in a water solution of methyldiethanolamine (MDEA) and diethanolamine (DEA). Then the CO_2 is desorbed in a stripping column, so that the MDEA/DEA solution is regenerated.
- Methanation. The still remaining CO and CO_2 traces can obstruct the utilization of H_2 in other applications. Accordingly these small traces are hydrogenated to CH_4 by reactions R9 and R10 respectively (Table 5.1). This reaction takes place at a Ni-catalytic bed reactor. Only residual CO and CO_2 traces remain in the purified stream.
- Final purification. Though CH_4 does not interfere in further processes, H_2O must be removed by cooling and condensation.

4.2. Evaluation of the main generic environmental impacts

Several LCA have addressed the environmental impact of H_2 produced from several sources, including natural gas, via steam reforming (Heracleous, 2011; Koroneos et al., 2004; Spath and Mann, 2001; Marquevich et al., 2002). All these studies conclude that the main impact of this process is CO_2 emissions. CH_4 emissions are also relevant, owing to its high Global Warming Potential (GWP). On the other hand, the high energy consumption of the process is also pointed out as a relevant impact of the process. All the consumptions and emissions derived from the process are analysed below.

CONSUMPTIONS

The typical consumptions in this type of plants are:

- Raw materials. The main raw material of the considered process is natural gas, consuming around 3 kg of natural gas per kg of produced H_2. Natural gas is also used as fuel in the process to supply the high energy demand.
- Water. Some 18-27 litres of water are consumed per kg of H_2 (Marquevich et al., 2002; Spath and Mann, 2001), 24% in reforming and shift operations, 71.22% in steam production and the rest in other stages of the process, as reported by Koroneos et al. (2004).
- Energy. Hydrogen production by natural gas steam reforming is an intensive energy consuming process. Energy is provided as fuel, natural gas normally, and as electricity. The average energy consumption rate is about 1.23-1.35 GJ of natural gas per GJ of H_2 (Jin et al., 2008), which is used as fuel for providing heat to the reformer and electricity for operation of pumps, also considering the energy efficiency losses (Heracleous, 2011).

Among the stages of the process, the most energy-demanding one is the reforming section. The reforming reaction is strongly endothermic and requires around 70% of the total energy input to the process, whereas pumps and refrigeration from the CO_2 removal section account for most of the rest (Ruddock et al., 2003).

EMISSIONS

The characteristic emissions derived from the analysed process are classified as atmospheric emissions, liquid effluents and solid waste:

- Atmospheric emissions. The main atmospheric pollutant released in H_2 production by steam reforming is carbon dioxide. In fact, authors estimate that some 6.3-8.9 kg of CO_2 are released per kg of H_2 (Marquevich et al., 2002; Muradov and Veziroğlu, 2005; Spath and Mann, 2001). Approximately 72-74% of the CO_2 comes from the steam reforming process (Marquevich et al., 2002), as well as large amounts of NO_x due to the high temperatures of the combustion process (IFA, 2009). Spath and Mann (2001) estimate that the average distribution of atmospheric emissions for the process is 83.7% CO_2, 7.3% NO_x (as NO_2), 1.4% CO and 1.1% PM. Not negligible either are the CH_4 emissions, mainly released as natural gas losses to the atmosphere during production and distribution (Koroneos et al., 2004), which are around 86 g of CH_4 per kg of H_2 (Marquevich et al., 2002). Considering all the above mentioned atmospheric pollutants, the average GWP of the process is 13.7 kg CO_2 equivalent per kilogram of net H_2 (Muradov and Veziroğlu, 2005).

Table 5.1: Chemical reactions at the natural gas steam reforming process

Stage	**Reaction**		**ΔH^0 (kJ/mol)**	**Modelled reactor**
Pre-reformer	R1: Steam reforming	$CH_4+H_2O \leftrightarrow CO+3H_2$	206	Gibbs reactor
	R2: Water gas shift	$CO+H_2O \leftrightarrow CO_2+H_2$	-41	
	R3: Steam reforming	$C_nH_m+nH_2O \rightarrow nCO+(n+m/2)H_2$	1175(1)	
Reformer I (radiant zone)	R1: Steam reforming	$CH_4+H_2O \leftrightarrow CO+3H_2$	206	Gibbs reactor
	R2: Water gas shift	$CO+H_2O \leftrightarrow CO_2+H_2$	-41	
	R3: Steam reforming	$C_nH_m+nH_2O \rightarrow nCO+(n+m/2)H_2$	1175(1)	
Reformer I (convection zone)	R4: Methane combustion	$CH_4+2O_2 \rightarrow CO_2+2H_2$	-80	Conversion reactor
	R5: Ethane combustion	$C_2H_6+3.5O_2 \rightarrow 5CO_2+3H_2$	-140	
	R6: Pentane combustion	$C_5H_{12}+8O_2 \rightarrow 5CO_2+6H_2$	-330	
Reformer II	R1: Steam reforming	$CH_4+H_2O \leftrightarrow CO+3H_2$	206	Conversion reactor
	R4: Methane combustion	$CH_4+2O_2 \rightarrow CO_2+2H_2$	-80	
	R7: Partial combustion	$CH_4+0.5O_2 \rightarrow CO+2H_2$	-71	
ATR (catalytic zone)	R1: Steam reforming	$CH_4+H_2O \leftrightarrow CO+3H_2$	206	Gibbs reactor
	R2: Water gas shift	$CO+H_2O \leftrightarrow CO_2+H_2$	-41	
	R3: Steam reforming	$C_nH_m+nH_2O \rightarrow nCO+(n+m/2)H_2$	1175(1)	
ATR (combustion zone)	R8: Methane combustion	$CH_4+1.5O_2 \rightarrow CO+2H_2O$	-519	Conversion reactor
HTS	R2: Water gas shift	$CO+H_2O \leftrightarrow CO_2+H_2$	-41	Conversion reactor
LTS	R2: Water gas shift	$CO+H_2O \leftrightarrow CO_2+H_2$	-41	Conversion reactor
Methanizer	R9: CO methanation	$CO+3H_2 \rightarrow CH_4+H_2O$	-206	Conversion reactor
	R10: CO_2 methanation	$CO_2+4H_2 \rightarrow CH_4+2H_2O$	-165	

(1) n-C_7H_{16}

- Liquid effluents. Emissions to water are very small if compared to other emissions (Ozalp, 2008; Spath and Mann, 2001). Practically, the only liquid effluents are associated to the formation of condensates or to the scrubbing of waste gases (IFA, 2009).
- Solid waste. The considered process does not really release any constant solid waste stream. The only waste stream is the spent catalyst from the reformer and shift reactors (IFA, 2009; Spath and Mann, 2001).

4.3. BAT Analysis

In chapter 2 a procedure to evaluate techniques candidate to be BAT based on the method set by the EIPPCB (European Commission, 2005) was proposed. Candidate techniques are selected according to the potential environmental impacts of the process concerned. Then, a technical sheet is elaborated for each candidate technique, including information about environmental aspects, technical description of the technique, the benefits it reports, the secondary effects derived from it, motivation for its implementation, considerations for its applications, related economical aspects, and examples of plants where the technique has already been implemented. BAT Analysis implies a deep knowledge of the sector analysed, and an intensive study of the process (Torres Rodríguez et al., 2011). Table 5.3 summarises the techniques (EFMA, 2000; European Commission, 2007b, 2008; US Department of Energy, 2008a, 2008b; Worrel and Blok, 1994) candidate to be BAT for the analysed process. They have been selected considering the main environmental impacts identified in the previous section, and classified according to the specific process step where they are likely to be implemented. 17 techniques have been identified. Six concern the reformer section mainly involving rearrangement of flows and the implementation of alternative equipment. One technique affects the shift converters, whereas two are meant to improve the CO_2 removal system. The rest of the techniques concern auxiliary equipment and operations, as combustion and steam system (three techniques each), heat recovery and cooling (one technique) and pumping system (one technique).

4.4. Process simulation to identify the IF

This stage of the methodology involves several steps intended to identify the IF of the industrial system analysed.

4.4.1. Software selection

Aspen HYSYS V7.1 (AspenTech, 2009) is the software selected to evaluate the base case. This software described in chapter 3.2.

4.4.2. Data acquisition

All data used in the model was supplied by the ammonia production plant. The input data fed to the model is shown in Table 5.2. Concerning natural gas, it was considered that the non-methane hydrocarbon in the reforming natural gas is n-heptane (C_7H_{16}), whereas natural gas for energy production considers both ethane (C_2H_6) and n-pentane (C_5H_{12}). In general terms, the operating pressure for the whole process is 3500 kPa, except for the absorption-desorption equipment, and no pressure drops are considered unless otherwise specified. The objective H_2/N_2 ratio for NH_3 production is 3.2. Energy is provided by natural gas combustion for the whole process.

In the base case almost 25% of the natural gas is used for H_2 production, whereas the rest is combusted to supply the energy needed in the radiant zone of reformer I. Half of the heat generated in this reformer is directly used for the endothermic reactions taking place inside the tubes. The rest is used in the convection section to heat the combustion air and the steam/air mixture fed to reformer II.

Table 5.2: Conditions of the input flows to the process

Parameter	Unit	Value
H_2/N_2 molar ratio	-	3.2
Natural gas		
Molar flow(1)	kmol/h	$1.295 \cdot 10^{6}$
Composition	Molar fraction	
CH_4		$9.45 \cdot 10^{-1}$
C_7H_{16}(2)		$4.18 \cdot 10^{-2}$
N_2		$7.73 \cdot 10^{-3}$
CO_2		$5.51 \cdot 10^{-3}$
Temperature	ºC	368.9
Steam temperature	ºC	560.0
Air		
Composition	Molar fraction	
O_2		$1.88 \cdot 10^{-1}$
N_2		$8.11 \cdot 10^{-1}$
Temperature	ºC	25.0
Pressure(3)	kPa	3500
Pressure drop(4)	kPa	0

(1) Total.
(2) Natural gas for energy production considers C_2H_6: $2.69 \cdot 10^{-2}$; C_5H_{12}: $1.48 \cdot 10^{-2}$ instead of C_7H_{16}.
(3) For the whole methane steam reforming process, except for the CO_2 removal section.
(4) In all the equipments except for the CO_2 absorption stage.

Table 5.3: Candidate BAT for the steam reforming of natural gas for H_2 production

Stage	Techniques		Environmental aspects
Reformer section	T.1.1	Selective non-catalytic reduction (SNCR) at the primary reformer	NO_x reduction rates of 40-70% and emission levels of 140-160 g/Nm^3
	T.1.2	Low NO_x burners	NO_x reduction rates up to 70%
	T.1.3	Revamp: increase capacity and energy efficiency	Global energy savings NO_x emissions < 200 mg/Nm^3
	T.1.4	Pre-reforming	Energy reduction rates of 5-10%
	T.1.5	Preheating combustion air with waste heat from flue gases	Global energy savings
	T.1.6	ATR (Auto-Thermal Reformer) system	Total integration of the consumption Reduction of global emissions
Converters	T.2	Pressure drop optimisation of HTS and LTS converters	Global energy savings
CO_2 removal system	T.3.1	Using MDEA technology	Global energy savings
	T.3.2	PSA (Pressure Swing Adsorption) system	Total saving of the energy consumed in absorption Reduction of CO_2 emissions
Combustion	T.4.1	Burner regulation and control by monitoring and controlling fuel flow, air flow, oxygen levels and heat demand	Energy savings and minimization of NO_x emissions
	T.4.2	Proper furnace insulation to reduce wall heat losses (mid-term implementation)	Estimated energy savings around 1-2%
	T.4.3	Clean heat transfer surfaces (short-term implementation)	Estimated energy savings around 1-5%
Steam system	T.5.1	Pre-heat feed-water by using economisers	Reduction in fuel requirements by 5-10% in 2 years
	T.5.2	Reduce total dissolved solids in the boiler water to reduce blow-down and energy loss (short-term implementation)	Estimated energy savings around 0.5-1%
	T.5.3	Optimise deareator vent rate (mid-term implementation)	Estimated energy savings around 0.5-1%
Heat recovery and cooling	T.6	Monitoring and maintenance of heat exchangers	Improving heat exchange for heat recovery
Pumping system	T.7	Control and maintenance	Reduction in energy consumption about 30-50%

4.4.3. Modelling and scenario building

The Peng-Robinson equation of state (Peng and Robinson, 1976) is used in all cases to model the process, owing to its suitability to evaluate the properties of pure substances and equilibrium ratios of mixtures. This equation (Equation 5.1) was properly defined in chapter 3.2.

$$P = \frac{R \cdot T}{V_m - b} - \frac{a \cdot \alpha}{V_m^2 + 2b \cdot V_m + b^2}$$

Equation 5.1

The equation of state is related with the rest of thermodynamic properties by means of the fundamental equations of thermodynamic.

Table 5.1 shows all the reactions modelled for the base case, indicating in which stage they are taking place. The desulphurisation stage has not been modelled, as it is assumed that the natural gas enters the process sulphur-free (Table 5.2). There have also been obviated the reactions which may cause carbon formation in the reformers, as they are suppressed by high temperatures and high O_2/C and S/C (steam/hydrocarbon) ratios (Halabi et al., 2008). Chan and Wang (2000) have proved that molar S/C ratios greater than 1.5 effectively avoid carbon formation.

The HYSYS function SET is used to fix the molar flow of steam regarding natural gas (specifically CH_4). Table 5.4 shows the S/C molar ratio for the base case. Another function, ADJUST, is used to calculate the amount of air entering the process, so that the H_2/N_2 molar ratio of the product stream is 3.2, as required for ammonia production. This function requires a spreadsheet which calculates the molar ratio and feeds the calculated value to the ADJUST function to recalculate the air flow in an iterative process until the desired ratio is reached.

Every specific consideration for the base case is included in Table 5.4. Figure 5.2 represents the model built in HYSYS. It includes six reactors.

Reformer I has been modelled as two reactors, representing the two zones, radiant and convection, which integrate it. The radiant zone has been modelled as a Gibbs reactor, defined on the basis of stoichiometric reactions and equilibrium parameters. In this type of reactors reactions keep going until minimum ΔG_0 is reached, meaning that the system is in equilibrium. The convection zone of reformer I and reformer II have been modelled as conversion reactors defined by the stoichiometry of the reactions taking place and by a conversion factor. The gas stream produced in the convection zone of reformer I is successively cooled down, so that the energy can be used in the radiant zone to fuel the endothermic reactions.

Both shift reactors have been modelled as conversion reactors, defining 75% conversion for the HTS and 416.2 ºC of operating temperature, and total conversion at 232.8 ºC in the LTS. The methanizer has been modelled as a conversion reactor considering total conversion of CO and CO_2 into CH_4.

The model of the CO_2 absorption stage includes an absorber where the reformate gas contacts the MDEA/DEA solution which absorbs the CO_2. This CO_2-rich solution is depressurized and heated so that CO_2 can be easily desorbed at the stripping column. The regenerated hot solution is used to heat the CO_2-rich solution, and it is then recycled to the absorber. 25 stages have been considered for the absorber, whereas the stripping column has been modelled as a component splitter column. To model the recycling of the MDEA/DEA solution HYSYS function RECYCLE has been used.

Water separation has been modelled as a cooler (to condensate water) followed by a flash separator. The model includes several mix and tee elements representing unions and divisions of streams, respectively.

4.4.4. Simulation

The model has been run in steady state, calculating the stationary material and energy flows for the base case.

The evaluation of the simulation results for the base case leads to the identification of the IF of the process. Two generic flows stand out as the most relevant in terms of quantity and environmental impact. They are the energy consumption (in terms of calorific energy from natural gas combustion for energy production, referred to the Low Heating Value (LHV)) and the CO_2 emissions.

Both reforming and CO_2 removal are energy-intensive processes. Between both of them they consume more than 90% of the energy input to the process. On the other hand, most of the energy produced in the convection zone of Reformer I is not used, resulting in a truly inefficient use of the energy. These flows require preventive techniques to avoid excessive energetic consumption, and to enhance the energetic integration of the process.

Reformer I and Reformer II generate more than $1.34\cdot10^7$ kg/h of CO_2 and $1.60\cdot10^7$ kg/h of CO, which is then turned into CO_2 in the shift converters. More than 95% of the CO_2 is emitted to the environment in the 'CO_2 absorption' stage, whereas the rest is converted into CH_4 in the methanizer. CO_2 emissions are unfortunately unavoidable for the analysed process. Therefore reduction techniques are required to minimize the emissions and to improve their management. Though CO_2 is released in the stripping column at the 'CO_2 absorption' stage, CO_2 and CO (which will be turned into CO_2 in the shift converters) are mostly generated in the reformers, so the suggested techniques should focus in those specific stages of the process.

4.4.5. Identification of the IF

According to the results from simulation, three IF have been detected, two inputs and one output:

- Inputs: both inputs correspond to energy flows as natural gas combusted to obtain energy for the process:
    - Energy input to Reformer I, most of it wasted as heat.
    - Energy input to 'CO_2 removal', this stage requires a quite big energy input to achieve the degree of purity required for the final product.
- Outputs: the only output flow pointed out as an IF is the CO_2 out of the stripping column in the 'CO_2 removal' stage. When selecting candidate techniques to avoid this flow it should be considered that CO_2 is generated at the 'reforming' stage.

Owing to the nature of the IF identified, they have been summarised in two categories, namely 'energy consumption in' (joining the two energy inputs identified as IF) and 'CO_2 emissions from'. This classification is intended to facilitate the selection of techniques from the inventory.

Table 5.4: Specific considerations for the modelled stages in the base case and in the alternative scenarios

Parameter	**Unit**	**Base case**	**Scenario 1**	**Scenario 2**	**Scenario 3**
S/C molar ratio	-	3.5	3	1	3.5
O_2/C ratio	-	0.31(1)	0.28(1)	0.55	0.28(1)
Pre-reformer					
Inlet temperature	ºC	-	503.9	-	-
Catalytic bed temperature	ºC	-	452.9	-	-
Natural gas for reforming flow	kmol/h	-	$3.208\cdot 10^5$	-	-
Reformer I					
Inlet temperature	ºC	503.9	500.0	-	503.9
Catalytic bed temperature	ºC	800.0	770.0	-	800.0
Convection zone pressure	kPa	3380	3380	-	3380
Natural gas for reforming flow	kmol/h	$3.208\cdot 10^5$	-	-	$3.208\cdot 10^5$
Natural gas for combustion flow	kmol/h	$9.738\cdot 10^5$	$9.738\cdot 10^5$	-	$9.738\cdot 10^5$
Reformer II					
Reactor temperature	ºC	818.2	797.4	-	792.2
ATR					
Inlet temperature	ºC	-	-	650.0	-
Combustion temperature	ºC	-	-	1521.0	-
Reforming temperature	ºC	-	-	894.0	-
Shift conversion					
HTS temperature (conversion)	ºC (%)	416.2 (75)	373.0 (75)	407.8 (75)	416.9 (75)
LTS temperature (conversion)	ºC (%)	232.8 (100)	244.8 (100)	237.4 (100)	233.1 (100)
CO_2 absorption					
Desorption pressure	kPa	1500	1500	1500	-
PSA					
Temperature	ºC	-	-	-	39.63
Pressure	kPa	-	-	-	2130
Methanizer					
Temperature	ºC	357.2	396.9	348.1	-
Pressure	kPa	3490	3490	3490	-

(1) In the radiant zone

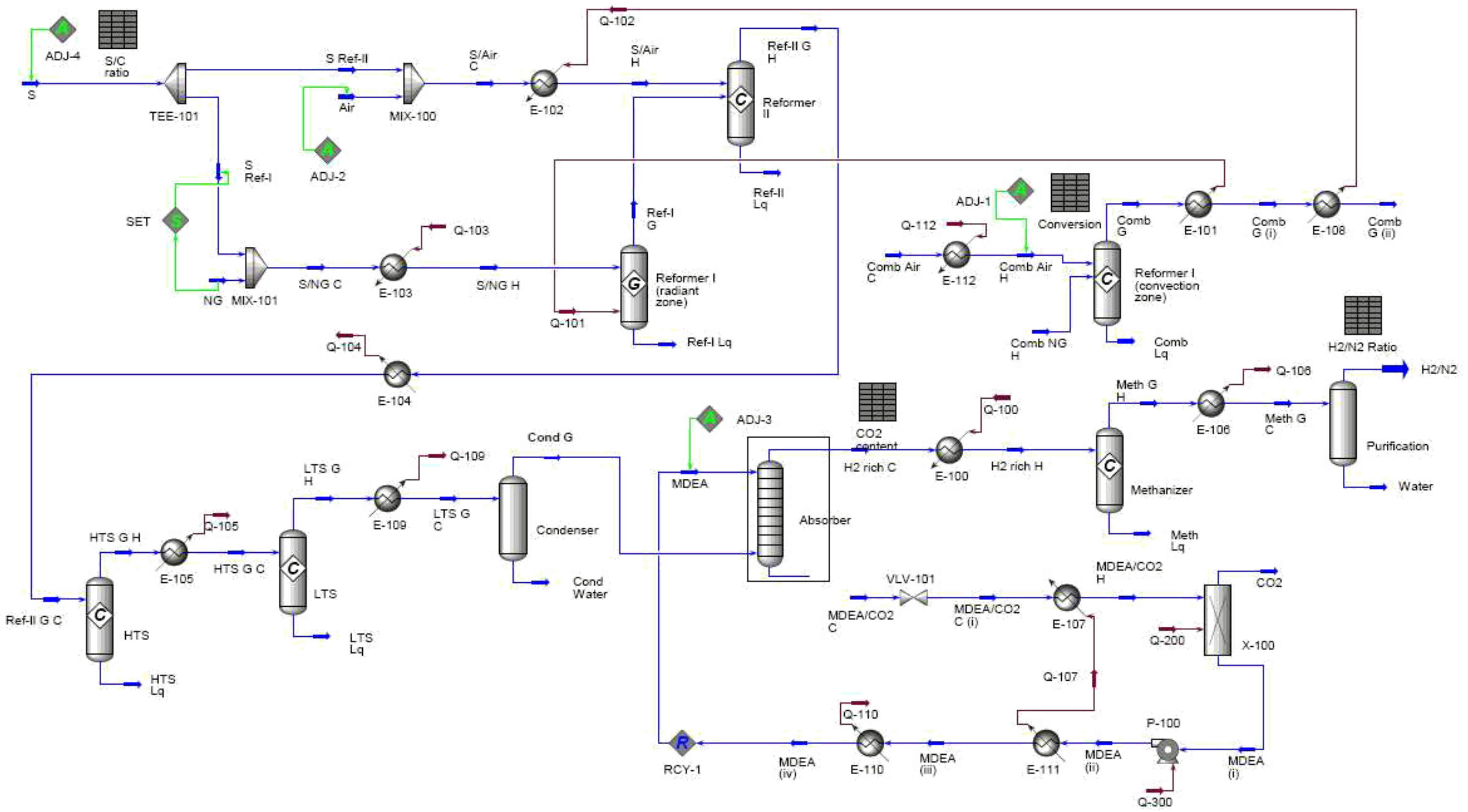


Figure 5.2: Aspen HYSYS model

4.5. Selection of the techniques to be evaluated by simulation

The three IF identified for this process (referred to energy consumption and CO_2 emissions) have pointed out ‘reforming’ and ‘CO_2 removal’ as the most impactful stages.

‘CO_2 emissions from’ and ‘energy consumption in’ have been pointed out as potential IF of the analysed process, being reformers and CO_2 removal columns the most impactful units. Accordingly, the chosen techniques should effectively reduce the IF ‘CO_2 emissions’ from the absorption stage and optimise the both IF regarding ‘energy consumption’, specially focusing on improving the performance of the reformer.

Due to the variety of options available, three different scenarios, implementing one or more than one candidate techniques, have been proposed (Table 5.5):

Table 5.5: Candidate BAT selected for implementation

Scenario 1	
T.1.3	Revamp: increase capacity and energy efficiency
	T.1.3.1 Extended pre-heating of the hydrocarbon/steam feed
	T.1.3.2 Reduce steam/carbon ratio to 3
	T.1.3.3 Reduce outlet temperature of the gases from reformer I
T.1.4	Pre-reforming
T.1.5	Preheating combustion air with waste heat from flue gases
Scenario 2	
T.1.6	ATR (Auto-Thermal Reformer) system
Scenario 3	
T.3.2	PSA (Pressure Swing Adsorption) system

- Scenario 1. Three techniques are suggested for implementation in the first scenario. One of the techniques is revamping to increase capacity and energy efficiency (Figure 5.3), specifically by extended pre-heating of the feed, reducing the S/C ratio, and reducing the outlet temperature of the exhaust gases. The other two techniques are installing a pre-reforming unit (Figure 5.4) and pre-heating the combustion air (Figure 5.5). This combination of techniques is meant to highly reduce the energy consumption of the process, as just pre-reforming units are estimated to reduce by 5-10% the energy demand (European Commission, 2007b). Moreover, pre-heating combustion air increases up to 91-92% the efficiency of the reformer (Molburg and Doctor, 2003), whereas revamping techniques can reduce NO_x emissions below 200 mg/Nm^3 (European Commission, 2007b).

- Scenario 2. Replacing primary and secondary reformers for an ATR system (Figure 5.6). ATR are highly energy efficient systems (Halabi et al., 2008; Souza et al., 2006) that can also reduce emissions to the atmosphere.

- Scenario 3. Implement a PSA system (Figure 5.7) instead of the CO_2 absorption. PSA units highly reduce CO_2 emissions (Gomes and Yee, 2002; Li et al., 2011) and produce high purity H_2 (Pena Lopez and Manousiouthakis, 2011). They also save all the energy consumed in other absorption options.

Each scenario will be modelled and simulated so that the three alternatives can be compared to select the best option to optimise the natural gas steam reforming process. Figure 5.8 shows the simplified flow charts for the alternative scenarios.

T.1.3 REVAMP: INCREASE CAPACITY AND ENERGY EFFICIENCY

ENVIRONMENTAL ASPECTS

Global energy savings and NO_x emissions reduced to < 200 mg/Nm^3.

TECHNICAL DESCRIPTION

The main purpose for revamping is optimising the energy consumption in the reformer and associated equipment as turbines. Some of the most typical measures are (European Commission, 2007b):

T.1.3.1. Extended pre-heating of the S/C feed. The S/C mixture fed to primary reformer is heated by the exhaust gases at the convection section of the reformer. This is one of the most effective modifications, as radiant duty and firing rate are reduced (Fleshman, 2001).

T.1.3.2. Reduce S/C ratio to 3. It reduces the heat absorbed in the radiant section of reformer I.

T.1.3.3. Reduce outlet temperature of the gases from reformer I. It reduces the energy demand in the radiant section of the reformer, reducing fuel consumption. High temperatures at the reformer outlet gases can be reduced by removing tubes from the coil, and the heat from the exhaust gas can be used for steam generation (Fleshman, 2001).

T.1.3.4. New gas turbines. If a second gas turbine is installed, the O_2 available in its exhaust gases closely matches the O_2 requirements of the reformer, so that the total flow through the radiant section of the reformer is minimised, and so the energy requirements of this unit.

T.1.3.5. Rearrangement of the convection coils and add additional surface. If energy utilization is optimised in the reformer, there is less energy available in the convection section. Accordingly convection coils must be rearranged to meet the new requirements.

T.1.3.6. Maintenance. The yield can be improved by 50% by proper maintenance programs.

BENEFITS / ENVIRONMENTAL DATA

Reduced NO_x emissions <200 mg/Nm^3 due to low O_2 surplus. Besides energy consumption can be reduced from 36.0 to 31.1 GJ/tonne (fuel + feed) (European Commission, 2007b).

Pre-heating allows increasing by 10% the capacity of the process (Fleshman, 2001).

SECONDARY EFFECTS

Not expected.

IMPLEMENTATION

Applicable in existing steam reforming plants.

APPLICATION AND CHARACTERIZATION

The proposed measures may require the installation of new equipment and/or the rearrangement of the existing one, so space limits and accessibility are quite relevant and conditioning.

ECONOMICAL ASPECTS

The expected pay-back time for the implementation of any measure is less than one year (European Commission, 2007b).

PLANTS WHERE THE TECHNIQUE IS ALREADY IMPLEMENTED

Foster Wheeler has supplied several revamping strategies.

Figure 5.3: Technical data sheet for candidate technique 'Revamp: increase capacity and energy efficiency'

T.1.4 PRE-REFORMING

Environmental Aspects

Energy reduction rates of 5-10% as well as reduced emissions to air.

Technical Description

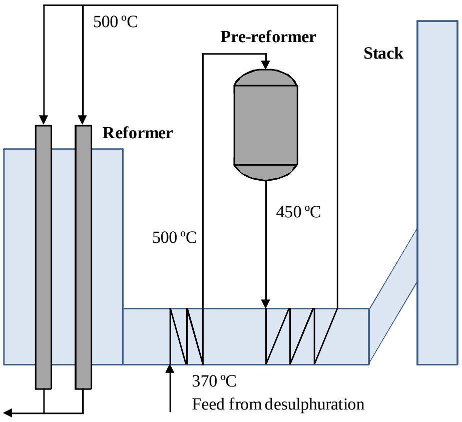
The pre-reformer is an adiabatic, fixed-bed reactor with a highly active Ni catalyst (Aasberg-Petersen et al., 2003). Adiabatic pre-reforming turns the hydrocarbons into CO and H_2 by low temperature steam reforming (350-550 °C) before the steam reforming stage. The reactions taking place are:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0_{298} = 206.2 \text{ kJ/mol}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41.2 \text{ kJ/mol}$$

The pre-reformer can be directly placed after the desulphurization section or after a pre-heater heating the feed gas before the pre-reformer. The preferred arrangement is placing the pre-reformer after a pre-heating section but re-heating the pre-reformed gas before entering the reformer, as shown in the figure.

The global chemical reaction is endothermic and, as it happens adiabatically through a fixed catalytic bed, the temperature is reduced by 50 °C.



To compensate this loss the feed is pre-heated in the convection zone of the reformer.

Benefits / Environmental Data

Significant energy savings by reducing the S/C ratio and the tube-walls temperature in the reformer. It has been reported that, in ammonia production processes by natural gas steam reforming, the installation of a pre-reformer yields about 1.4 GJ/t NH_3 in energy savings (Rafiqul et al., 2005).

Secondary Effects

Avoids carbon formation because of cracking of higher hydrocarbons in the reformer tubes (Christensen, 1996; Yang et al., 2011). The capacity of the reformer is increased, and also the lifetime of the catalyst.

Implementation

New chemical plants, but also for de-bottlenecking or revamping existing plants in order to increase production capacity or improve energy efficiency (Christensen, 1996). It can be installed upstream of a fired tubular reformer, a heat exchange reformer or an ATR (Aasberg-Petersen et al., 2011).

Application and Characterization

Process design and equipment sizing requires knowledge about reaction kinetics, potential catalyst-poisoning and carbon formation limits (Christensen, 1996). The low operating temperatures require a Ni-catalyst with high surface area, moderate size, and resistance to poisoning, with S/C ratios in the range 0.1-0.5 (Aasberg-Petersen et al., 2011; Christensen, 1996).

Economical Aspects

Energy consumption is reduced 5-10% (European Commission, 2007b). The overall investment is slightly reduced in spite of the additional investment for the pre-reformer and catalyst (Christensen, 1996).

Plants where the Technique is Already Implemented

Technique widely used in the chemical process industry (Christensen, 1996): H_2 production at refineries, plants for synthesis of methanol and NH_3, and plants producing syngas.

Figure 5.4: Technical data sheet for candidate technique 'Pre-reforming'

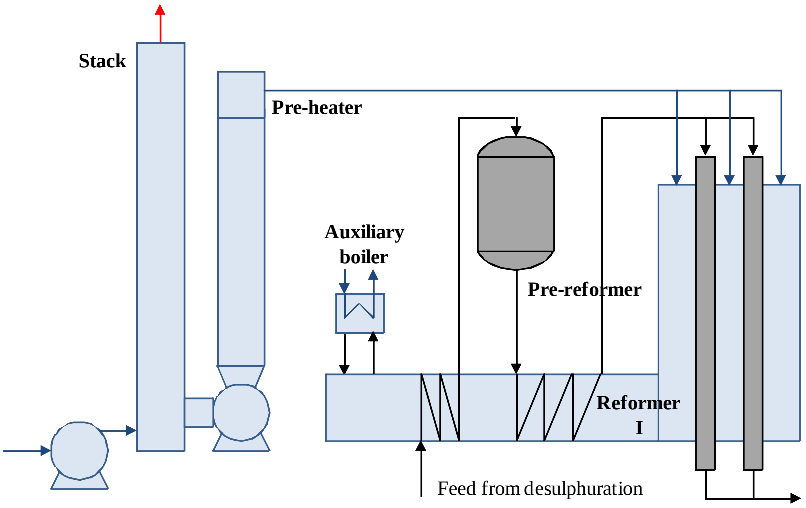
T.1.5 PRE-HEATING COMBUSTION AIR WITH WASTE HEAT FROM FLUE GASES

ENVIRONMENTAL ASPECTS

Global energy savings.

TECHNICAL DESCRIPTION

Combustion air can be heated with waste heat from the primary reformer or auxiliary boiler flue-gases (European Commission, 2007b), by implementing a pre-heater with a similar configuration as the one shown in the figure. The combustion air pre-heater is normally plate-type and is placed downstream of the convection bank.



BENEFITS / ENVIRONMENTAL DATA

The efficiency of the reformer can be increased by 87-89% to 91-92%. High combustion air pre-heat temperatures reduce the fuel demand of the reformer (Molburg and Doctor, 2003) and the steam production (Udengaard, 2004).

SECONDARY EFFECTS

CO_2 emissions are reduced, though NO_x emissions are increased. The increased flame temperatures in the air pre-heater lead to higher NO_x emission levels, increasing emission values from 90 mg/Nm^3 to 130 mg/Nm^3 (European Commission, 2007b).

IMPLEMENTATION

New plants and also existing plants where there is space available.

APPLICATION AND CHARACTERIZATION

An abatement technique is required to reduce NO_x emissions.

ECONOMICAL ASPECTS

Cost benefits (European Commission, 2007b). Depending on the value of fuel and steam, combustion air pre-heat can provide substantial operating cost savings.

PLANTS WHERE THE TECHNIQUE IS ALREADY IMPLEMENTED

It is a common practice.

Figure 5.5: Technical data sheet for candidate technique ‘Pre-heating combustion air with waste heat from flue gases’

T.1.6 ATR (Auto-Thermal Reformer) SYSTEM

ENVIRONMENTAL ASPECTS

Total integration of the consumption.

TECHNICAL DESCRIPTION

ATR is a combined combustion and catalytic process carried out in an adiabatic reactor. The reactions combined are partial oxidation (1) and steam reforming (2), (3) (Aasberg-Petersen et al., 2003; Souza et al., 2006), normally catalyzed by a Ni-based catalyst (Zahedi Nezhada et al., 2009).

(1) $CH_4 + 1.5.O_2 \rightarrow CO + 2H_2O \quad \Delta H^0_{298} = -520$ kJ/mol

(2) $CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = 206$ kJ/mol

(3) $CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41$ kJ/mol

The process is ‘auto-thermal’ as the heat needed for the endothermic reforming is provided by the oxidation of a portion of the hydrocarbon feed (Wilhelm et al., 2001).

ATR reactors include a burner, a combustion chamber and a catalyst bed, all included in a refractory lined pressure shell. In the burner the feed streams are mixed in a turbulent diffusion flame (Dybkjær, 1995), and the hydrocarbon sub-stoichiometrically reacts with a mixture of O_2 and steam (Aasberg-Petersen et al., 2011). In the fixed catalytic bed the reacting gas is further equilibrated, producing a soot-free synthesis gas (Aasberg-Petersen et al., 2001) with H_2/CO ratios ranging from 2-1 (Halabi et al., 2008). ATR schemes include feed pre-heat, a reactor, a heat recovery section and a gas separation unit (Dybkjær, 1995).

BENEFITS / ENVIRONMENTAL DATA

Higher energy efficiency, as exothermic CH_4 oxidation provides energy for endothermic steam reforming (Halabi et al., 2008; Souza et al., 2006). Lower temperatures, smaller size and easier start up are required. It allows a wider range of H_2/CO ratios by simply adjusting CO_2, H_2O and O_2 inlet flows (Halabi et al., 2008; Souza et al., 2006). Emissions to air are significantly reduced by eliminating flue gas from the primary reformer. NO_x emissions can be reduced by more than 50% (European Commission, 2007b).

SECONDARY EFFECTS

Higher total energy consumption if compared with other techniques (European Commission, 2007b).

IMPLEMENTATION

Applicable for new plants (European Commission, 2007b), though there is limited commercial experience and the technique normally requires extra O_2 (Wilhelm et al., 2001).

APPLICATION AND CHARACTERIZATION

Careful design to avoid excessive temperatures and soot formation (Aasberg-Petersen et al., 2011). Including a pre-reformer upstream the ATR reduces O_2 demand (Aasberg-Petersen et al., 2003).

ECONOMICAL ASPECTS

ATR is the preferred option for large-scale safe and economic syngas production (Wilhelm et al., 2001). The low S/C ratios improve the process economics (Aasberg-Petersen et al., 2003). Up to 40% of the costs are related to the oxygen plant (Aasberg-Petersen et al., 2001), though using air instead of O_2 results in big volumes of gases, not-viable for large-scale plants (Aasberg-Petersen et al., 2001).

PLANTS WHERE THE TECHNIQUE IS ALREADY IMPLEMENTED

Danish company Haldor Topsøe has developed a technology for ATR-based processes applied in more than 60 locations worldwide (Haldor Topsøe, 2008).

Figure 5.6: Technical data sheet for candidate technique ‘ATR system’

T.3.2 PSA (Pressure Swing Adsorption) SYSTEM

Environmental Aspects

Total saving of the energy consumed in absorption. Reduction of CO_2 emissions.

Technical Description

PSA separates CO, CO_2, CH_4 and H_2O from H_2 by adsorption of these components on a solid adsorbent at relatively high pressure (Behroozsarand et al., 2010). The process achieves high purity H_2 (99.99%) (Pena Lopez and Manousiouthakis, 2011) and moderate H_2 recovery (65-90%) (Peramanu et al., 1999). The adsorbent solid bed is rapidly regenerated by lowering the pressure and purging with high purity H_2 (Yang et al., 1995). The resulting PSA waste gas contains 50–55 vol.% CO_2, 24–26 vol.% H_2, 15–20 vol.% CH_4, 0–2 vol.% CO and 0–5 vol.% H_2O (Ortiz et al., 2011), so it can be used in the reformer to fuel the endothermic reforming reaction (Heracleous, 2011). According to Spath and Mann (2001), an additional small amount of natural gas is needed to supply the balance at the reformer. Continuous H_2 flow is maintained by synchronized multiple adsorption beds (Behroozsarand et al., 2010).

The adsorbent solid bed is typically made of 3 different adsorbent layers (Bastos-Neto et al., 2011):

- First layer, composed of alumina or silica gel to adsorb H_2O;
- Second layer, made of activated carbon to adsorb CH_4, CO, CO_2 and traces of S components;
- Third layer, made of zeolites to improve the adsorption of CO, N_2 and other trace components.

Efficiency can be improved by modifying operating parameters (pressure, purge/feed ratio, step times) which influence H_2 purity and the recovery yield (Yang et al., 1995). Accurate process control is required to continually cycle the valves through their pressurization and depressurization sequence. Despite the complex valve system, the system is very reliable (Peramanu et al., 1999).

Benefits / Environmental Data

CO_2 emissions are highly reduced (Li et al., 2011). Martunus et al. (2012) estimated that PSA for treating hot flue gas from a power plant demands 230 kWh/t of CO_2, and only 27 kg CO_2/h are released for every 1000 kg/h captured from the flue stream. Pena Lopez and Manousiouthakis (2011) even claim that “H_2 can be produced from fossil fuels without generation of CO_2 emissions”. They propose producing valuable carbon-containing chemicals with the retained CO_2, which will reduce H_2 price.

Secondary Effects

None.

Implementation

It is suitable for CO_2 removal and recovery over a wide range of temperature and pressure conditions, with low energy requirements, cost advantages and high energy efficiency (Gomes and Yee, 2002).

Application and Characterization

Design is based on adsorption equilibrium and kinetics, requiring operating variables (composition, pressure and temperature) and process variables (step times, cycles proposed, blow down and purge pressures) (Lopes et al., 2011). Jain et al. (2003) have proposed a set of heuristic rules for designing PSA units considering several parameters. Typical operating conditions for PSA units are 21.3 bar maximum pressure and 37.85ºC (Pena Lopez and Manousiouthakis, 2011).

Economical Aspects

Low operating costs, which are only more significant for large-scale units (Chang et al., 2004; Kearns and Webley, 2004). Too strict product specifications may increase capital cost (Bressan et al., 2010).

Plants where the Technique is Already Implemented

Since being marketed in 1966, more than 600 PSA have been installed all over the world (Tagliabue and Delnero, 2008), many of them by Linde, one of the world leader companies.

Figure 5.7: Technical data sheet for candidate technique ‘PSA system’

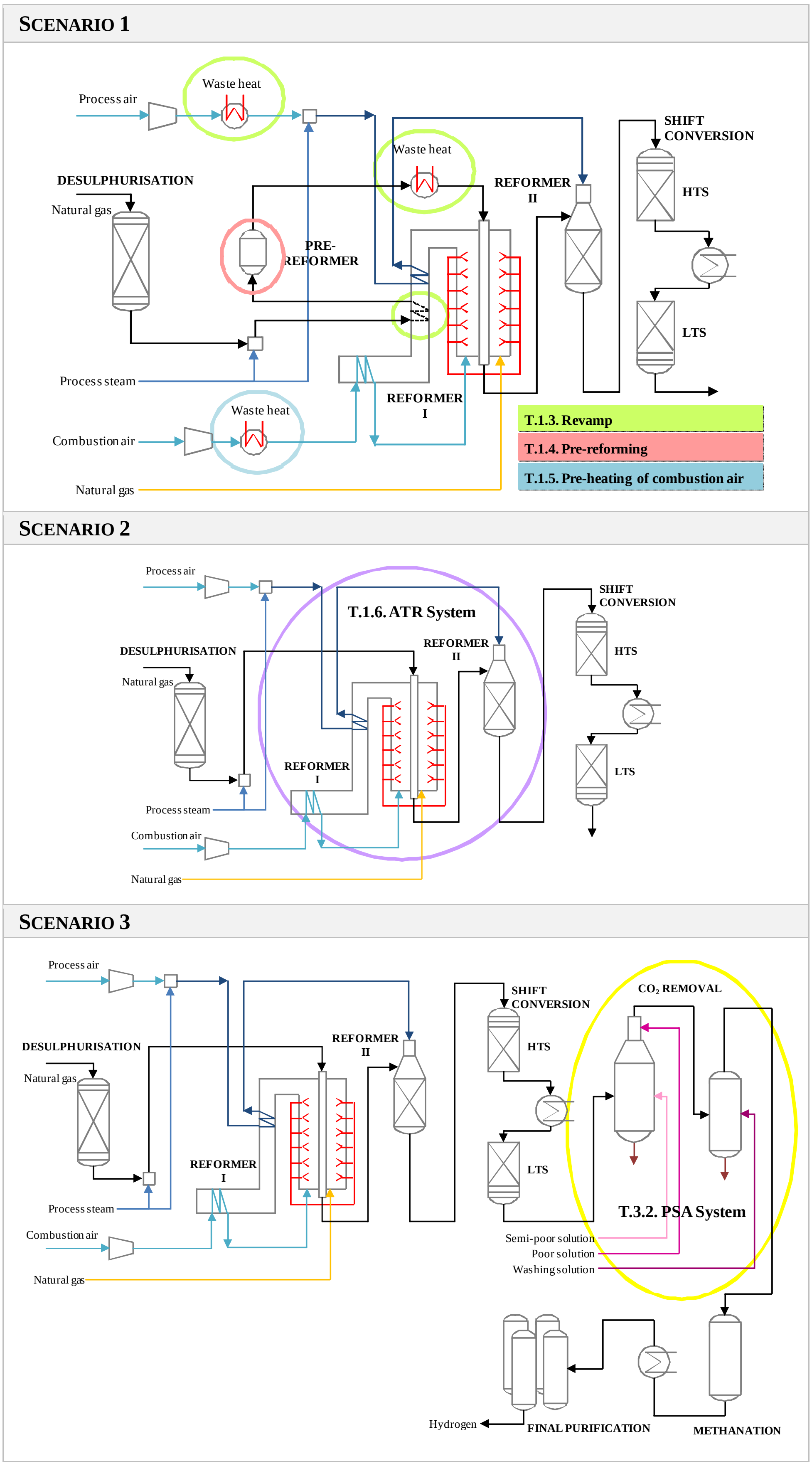


Figure 5.8: Proposed scenarios to improve the process by applying the selected candidate BAT

5. Application of the methodology: alternative scenarios analysis

The second module of the methodology is applied step-by-step to all the alternative scenarios proposed to improve the sustainability of the industrial system considered.

5.1. Qualitative description of the proposed scenarios

The input data fed to the model in all the alternative scenarios is shown in Table 5.3. The specific considerations for each scenario are described below:

- Scenario 1. This scenario highly takes advantage of the residual heat dispersed in the convection zone of reformer I. On the other hand, a pre-reformer has been included before reformer I, so that the reforming reactions had already begun before entering reformer I. The S/C ratio has been reduced to 3, as well as the catalytic bed temperatures in reformer I and reformer II.
- Scenario 2. The original reforming section is substituted by an ATR system where exothermic combustion directly fuels endothermic reforming. Accordingly, S/C ratio is reduced to 1, and O_2/C is adjusted to 0.55, to guarantee that the required energy is supplied to the reforming reactions.
- Scenario 3. The CO_2 absorption stage is substituted by a PSA unit where H_2 is separated and purified. PSA recovers 90% of the H_2 and retains 99% of the CO_2, producing a high purity mixture of H_2 and N_2.

5.2. Process simulation to evaluate each scenario

This stage of the methodology involves several steps intended to evaluate the consequences of implementing each of the proposed scenarios, and to analyse their effect over the IF of the process.

5.2.1. Software selection

Aspen HYSYS V7.1 is again selected to evaluate all the alternative scenarios.

5.2.2. Modelling and scenario building

As in the base case, the Peng-Robinson equation of state (Equation 5.1) is used to model all the proposed scenarios. All the reactions modelled in each alternative scenario are shown in Table 5.1, indicating in the stage in which they are taking place. The desulphurisation stage has not been modelled in any case, as none of the modifications proposed after BAT Analysis affects it. As in the base case, it is assumed that the natural gas fed to the reformers is sulphur-free (Table 5.3). There have also been obviated the reaction causing carbon formation in the reformers, owing to the working conditions.

HYSYS functions SET and ADJUST are used for the same purposes as in the base case. Every specific consideration for the alternative scenarios is included in Table 5.4, and the models built for each scenario are described below:

- Scenario 1. In this scenario waste heat from the convection zone of reformer I is used to heat several streams of the process. The gas stream leaving the convection zone is sequentially cooled down, so that the dissipated heat can be used to heat other streams. Six coolers have been modelled representing the thermal integration of the process. Besides fuelling the endothermic reactions on reformer I, the combustion energy heats the combustion air, the steam/natural gas mixture fed to pre-reformer, the inlet flow to reformer I, the process air and the steam/air mixture fed to reformer II.

  The pre-reformer, placed before reformer I, has been modelled as a Gibbs reactor, defined on the basis of stoichiometry and equilibrium parameters, with low catalytic bed temperature.

  The rest of the process has been modelled with the same criteria as in the base case, though considering the parameters included in Table 5.4.

- Scenario 2. The reforming section has been substituted by an ATR, which has been modelled as two reactors. The first one is a conversion reactor, where the combustion reactions that fuel the rest of the process take place. This reactor represents the combustion section of the ATR. The second is a Gibbs reactor, where the reforming reactions have been modelled considering stoichiometry and equilibrium relations. ATR considers lower S/C ratio than the rest of the scenarios (it is set on 1) and it is the only scenario fixing (by means of the ADJUST function) a specific value for the O_2/C ratio. It has been set on 0.55 to guarantee that the required energy is provided to the reforming reactions. Owing to the increased O_2/C ratio, it is not possible to achieve the objective H_2/N_2 ratio. It would be necessary to make up the N_2 content of the product stream so that it could be used in ammonia synthesis.

  The rest of the process has been modelled with the same considerations that the base case, though updating some parameters according to Table 5.4.

- Scenario 3. The reforming section has been modelled with the same criteria as in the base case, as well as the shift reactors. However, the CO_2 removal section has been substituted by a PSA, which has been modelled as a component splitter. According to the specifications for PSA (Figure 5.7), temperature has to be adjusted to 37.85 ºC and pressure has to be reduced to 2130 kPa, staying in this value for the rest of the process. For the component splitter is has been considered that 99% of the CO_2 is removed from the product stream, which retains some traces of CH_4 and losses 10% of the H_2 and N_2 content.

5.2.3. Simulation

All models have been run in steady state, calculating the stationary material and energy flows for each case. The simulation of the base case and the alternative scenarios has led to the results shown in Table 5.6.

The simulation of the base case, which represents the current situation, is the benchmark for the rest of the analysed scenarios. According to the simulation, $2.47 \cdot 10^6$ kg/h of H_2 are produced, meaning $1.35 \cdot 10^7$ kg/h of a mixture of H_2 and N_2 with a 3.2 H_2/N_2 ratio and 98.57% purity. $5.06 \cdot 10^7$ kg/h of air are fed to the process, 72.50% used in the convection zone of the reformer. As the S/C ratio is 3.5, the amount of steam consumed in the process is $3.01 \cdot 10^7$ kg/h. The total normalized energy consumption (regarding the calorific energy derived from natural gas combustion) is $9.65 \cdot 10^4$ kJ/kg H_2 and the CO_2 emissions are 11.88 kg CO_2/kg H_2.

Table 5.6: Simulation results for the outputs (H_2) and inputs (air and steam) and for the IF ('energy consumption in' and 'CO_2 emissions from') for the base case and for the alternative scenarios

	Unit	Base case	Scenario 1	Scenario 2	Scenario 3
H_2 produced	$10^7 \cdot$ kg/h	0.25	0.25	0.66	0.24
Air consumed	$10^7 \cdot$ kg/h	5.06	5.07	10.30	5.13
Steam consumed	$10^7 \cdot$ kg/h	3.01	2.81	2.33	3.01
Purity of the H_2/N_2 mixture	%	98.57	98.67	95.12	99.74
IF 'ENERGY CONSUMPTION IN'					
Energy input to the process (not reforming)	$10^{11} \cdot$ kJ/h	1.35	1.05	3.50	0.30
Energy input to Reformer I (radiant zone)	$10^{11} \cdot$ kJ/h	0.66	0.50	0	0.66
Non-used energy from Reformer I (convection zone)	$10^{11} \cdot$ kJ/h	1.03	0.76	0	1.03
Total energy consumption normalized	**kJ/kg H_2**	**$9.65 \cdot 10^4$**	**$7.34 \cdot 10^4$**	**$5.26 \cdot 10^4$**	**$5.65 \cdot 10^4$**
IF 'CO_2 EMISSIONS FROM'					
CO_2 from reformer I (convection zone)	$10^7 \cdot$ kg/h	0.61	0.61	0	0.61
CO_2 from CO_2 removal stage	$10^7 \cdot$ kg/h	1.65	1.64	5.50	0
CO_2 from energy consumption	$10^7 \cdot$ kg/h	0.67	0.64	1.71	0.15
Total CO_2 emissions	**$10^7 \cdot$ kg/h**	**2.93**	**2.89**	**7.21**	**0.76**
Total CO_2 emissions normalized	**kg CO_2/kg H_2**	**11.88**	**11.71**	**10.83**	**3.21**

In scenario 1 the data concerning H_2 production and purity, and the consumption of air is quite similar than for the base case, as well as for scenario 3. The steam consumed is quite lower for scenario 1, as the S/C ratio is reduced to 3. The different configuration modelled in scenario 2 results on an incremented H_2 production, as well as higher air consumption.

The evolution of the H_2/N_2 product stream composition is shown in Figure 5.9. The base case and scenario 1 produce similar products, with high purity (over 98%) and a proper H_2/N_2 ratio. Scenario 3 is the one producing a highest purity product, as only traces of other products are found. The purity on scenario 2 is quite lower than for the rest of the models, due to the non-combusted CH_4. This compound does not affect to the ammonia production process, so it can be further removed. The H_2/N_2 ratio is reduced to 1.17.

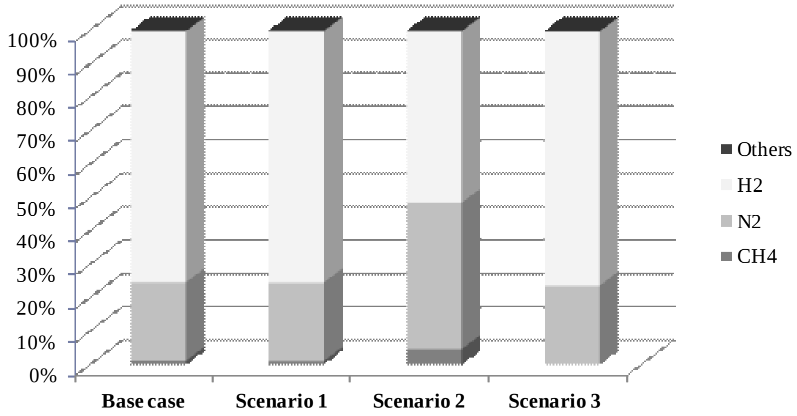


Figure 5.9: H_2/N_2 product stream composition ('Others' includes H_2O, MDEA and DEA)

5.3. Evaluation of the alternatives

The evolution of the IF detected, 'CO_2 emissions from' and 'energy consumption in', through the considered scenarios is analysed.

5.3.1. IF 'energy consumption in'

For 'energy consumption in', energy inputs to the 'reforming' and 'CO_2 removal' stages are considered (table 5.6). The energy input to the process (not reforming) covers all the energy provided through the process to heat streams and to fuel equipment (not the reformer). Coolers have not been considered, as cooling is provided by cool water. The energy input to Reformer I (radiant zone) is the energy provided by the natural gas combusted in Reformer I (convection zone) (Figure 5.2). Non-used energy from Reformer I (convection zone) considers the energy from the convection zone which has not been consumed in integrated heat exchangers.

The total energy consumption for the base case and each individual scenario has been calculated and normalized regarding the H_2 produced (kg/h) (Figure 5.10), so that it can be easily compared among scenarios. The relative energy consumption in the base case is $9.65 \cdot 10^4$ kJ/kg H_2. $6.63 \cdot 10^{10}$ kJ/h are consumed in Reformer I (radiant zone), whereas $1.03 \cdot 10^{11}$ kJ/h of energy is lost, as it is produced in the convection zone of Reformer I but not used in the process. This situation is highly improved in scenario 1, as the installation of a pre-reformer and the energetic integration of the process reduces energy consumption. The implementation of the pre-reformer reduces by 23% the energy required in Reformer I. On the other hand, taking advantage of the non-used energy from the conversion zone of Reformer I reduces energy losses by 26%. Accordingly, the overall energy consumption of this scenario is $7.34 \cdot 10^4$ kJ/kg H_2.

The ATR implemented in scenario 2 does not require any external energy input, so energy is only consumed in not-reforming processes. H_2 production is highly incremented, as well as the energy demand of the process, as all the flows are incremented regarding the other scenarios. The energy demand in the CO_2 removal stage is particularly high, as the amount of MDEA/DEA solution required is much bigger, and so the energy consumed in CO_2 desorption. However, the energy consumption regarding the H_2 production is the lowest of all of the analysed models, as it is set on $5.26 \cdot 10^4$ kJ/kg H_2.

In Scenario 3 the total energy consumption is reduced due to the implementation of the PSA unit. Unlike the absorption-desorption configuration modelled in the rest of the scenarios, the PSA does not require any external energy input. Although the energy input to Reformer I (radiant zone) and the non-used energy from the convection zone are the same than for the base case, the overall energy consumption is reduced to $5.65 \cdot 10^4$ kJ/kg H_2.

Scenarios 2 and 3 show the best results on energy consumption reduction, as they provide the most important reductions of the IF involved in this category (Figure 5.10). Scenario 2 mainly affects the energy consumed in the reforming process, so it reduces the IF 'energy input to Reformer I'. On the other hand, scenario 3 eliminates the energy input to the 'CO_2 removal' stage, effectively eliminating IF 'energy input to CO_2 removal'.

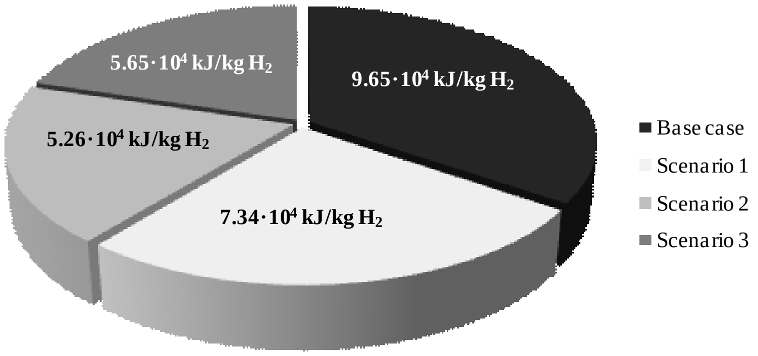


Figure 5.10: Total energy consumption for the base case and the alternative scenarios (referred to the kg of H_2 produced in each case)

5.3.2. IF 'CO_2 emissions from'

'CO_2 emissions from' takes into consideration the CO_2 generated in Reformer I (convection zone) as a result of the natural gas combustion for energy production (not reforming), and released in the 'CO_2 removal' stage. CO_2 emissions from both Reformer I (convection zone) and 'CO_2 removal' stage are directly gotten from the simulation results. Emissions from energy consumption have been calculated (Equation 5.2) on the basis of the emission factor for CO_2 emissions from natural gas combustion, $f=5.0576 \cdot 10^{-5}$ kg/kJ (US EPA, 1998).

$$E = f \cdot \sum_i G_i \qquad \textit{Equation 5.2}$$

E is the total CO_2 emissions derived from energy consumption in each of the analysed situations, and G_i is the energy consumption in unit i (kJ/h). The summation covers, for each model, all the elements consuming energy, except the reforming section. The total CO_2 emissions have calculated and normalized regarding the H_2 produced (kg/h) in each situation.

As already reported by other authors, energy-related BAT play a significant role in emission reduction (Mavrotas et al., 2007), and so the CO_2 emissions derived from the analysed process are highly affected by the techniques which reduce energy consumption.

The reference CO_2 emissions are provided by the base case, which releases 11.88 kg CO_2/kg H_2. Not-reforming energy input to scenario 1 is quite reduced, so CO_2 emissions are decreased to 11.71 kg CO_2/kg H_2 (Figure 5.11). This reduction is due to the reduced energy consumption, as the corresponding CO_2 emissions have been reduced from $6.71\cdot 10^6$ kg/h in the base case to $6.45\cdot 10^6$ kg/h in scenario 1.

As energy consumption is highly reduced in scenario 2, so are the CO_2 emissions, which are brought down to 10.83 kg CO_2/kg H_2. As this scenario performs combustion for energy production and reforming together, the CO_2 content of the reformate gas is bigger than for the other models, and so the amount of CO_2 released in the removal section is rather superior.

Scenario 3 is by far the one releasing less CO_2, as only 3.21 kg CO_2/kg H_2 are emitted to the atmosphere. The CO_2 removed is retained in an adsorbent matrix, instead of being emitted to the atmosphere. This high-purity CO_2 can be desorbed from the solid matrix and being used as syngas in other processes, turning the waste stream into a by-product. This scenario is clearly the best one regarding CO_2 emissions reduction, although the improvements obtained in scenario 2 are also quite remarkable (Figure 5.11).

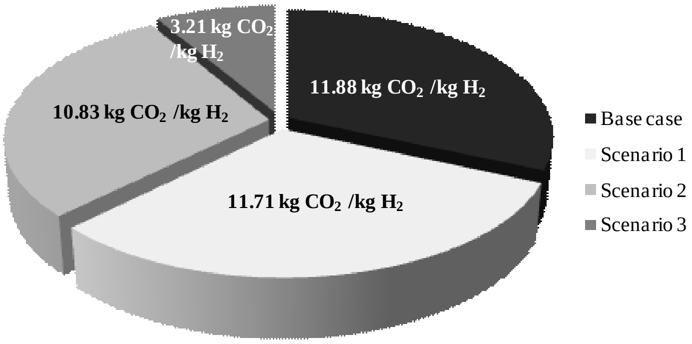


Figure 5.11: Total CO_2 emissions for the base case and the alternative scenarios (referred to the kg of H_2 produced in each case)

6. Results and discussion

This chapter has presented a methodology combining a technical inventories method, BAT Analysis, and an IF identification tool, process simulation, to get sustainable industrial systems. The methodology includes two sections. The first one thoroughly analyses the process to develop an inventory of candidate techniques and to quantitatively identify, by process simulation, the IF of the system. The second section evaluates, by process simulation, the suitability of the resulting alternative scenarios.

The methodology has been applied to an industrial system, a hydrogen production plant applying the natural gas steam reforming process. As a result the IF of the system have been identified by process simulation and a set of scenarios implementing different combinations of BAT, each of them evaluated by process simulation, has been proposed.

The application of the methodology has led to the selection and evaluation of the most appropriate techniques to enhance the IF identified for the process. The first important result is the elaboration of an inventory of candidate BAT for the generic natural gas steam reforming process. It includes 17 techniques affecting different stages of the process and covering a variety of environmental aspects. This inventory can be used in any other plant performing the same process.

The other relevant contribution of the methodology is the proposal of three alternative scenarios to improve the original process. These alternatives are meant to reduce the IF identified in the base case. Two generic IF were identified, 'energy consumption in' and 'CO_2 emissions from'. Each scenario includes one or a set of BAT whose implementation on the process is modelled and simulated using Aspen HYSYS.

The simulation results show up the benefits on implementing each of the proposed scenarios. Scenario 1 provides good results, as energy integration highly reduces energy consumption, which effects CO_2 emissions. However, the benefits derived from the implementation of scenario 2 and scenario 3 are much more striking. Scenario 2 highly reduces energy consumption, which is 45.5% lower than for the base case. CO_2 emissions are also rather decreased, although the major reductions are provided by scenario 3, which minimizes the emissions to 3.21 kg CO_2/kg H_2.

The decision of whether selecting scenario 2 or scenario 3 for implementation on the plant should rely now on economical factors. According to the technical data sheet for candidate technique ATR (Figure 5.6), this technique is a good option for large scale production, as the low S/C ratios reduce operating costs. On the other hand PSA (Figure 5.7) is a low operating cost technique, especially for small-scale production. A proper economical analysis, out of the scope of this work, will be needed to make a based decision.

According to the results, it will also be interesting to analyse the effect of combining ATR and PSA into a single scenario. Both energy consumption and CO_2 emissions will be highly reduced, probably providing the most appropriate option to improve the sustainability of the industrial system in the long term.

7. Conclusions

The proposed methodology was intended to design sustainable industrial systems on the basis of BAT by simulating different alternatives. The method combines two known tools to identify the IF of the process and to propose a suitable enhanced scenario to get a sustainable industrial system. The methodology has been satisfactorily validated in a H_2 production plant. Three alternative scenarios have been proposed for an obsolete process, and they have been modelled and simulated in order to quantify their effects over the process.

Although laborious in terms of data recompilation and evaluation, qualitative process analysis provides the basis of the methodology. It allows dividing the process into clearly differentiated stages and also identifying all the flows involved. This information is directly used to evaluate the environmental impacts of the process, as flows can be one by one evaluated regarding other similar processes. This evaluation points out which are the most disturbing flows in terms of quantity and impact over the environment, which are selected as the IF of the process.

BAT Analysis provides support on decision-making when selecting the most appropriate techniques. Besides technical inventories especially adapted to the analysed process, it includes complete and individualized information for each technique. This information, summarized in individual technical data sheet, is a good support for evaluating and selecting candidate techniques.

Though model building may be arduous, process simulation allows modelling and simulating all the alternatives so that they can be effectively compared. The three proposed scenarios have been simulated, so that the potential improvements can be predicted. These results will provide decision-makers with qualitative information about the improvements to be expected after implementing any of the proposed techniques. It even allows the possibility of modelling and analyzing any combination of techniques to identify the optimal set.

The methodology could be improved mainly in two ways. Firstly the identification of the IF could be improved by applying a quantitative material and flow analysis of the base case, so that all the streams of the process could be quantified and compared. This could be provided by MEFA, as presented on the methodology proposed in chapter 3.1. MEFA is a more suitable tool for IF identification, though process simulation is better to test and evaluate alternative scenarios implementing different techniques. It allows quantitatively comparing the IF in the different scenarios.

On the other hand, an economic analysis will facilitate decision-makers to decide, between similar options, which are the economic consequences of implementing the options in consideration.

Methodologies proposed in chapter 4 and chapter 5 have been effectively validated in case studies representing different industrial systems. However both methodologies have been developed considering individual plants, not systems involving more than one plant. Moreover these methodologies are actually conceived for quite big plants whose processes can be divided into stages, their consumptions and emissions can be easily allocated, and are able to provide abundant and accurate data. Complex industrial systems and smaller plants are also in need of methodologies to improve their sustainability, which take into consideration their specific features.

CHAPTER 6

COMBINING WMH AND BAT ANALYSIS: APPLICATION TO A WASTE MANAGEMENT SYSTEM

Summary

In previous chapters methodologies combining BAT Analysis with MEFA and process simulation have been developed and validated. These methodologies have been proved to be quite suitable to identify the IF and propose techniques to enhance them and get a sustainable industrial system. However these methodologies have been developed mostly considering single industrial plants. Specific methodologies combining and adapting the tools analysed in previous chapters are required to get sustainable industrial systems integrated by smaller plants in complex systems.

This chapter proposes a methodology to improve the sustainability of waste management in an industrial system represented by an atomised sector, integrated by highly dispersed small enterprises. Two of the actors involved on waste management strategies are considered: the waste producers and the intermediate waste manager. The IF between both actors are identified and techniques from an inventory are proposed to get a sustainable symbiotic system. The methodology considers the WMH, settled by the European waste Directive, and the IPPC philosophy. Both elements are combined, and the IPPC philosophy is adapted to the small and medium sized enterprises.

The methodology is applied and validated in a system where the producers are the Galician (NW Spain) printing plants belonging to a regional association, and represented by a reference plant. The intermediate waste manager is a local waste transfer station.

This methodology provides extensive information about the considered system regarding the geographical area considered, the processes performed, the consumptions and emissions associated, and the waste flows between the waste producers and the waste manager. The IF are identified according to their amount and hazards associated. Alternatives to enhance their management are proposed on the basis of WMH and BAT Analysis, so that the waste producers focus their initiatives on prevention and preparation for re-use techniques, whereas the intermediate waste manager focuses on preparation for re-use, recycling and recovery options.

Techniques and treatments are selected aiming to establish or improve the symbiosis between waste producers and intermediate managers.

The original system, integrated by a printing plant and a waste transfer station, is analysed to detect the IF. A series of alternatives are proposed to improve the system, and some of them are selected for being implemented. After implementation, the improved system is compared with the original one, showing that, besides reducing the amount of waste managed in the system, a symbiotic relationship between both actors has been settled.

In this chapter, principles established considering big installations have been adapted to sectors that, in spite of being mainly integrated by small and medium-sized enterprises, generate a not negligible amount of diverse hazardous wastes.

1. Introduction

Methodologies combining technical inventoreis, by means of BAT Analysis, and IF identification tools, as MEFA and process simulation, have been proposed and validated in previous chapters. But these methodologies are really intended for big single industrial plants, as they have been developed under the requisites of the IPPC Directive.

Nevertheless the principles established with the IPPC Directive about the integrated pollution prevention of the environment can be extrapolated to industrial systems not listed in its Annex I. That is the case of the sectors mostly integrated by Small and Medium-sized Enterprises (SME).

The objective of this chapter is to propose a methodology to get a sustainable industrial system to manage hazardous waste generated by an atomised sector, integrated by highly dispersed SME. The methodology considers two actors: the waste producers and the intermediate waste manager. The WMH and the IPPC philosophy are combined and adapted to a complex system integrated by SME to detect the IF and enhance them by industrial symbiosis.

The methodology is validated in an industrial system where the producers are the Galician (NW Spain) printing plants belonging to a regional association, and represented by a reference plant. The intermediate manager is a local waste transfer station. This type of installation serves as a link between waste collection areas and waste treatment facilities, and they are used to bulk up the waste for more efficient transport by a larger truck (Bovea et al., 2007; Eshet et al., 2007).

1.1. Small and Medium-sized Enterprises

SME are defined as those enterprises which employ fewer than 250 persons and which have an annual turnover not exceeding 50 million euro, and/or an annual balance sheet total not exceeding 43 million euro (Commission of the European Communities, 2003c). They represent 99% of all the European enterprises and 57% of the economic value added. Being such an important part of the European economy, they have a significant impact on the environment, not as individuals, but as a combined total impact across sectors (Commission of the European Communities, 2007a).

Small enterprises are often not fully aware of the environmental impact of their activities. In fact, between 75-90% of them think that their activities do not have any impact on the environment (Commission of the European Communities, 2007a). However, despite having little evidence of their specific impacts on the environment, research has pointed out SME as a particularly problematic group in terms of compliance with environmental legislation (Commission of the European Communities, 2007b). The main reasons are their lack of awareness of their environmental impact, their ignorance about the environmental legislation, their incapacity to tackle their impacts, and sometimes the excessive administrative and financial burden of compliance (Commission of the European Communities, 2007a; Commission of the European Communities, 2007b; EU, 2009b; Redmond et al., 2008).

A recent initiative aiming to make it easier for SME to comply with their obligations and improve their environmental performance was the “Environmental Compliance Assistance Programme for SME” (EU, 2009b). It is a strategic approach to implement one of the principles of the 6th Environmental Action Programme: “the environmental action should be related to the nature and magnitude of the environmental problem rather than the size of the enterprise" (EU, 2002), and proposes a series of actions which included more accessible environmental management schemes (EU, 2009b).

1.2. Waste management strategies in SME

As explained in chapter 3.2, literature provides a wide variety of examples of strategies and methodologies to facilitate decision-making on designing waste management systems, normally concerning MSW (Abou Najm and El-Fadel, 2004; Fiorucci et al., 2003; Galante et al., 2010; Salvia et al., 2002; Shmelev and Powel, 2006). But strategies developed considering large business perspective cannot be simply adapted to small business, as they are not scaled down versions of big business.

SME have several advantages over large business that help them to address the environmental impact of their wastes (Redmond et al., 2008). On the one hand, their size enables them to react quicker than bigger enterprises to changes in the business environment (Condon, 2004). On the other hand, once an environmental strategy is decided upon, the costs of learning the new routine and renegotiating responsibilities is less than for a bigger enterprise, thanks to the relatively small staff numbers (Wills, 2003).

In spite of the significant advantages over big enterprises, SME are quite reluctant to implement any management system. As early as 2001, a study carried out by Ilomäki and Melanen (2001) showed that innovative and proactive enterprises implemented EMS only if they were demanded by external stakeholders. Three years later Hillary (2004) confirmed this behaviour after a study that also showed that, despite being the driving force for implementing EMS, customers had a striking lack of interest in the environmental performance of SME. Micro business in particular found that their customers were absolutely uninterested in their environmental behaviour, as they considered that the impact of their activities could be neglected.

SME are very sceptical of the benefits to be gained from making environmental improvements (Hillary, 2004). In 2005, Worthington and Patton (2005) concluded that although SME were realizing that voluntarily embracing environmental good practices could improve their performance, the general environmental behaviour was limited and compliance-driven. In fact, legislation has been pointed out as the most important driver for environmental improvements (Hillary, 2004). Other good-known drivers for environmental improvement in SME are customers. In fact Vachon and Klassen (2006) went even further, as they concluded that the interaction between a plant and its primary suppliers was associated with better delivery performance, whereas partnership with customers was positively linked to quality, flexibility and environmental performance. More recent works show that the decision of the SME owner-manager is the main reason to introduce any EMS (Zorpas, 2010) or even any waste management practice (Redmond et al., 2008). Therefore, to achieve a better implementation of environmental good practices in SME, the owner-managers should be informed about how to make appropriate changes in their business to take advantage of the benefits (Redmond et al., 2008). Though the aims and conclusions from these works consider general environmental performance, they also apply over the specific case of waste management in SME. The considered experiences suggest that strategies aiming to improve the environmental performance, and therefore waste management, of SME must be strongly based on legal requirements, as legislative compliance is a major driver for environmental initiatives in SME (Hillary, 2004; Worthington and Patton, 2005).

The needs, requirements and particularities of the actors affected by the production process must be considered, as they are precursors, in many cases, of the application of good practices in small enterprises. Finally, benefits derived from implementing any strategy must be evident and well defined.

IPPC-focused strategies are an important resource for encouraging environmental improvements in SME, owing to its integrated approach based on the implementation of techniques with environmental, economic and technical benefits. In addition waste is specifically considered, focusing on its prevention and reduction. BAT Analysis, as proposed in chapter 2, is a methodology based on the IPPC philosophy only focused on the affected sectors, normally integrated by big installations, and it considers general environmental aspects without focussing on waste. The methodologies proposed by other authors face similar limitations, as the method for emission data comparisons by Saarinen (2003) or the quantitative integrated assessment of pollution prevention by Styles et al. (2009). Other IPPC-based initiatives are mostly focused on evaluating the implementation of the IPPC Directive in the affected sectors (Pellini and Morris, 2001; Silvo et al., 2009). The methods they propose include LCA for BAT selection (Nicholas et al., 2000), others propose indicators to assess environmental performance (Karavanas et al., 2009) and more recent works qualify BAT and analyse their suitability for the considered process (Samarakoon and Gudmestad, 2011; Schoenberger, 2011). In all cases these methodologies only apply over IPPC affected installations, never considering other sectors such as those typically integrated by SME.

In spite of not being frequently included on the scope of the IPPC Directive, SME are important sources of pollution and generate a not negligible amount of diverse hazardous wastes. In this chapter the principles established considering big installations have been adapted to sectors mainly integrated by SME.

An example of a sector mainly integrated by SME is the printing industry. Though some authors have analysed the implementation of environmental management initiatives in the sector (Kiurski et al, 2012; Vachon and Klassen, 2006; Worthington and Patton, 2005), most of the experience is gotten from regional and national associations worldwide. These associations have developed different activities and initiatives for the printing sector (Table 6.1) aiming to improve the environmental performance of the involved installations. Most of them are recommendations proposed by the Administration or associations which are mostly focused on pollution prevention and control in the printing processes. However, no methodology involves the printing industry together with upstream or downstream stakeholders, so there is no evidence of the iteration between these elements.

2. Case study

The methodology applies the management alternatives set by the WMH and the IPPC philosophy to two main actors considered (Figure 6.1):

- The atomised SME sector, integrated by highly dispersed small plants, is the waste producer, mainly focussed on prevention and, in those cases where waste could not be avoided, preparation for re-use.

- The intermediate manager is a waste transfer station that manages waste from SME and delivers it to a final manager who frequently disposes it without further treatments. The methodology considers preparing wastes for their re-use, recycling and recovery as the main alternatives for this actor.

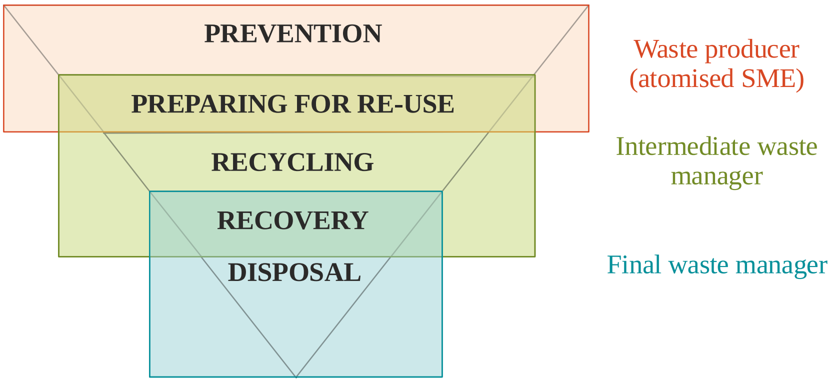


Figure 6.1: Roles of the actors involved in the methodology (Cristóbal Andrade et al., 2012)

3. Methodology

Although limited, literature about waste management strategies in SME is clear about the driving forces in such enterprises. Authors suggest that legislation is a main driver for environmental initiatives in sectors integrated by SME, as well as the criteria of the owner-managers. Furthermore the pressure from customers and the collaboration with stakeholders is also needed. These factors are the foundations for developing the methodology for SME.

As main drivers for environmental performance improvements in SME, two legal approaches have been used as basis for the methodology: IPPC philosophy and WMH. IPPC has been proved to be quite useful when improving environmental performance on industrial systems, mainly by the application of BAT (Georgopoulou et al., 2008; Mavrotas et al., 2007; Torres Rodriguez et al., 2011). Accordingly, some aspects typical from IPPC-based methodologies have been selected and adapted to SME. Firstly the need to deeply know the processes performed by the concerned installations, as well as the inputs and outputs involved, by an exhaustive qualitative process analysis. This step is particularly relevant in SME, as these plants do not have the resources to provide a detailed description of their environmental situation and identify the relevant flows (Laner and Rechberger, 2009). Secondly the waste prevention approach and the recovering the unavoidable wastes policy set by the IPPC Directive are also applicable for SME. Finally, improving environmental performance by implementing preventive or correctives measures, such as BAT, is highly interesting when considering SME. However, as SME are known to have very limited financial resources and capabilities (Kim et al., 2008), the proposed techniques must be economically reasonable and depend on the sector structure (Schollenberger et al., 2008). BEP seem appropriate, as they normally do not involve relevant economic investments, neither big technological change, and they provide short steps with quick wins, as needed in such sectors (Tischner and Nickel, 2003).

Table 6.1: Worldwide activities and initiatives in the printing industry

Country	Organization	Year	Title	Objectives and other important remarks	Reference
Australia	Australian Environment Business Network	2003	“Waste reduction in the printing industry”	Identify and promote effective waste minimisation printing practices by proposing a set of drivers for printers.	(Australian Environment Business Network, 2003)
US	Environmental Protection Agency	1990-1995	Guidelines and proposal of pollution prevention opportunities	18 activities or initiatives undertaken to voluntarily improve the environmental performance of the sector.	(US EPA, 1990, 1995)
US	Environmental Protection Agency	1994-1995	“Lithographic Printing Partnership”	Evaluation of printing centres to identify simple workplace practice changes mostly focused on pollution prevention options that printers could implement easily and cheaply.	(US EPA, 1997, 2010)
US	Printing Industries of America	2009	“Green Guide for Graphic Communications”	Evaluate green performance and communicate the “green” behaviour of the company to prospects, customers and other stakeholders.	(Printing Industries of America, 2009)
UK	Envirowise	1997-2004	Articles and leaflets for small printing business about environment-related topics.	Development of environmental policies, implementation of EMS, management of cleaning materials, reduction of fugitive solvent emissions and proposal of techniques for solvent capture and recovery.	(Envirowise, 1997a, 1997b, 1999c, 2000a, 2000b, 2002, 2004)
Europe	Intergraf	2009-2010	“Best practices in socially responsible restructuring for printing companies”	Exchange of information and best practices between several printing companies aiming to identify and tackle the challenges of the sector.	(Intergraf, 2010)
EU	EIPPCB	2007	“Reference Document on BAT on Surface Treatment using Organic Solvents”	Proposal of 60 generic BAT for the surface treatments using organic solvents sector, and 13 specific BAT for the printing industry, mostly aiming to reduce the emissions of pollutants.	(European Commission, 2007c)

Table 6.1: Worldwide activities and initiatives in the printing industry

Country	**Organization**	**Year**	**Title**	**Objectives and other important remarks**	**Reference**
Japan	Japan Federation of Printing Industries	2001-2007	“Print Service Green Standards Guideline”	Green standards for the off-set printing, gravure and screen printing. It includes detailed best practices and standards for materials, processes and projects.	(JFPI, 2010)
Brazil	Abrigraf	2003-2009	Guidelines for regional printers.	Implementation of legal requirements, adoption of clean production practices, waste management, and improvement of the environmental behaviour.	(Abrigraf Nacional, 2010)
Spain	Spanish Regional Governments and associations	2001-2003	Guides and manuals of good environmental practices.	Proposal of tools, good practices and new technologies to improve the environmental performance of the printing industries.	(*Generalitat de Catalunya*, 2003; *Generalitat Valenciana*, 2003; *IHOBE*, 2001; Spanish Government, 2002c)

On the other hand, WMH, settled by European Directive 2008/98/EC, provides the guidelines for waste management in any sector, even in those mainly integrated by SME. The hierarchy sets the necessity of preventing waste as a key factor for performance in any enterprise. After prevention, the next priority options are preparing waste for its re-use, recycling and recovery, being disposal the less desirable option. Appropriate technologies and techniques respecting this hierarchy must be selected to implement producer responsibility collectively (Pires et al., 2011).

Besides the IPPC philosophy and WMH approaches, other important driver in environmental strategies for SME is the relationship with the stakeholders. Being a waste management-oriented methodology, waste managers have been selected as the most relevant stakeholder. However, the particularities of SME make it necessary to consider a special type of manager: the intermediate ones. As discussed, SME typically lack resources enough to manage their own waste. Accordingly, they rely on intermediate waste managers who collect and manage waste from SME before drawing on final waste managers. The benefits of considering such a manager in waste management strategies for SME will be discussed.

The methodology proposed in this chapter is based on the WMH and the IPPC philosophy, and considers two actors: the waste producer and the intermediate waste manager. It includes a series of consecutive steps intended to enhance waste management on sectors mainly integrated by atomised SME by setting symbiotic relations with the intermediate waste manager. The steps of the methodology are defined below.

- Identification of the system. The two actors involved, namely the waste producer and the intermediate waste manager should be identified and defined.
- Evaluation of the sector in the affected geographical area. It includes the selection of a reference waste producer plant and the analysis of the role of the intermediate waste manager in the considered system. The selected reference plant should be representative of the whole system and should meet all the characteristics identified for the sector in the region concerned.
- Qualitative analysis of the process at the reference waste producer plant: identification of its limits, definition, and description of its stages. This analysis should be supported by technical visits to the reference plant, together with a bibliographic review.
- Identification of the potential pollutant flows. Qualification of the potential pollutants released by the reference waste producer plant. Classification, according to hazardousness criteria, and quantification of the total waste managed by the intermediate waste manager. This evaluation should be supported by technical visits to the intermediate waste manager installation.
- Selection of the IF of the system, which are selected considering their relevance over the whole system in terms of quantity.
- Alternatives to enhance the management of the identified IF, according to the WMH and BAT.
  - Definition and inventory of the good practices (BEP) for the waste producer focused on prevention and preparation for re-use. The opinions of experts from the considered sector are relevant in this part of the methodology.
  - Proposal of alternatives for treating the unavoidable inputs to the intermediate waste manager. They have to be based on the WMH objectives preparation for re-use, recycling and recovery.

- Implementation. Selection of improvements to be applied in the system (waste producer and intermediate waste manager), considering the possible symbiosis between them. Comparison of the differences between the base case and the improved system.

4. Application of the methodology

The proposed methodology is applied, step by step, to a real system for validation. The Galician printing industry is the sector selected for this purpose.

4.1. Identification of the system

The two actors involved on the considered system are:

- Waste producers: the Galician (NW Spain) printing plants belonging to a regional association, *AEAGG* (Association of Graphics Arts Entrepreneurs of Galicia) (*AEAGG*, 2010). This association represents the Galician printing industry, joining 146 regional printing plants, all of them SME.
- Intermediate waste manager: the local waste transfer station that regularly manages the hazardous waste from more than half of the printing plants included in the association.

4.2. Evaluation of the Galician printing industry

Printing industry, one of the largest manufacturing industries in the EU, produces manufactured products such as books, newspapers or magazines to all sectors of the economy (European Commission, 2007c). It is an industrial sector traditionally integrated by SME, as 85% of the enterprises have less than 20 employees (*AEAGG*, 2005; *IHOBE*, 2001). The European printing industry is integrated by more than 80000 enterprises which employ almost 962000 people, generating a total turnover of 80 billion euro (data from 2005) (*AEAGG*, 2005).

The process developed by the printing industry covers all the steps required to transform a creative work into a manufactured product. It includes activities such as illustrating, photo processing, painting or graphic design, among others. The ones related with printing operations can be classified as engraving or planography activities, according to the nature of the processes involved (Table 6.2).

The printing industry is closely linked with other sectors of the economy. As a result, a strong relationship between production and demand has been set, so the enterprises of this sector tend to be located around the demanding centres (*AEAGG*, 2005). In Spain almost 50% of the printing enterprises are placed in Madrid and Cataluña, where most of the Spanish industry is settled. However, as industry spreads through the Spanish geography, the printing industry is becoming more relevant in other regions. That is the case of Galicia, where 4.45% of the Spanish printing sector is located (data from 2009).

Table 6.2: Classification of printing activities

Engraving	Planography
Chalcography	Collotype
Flexography	Driography
Rotary press	Laser printing
Letterpress	Lithography
Block printing	Offset
Zincography	Screen printing

In 2009 there were 17401 printing plants in Spain, 775 of them located in Galicia. 93.42% of these enterprises were focused on printing and service activities related to printing, whereas the remaining 6.58% performed pre-press activities. Considering the number of employees, 91.74% of these enterprises had fewer than 10 employees. In general terms, the representation of the printing industry relevance on the Spanish industry is shown in Table 6.3.

Table 6.3: Comparison between Galician and Spanish enterprises, 2009 (data source: *INE*, 2010b)

Parameter	Galicia	Spain
Number of printing enterprises	775	17401
Total number enterprises	201263	3355830
% of enterprises belonging to the printing industry sector in relation with the total amount of enterprises	0.38	0.51
% of Galician enterprises in relation with the total amount of enterprises in Spain	6.00	
% of Galician printing enterprises in relation with the total amount of printing enterprises in Spain	4.45	

More than half of the Galician enterprises are principally dedicated to the offset printing, whereas the rest of the sites perform activities such as pre-press and design, screen printing or bookbinding (Figure 6.2). Nevertheless, it is uncommon to find sites exclusively dedicated to a single activity, as the majority prefer to diversify, complementing the main process with supporting activities. An example of this tendency is the offset printing, which is usually complemented by pre-press and design activities, as well as bookbinding processes (*AEAGG*, 2005).

Offset printing is clearly the most competitive and relevant printing activity in Galicia. It is also the most attractive to new investors, mainly due to its versatility, speed, quality and cost-effectiveness (*AEAGG*, 2005; European Commission, 2007c).

4.2.1. Selection of the printing reference plant

A printing plant, belonging to *AEAGG*, has been selected as a reference for the purposes of this chapter, taking into account the considerations of the previous section. The selected plant is one of the biggest printing installations of Galicia, and it applies the most complete version of the offset process in the region.

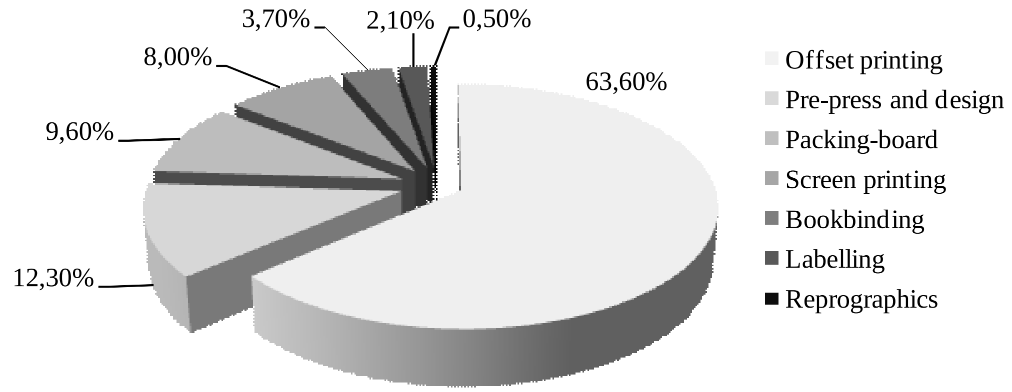


Figure 6.2: Distribution of activities in the Galician printing industry based on the number of companies (data adapted from *AEAGG*, 2005) (Cristóbal Andrade et al., 2012)

4.2.2. The role of the intermediate waste manager

In 2002 the Galician printing industry generated 60712 tonnes of waste (*IGE*, 2010). This data represented 1.48% of the waste produced in the region, and 3.27% of the total waste produced in Spain.

The intermediate waste manager considered is a regional waste transfer station. It is a local micro-business that manages an important part of the diverse hazardous wastes produced by the regional printing industries. This plant deals with the wastes produced by 93 of the Galician printing installations. It annually manages about 193.50 tonnes of hazardous wastes from these enterprises, representing 26.07% of the hazardous wastes generated by the Galician printing industry. Such an important percentage justifies the need of developing an appropriate methodology involving both the printing industry and the waste manager.

As discussed, printing plants are mainly SME. Moreover they are numerous and atomised, and normally they are not able to handle their own residues due to their limited resources. On the other hand, the final waste manager frequently is a big installation whose activities do not include collection from small production centres. Therefore, an intermediate actor is needed to transfer residues from the production centres to the final management facilities. A waste transfer station is the most suitable intermediate waste manager. It can collect waste from the small, numerous and atomised printing plants, and transport, classify and store it until it is delivered to the final waste manager. It is a privileged role for the application of the WMH as:

- The close relationship with both the printing plants and the final waste manager can be used to promote the implementation of the hierarchy by both actors.
- The waste transfer station receives and manipulates all the waste before delivering it to the final manager, so it can apply any alternative of the WMH in its own installations.

The considered waste transfer station collects the different types of waste from all the dispersed waste producer centres. Waste is transported to the transfer station where it is classified and stored before final disposal.

4.3. Qualitative analysis of the printing process

Offset is a planographic printing technique where the image and non-image areas are on the same plane as the image carrier. The non-printing areas are kept free of ink by being ink-repellent while the printing areas are ink-receptive, as the offset ink is oil-based while the non-printing areas are kept clean with water-based solutions. The image is transferred to the substrate (paper, board, etc.) from a rubber blanket, which previously receives the image from a plate.

After some technical visits to the reference printing plant, all the elements of the offset process were identified. These visits were scheduled with the owner-manager, who actively participated in them. In all cases previous reports were prepared to define the expected processes according to literature, to enumerate the data required for research and to summarize bibliographic background. During the visits the whole plant was analysed, identifying the processes, the inputs, outputs and intermediate flows, as well as the habitual performance of the plant. Information gathering was supported by the advice and expertise of the technicians from the plant, as well as by the opinion of the professionals from *AEAGG*. The visits resulted in a draft document that was evaluated by the already mentioned experts, who made some contributions. Finally, all the information collected from literature (bibliographic review oriented to the foundations, statistics, technology and environmental impact or the sector) and from the technical visits was included in a final report, used as starting point for the qualitative analysis of the printing industry.

The steps integrating the analysed offset process have been classified in three modules, namely pre-printing, printing and post-printing. The result of this qualitative analysis is shown in Figure 6.3, and it is briefly explained below.

PRE-PRINTING

It involves two sub-stages namely imaging and plate preparation.

- Imaging. The image is created using computational applications. As the plate is going to be conventionally processed, the designed image is developed as a film.
- Plate preparation. Plates are prepared by the conventional process. After placing the film over the plate, a vacuum is created to improve contact between both surfaces, and the whole pack is exposed to UV light. The plate is introduced in the developer bath, to make visible the light sensitive areas, and then in the fixer bath, to remove the non-photosensitive halogenated silver salts. Finally the film is water-washed and gummed. The image areas become ink-receptive thanks to a chemical change on the previously coated plate surface, triggered by a photochemical process in the light sensitive coating. The non-image areas stay water-receptive.

PRINTING

The plate is attached to the cylinder of the press. Since plates are typically made of thin flat aluminium sheets, they can be easily wrapped around the plate cylinder. As the cylinder rotates, a water-based dampening solution followed by an oil-based ink is transferred to the image area of the plate. The image repels the solution and accepts the printing ink, while the non-image areas accept the dampening solution and repel the ink. As the cylinder keeps rotating, the inked image is transferred to a blanket and then onto the substrate.

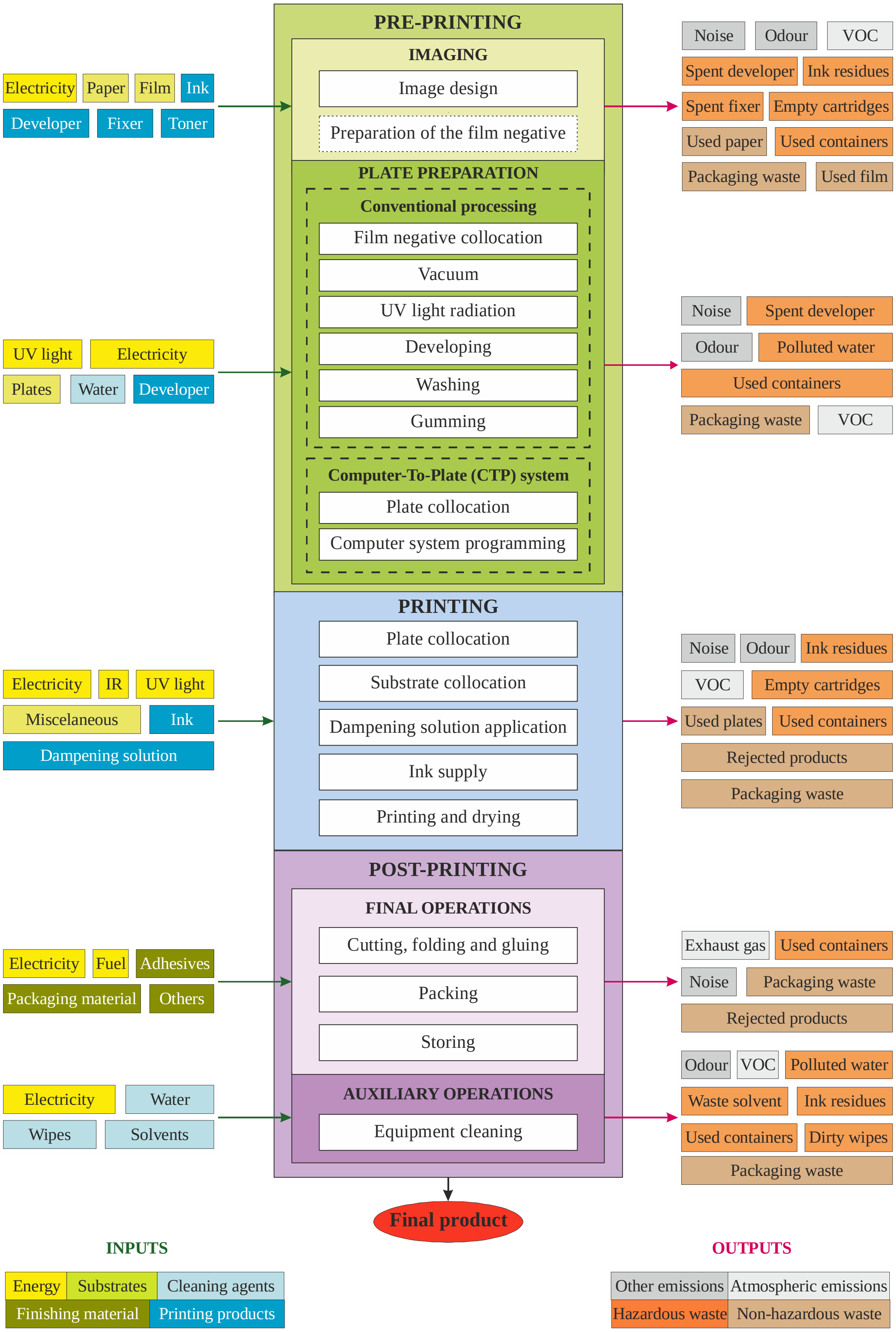


Figure 6.3: Flowsheet and environmental aspects of the offset printing process (Cristóbal Andrade et al., 2012)

POST-PRINTING

It involves two stages, which are final operations and auxiliary operations.

- Final operations. According to the demanded specifications, the printed substrate is cut, folded, glued or clamped. Then the final products are packed and stored until delivery.
- Auxiliary operations. Cleaning operations take place after finishing the printing process or when ink colours need to be changed. Cleaning requires wipes impregnated with solvents, detergents or even water, when the used inks are water-based.

4.4. Identification of potential pollution flows

This stage involves the identification of the potential pollution flows in the printing plants and in the waste transfer plant.

4.4.1. Printing plant

The typical inputs and output of the offset process have been assigned to the corresponding step, so that the limits of the system are clearly established, facilitating the identification and qualification of waste streams (Figure 6.3), as explained below.

PRE-PRINTING

Pre-printing activities release VOC that evaporate from the developing baths. Hazardous wastes are also generated. They are mainly spent chemicals as developer, fixer or ink residues, as well as polluted water from washing. Hazardous solid waste includes empty cartridges and used contaminated metallic and plastic containers. The process also generates non-hazardous waste, as used paper and film, and packaging waste.

PRINTING

This stage releases VOC and produces noise and odours. Ink residues are generated, as well as used plates and rejected products. Besides them, the other relevant waste streams are solid wastes such as packaging waste, used containers and empty cartridges.

POST-PRINTING

Final operations mainly generate packaging waste and rejected products. They also result in used containers and exhaust gases. Regarding auxiliary activities, dirty wipes are the main residue, together with waste solvent and polluted water. Ink residues are generated during maintenance operations. VOC are released, and used containers and packaging waste are generated.

4.4.2. Inputs to the waste transfer station

The considered waste transfer station manages the hazardous waste produced by the printing plants. Several technical visits have been needed to analyse and evaluate the activity and possibilities of this plant. As in the reference printing plant case, these visits involved previous reports about the processes expected, the data needed and the information gotten from bibliography. In the visits the whole plant was analysed. Supported by technicians from the plant the processes were defined, material flows were identified and the performance layout of the plant was described. All these information was included in a draft document that was reviewed by experts from the plant. The revised document, together with the literature review (focused on the foundations, statistics, technology and environmental impact of waste transfer stations), were included in a final report, used to identify the waste managed in this installation. After this exchange of information period, the waste collected from the printing industry was identified and quantified. Consequently, a classification method based on the hazardousness of waste was adopted.

The hazardousness criterion is based on the Spanish legislation, specifically to the Royal Decree 833/1988 on hazardous and toxic wastes (Spanish Government, 1988). It establishes that toxic and hazardous wastes are those wastes, including containers and packaging that have contained some, whose composition, shape or any other characteristic can be considered as such. This Royal Decree includes in its annex I a series of tables considering generic types of hazardous wastes, possible components of the waste that can make it dangerous and some characteristics of the hazardous wastes. These tables are complemented by the amendment of that legislation, the Spanish Royal Decree 952/1997, which sets down an extensive list of the wastes that are considered as hazardous (Spanish Government, 1997), and also by the transposition to the Spanish legal framework of the European list of hazardous wastes, Spanish Order MAM/304/2002 (Spanish Government, 2002b).

According to the Spanish legislation, there have been identified three different hazards among the wastes managed at the considered waste transfer station (Figure 6.4): flammability, harmfulness and ecotoxicity.

Table 6.4 presents the classification of the input waste to the waste transfer station. It includes the definition of each hazard according to the Spanish legislation, as well as a description of the waste itself. 38% of the waste managed at the waste transfer station is flammable, though spent developer is the most abundant waste dealt with.

4.5. Selection of Improvable Flows (IF)

Figure 6.4 represents the whole system, meaning the printing industry and the intermediate waste manager, the inputs and outputs, and the connexions between the actors. The dotted line represents the system boundaries.

All the waste streams generated by the printing plant, except atmospheric and other emissions, are delivered to the appropriate waste manager. Waste classified as non-hazardous is treated at a MSW plant. The hazardous waste, which requires special management, is sent to the intermediate waste manager.

The selected IF have been highlighted in bold in the diagram. Inputs of the printing process identified as IF are those materials that, after the printing process, can result in a hazardous waste. The selected outputs are all the hazardous waste resulting from the printing process that is managed at the intermediate installation.

Atmospheric emissions and the so-called "other emissions" are not relevant in comparison with residues, which are the main waste stream; therefore they have not been identified as IF.

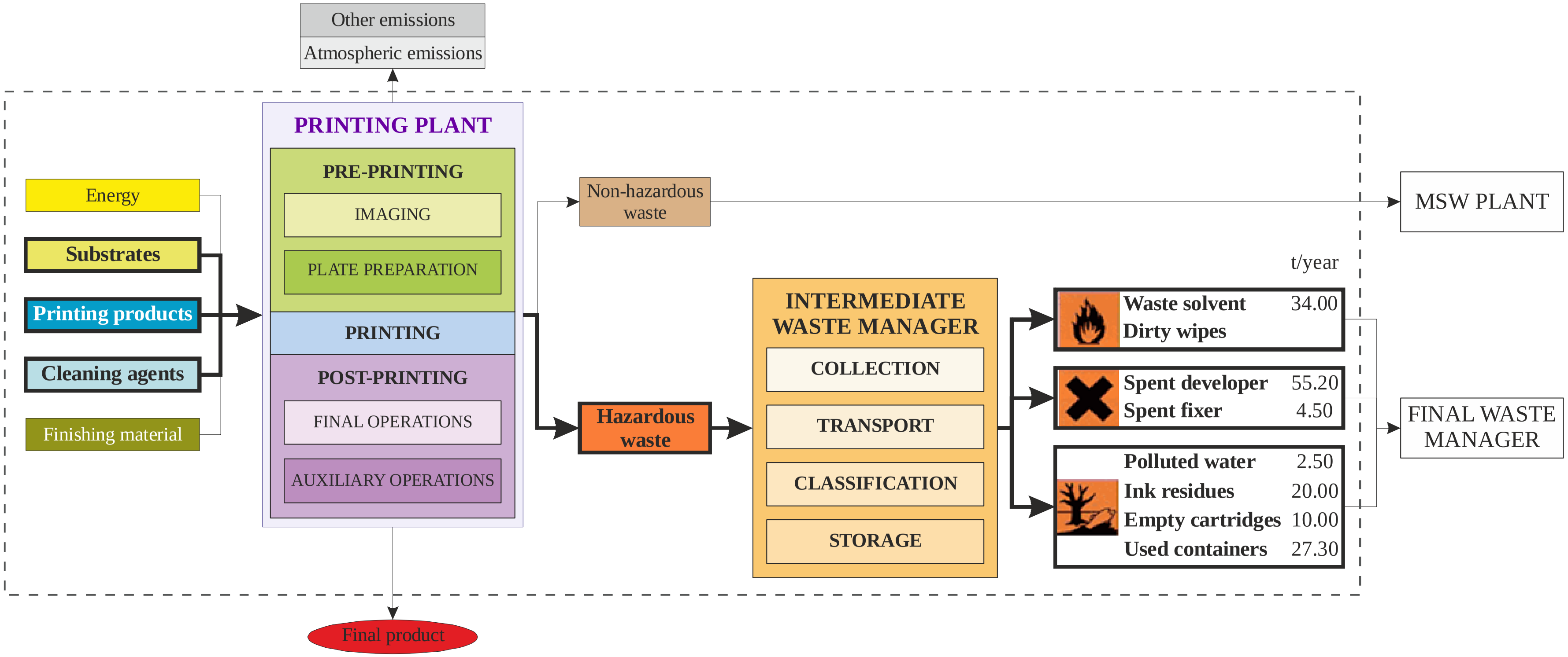


Figure 6.4: IF in the original system, integrated by the printing industry and the intermediate waste manager (Cristóbal Andrade et al., 2012)

Table 6.4: Definition and classification of the hazardous waste managed at the waste transfer station

Hazard	**Definition**[1]	**Waste**	**Description**
Flammable	Liquid substances and preparations whose flash point is equal to or greater than 21 ºC and less or equal to 55 ºC	Waste solvents	Mixture of different solvents, typically aliphatic, cyclical and naphthenic hydrocarbons, although sometimes they may also contain aromatic hydrocarbons such as toluene or xylene (European Commission, 2007c). They are polluted with inks, other printing products and water.
		Dirty wipes	They are soaked with solvents, inks and traces of all the chemicals used during the printing process.
Harmful	Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risk	Spent developer	Basic products whose pH varies between 10 and 12. They are water soluble and mainly composed by KOH, diethanol amine and 1-4 dihydroxybenzene. They may also contain heavy metals such as chromium VI, arsenic or lead.
		Spent fixer	Acid product, pH between 3 and 6. Its standard composition is ethanol, acetic acid and ammonium thiocyanate, though it may also contain mineral acids and their salts.
Ecotoxic	Substances that present or may present immediate or delayed risks for one or more sectors of the environment	Polluted water	- Plate preparation effluent: aqueous solution containing sulphuric acid, defoamer, fungicides and between 5 and 15% of isopropyl alcohol. - Cleaning operations effluent: water polluted with inks, other printing products, solvents and dirt from the machines.
		Ink residues	Unused and rejected mixtures of different inks sometimes polluted with other chemicals.
		Empty cartridges	Spent toner and cartridges containing traces of ink.
		Used containers	They are polluted with chemicals remains and cleaning agents, and their hazardousness is associated to the hazards of the products they initially contained (*IHOBE*, 2001).

[1] (Spanish Government, 1997)

Table 6.5: BEP for the offset printing process (techniques in italics are selected for implementation)

IF	Prevention	Preparing for re-use
Substrates	· *Recycled paper for testing.* · *Adjust the size of the plate to the dimensions of the image.* · *Substrates with the appropriate dimensions.*	· *Segregate the waste paper.*
Printing products	· Plan the acquisition of printing products. · Buy printing products in appropriate sized containers, regarding the production rate. · Operational practices to increase the lifetime of the baths. · Planning to avoid unnecessary ink changes. · Promote the use of silver-free film. · Avoid using inks containing heavy metals or hazardous pigments. · *When possible, use specific cartridges for each ink colour.* · Replace printing products containing VOC for water-based ones. · Spend developer baths completely. · *Operational practices to reduce the consumption of printing products.* · Reduce the size of the developer baths. · Floating plastic lids to prevent the oxidation of the developer. · *Use the ink remains.*	· Filtrate dampening solutions. · *Segregate liquid effluents such as developer, fixer and washing water.*
Cleaning agents	· *Start cleaning operations with used cleaning agents and finish with fresh ones.* · *Re-usable wipes.* · *Recirculation of the washing waters used in cleaning operations.* · Accurate systems to measure and dose solvents. · Automatic cleaning systems.	· *Avoid mixing cleaning agents.*
Waste	· *Print similar works together to reduce the amount of waste generated while cleaning.* · Store, when possible, products and input materials in recyclable containers. · Exclusive cartridge for inks with solvents or hazardous pigments. · Apply dry cleaning when possible. · Minimise the consumption of packages. · *While possible, prepare the image using electronic methods.* · *When possible, applying CTP technique.* · Adequate speed to optimise production and minimise wastes.	· Store liquids in covered containers. · Store the empty containers so that they do not get deteriorated. · Store the used wipes correctly. · Clean and recover containers, especially metallic cylinders. · *Remove the excess of ink before cleaning.* · *Appropriate segregation of all wastes generated during printing.* · Collect recyclable materials. · *Segregate the waste generated.* · Classify waste solvent according with the colour and type of ink. · Collecting inks and solvents before cleaning.

4.6. Alternatives to enhance the management of the IF

Measures to be applied by the printing plant and by the waste transfer station are proposed to enhance the management of the IF identified.

4.6.1. Definition and inventory of good practices for the printing plant

The printing industry is mostly integrated by SME that frequently do not have resources enough to manage their own waste. In spite of that, they have to make sure that an authorised and appropriated waste manager gets the generated wastes and takes care of their treatment (US EPA, 2001). In addition, a generic good practice to be applied, even defined as a BAT for the sector, is to “reduce material usage, prevent material losses and recover, re-use and recycle materials” (European Commission, 2007c). Both measures are the nexus between the printing industry and the waste management plants.

As hazardous waste producers, the offset printing sites should apply measures firstly focused on prevention and then on preparation for re-use, as settled by the WMH (Table 6.5).

PREVENTION

Prevention involves measures taken before a substance, material or product has become waste, that reduce their quantity, their adverse impacts on the environment and human health, or the content of harmful substances in materials and products (EU, 2008b).

29 BEP have been included in the inventory, classified according to the IF they affect:

- Substrates. These good practices promote the proper sizing of printing materials.
- Printing products. Some practices concern planning the execution of projects and the acquisition of the raw materials. These measures avoid chemicals to get out of specification because of long periods of storage. Others promote the use of less hazardous and reusable materials, which reduces the amount and the hazardousness of the generated residues. The rest is related to the improvement of the consumption of raw materials.
- Cleaning agents. Most of the practices proposed encourage the reutilization of used products in cleaning operations.
- Waste. 8 measures are proposed, and some of them involve automating the printing process. That is the case of applying the Computer-To-Plate (CTP) system during plate preparation, instead of the conventional process. This system obtains the plate directly from the computer, not requiring any photo-mechanic process. CTP process is much cleaner than the conventional one, as its waste stream is limited to packaging waste. Other practices, as storing products and input materials in recyclable containers, should be extensively applied in the sector, as more than 14% of the wastes managed at the waste transfer station (Figure 6.4) are used containers.

PREPARING FOR RE-USE

Preparing for re-use involves checking, cleaning or repairing operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing (EU, 2008b).

14 good practices have been included in the inventory and classified according to the IF they influence (Table 6.5), though most of them concern waste. These good practices are useful not only to re-use wastes directly in the printing plant, but also to help the intermediate waste manager to recover them. Proper segregation and classification of residues facilitates applying further treatments aiming to recover the waste or any material it may contain.

4.6.2. Proposal of alternatives for treating the unavoidable waste at the transfer station

The considered waste transfer station annually manages 193.5 tonnes of hazardous waste, which is collected, transported, classified and stored until it is delivered to the final waste manager. The alternatives proposed to improve the management of the selected IF correspond to the WMH options preparing for re-use, recycling and recovery (Table 6.6).

Table 6.6: Management alternatives at the intermediate waste manager plant

IF	**Preparing for re-use**	**Recycling**	**Recovery**
Waste solvent	Mixture with ink (residual or fresh)	Distillation (Filtration)	Energy recovery
Dirty wipes	Centrifugation	-	Distillation of the recovered solvent
Spent developer	Chemical make-up	Ion exchange	-
Spent fixer	-	Electrolysis and chemical make-up	Electrolytic recovery Metallic replacement
Polluted water	-	Ion exchange	Nanofiltration
Ink residues	Mixture with solvent Mixture with other inks	Ultrafiltration	-
Empty cartridges	Recharging	Plastic/metal recycling	-
Used containers	Cleaning	Plastic/metal recycling	-

Some of the alternatives focussed on preparing for re-use should take place at the printing site, as it would be nor environmental neither economically sustainable to prepare them off site. However, as some of these techniques require equipment that not all the printing plants can afford, they are likely to be performed by an intermediate waste manager.

- Waste solvent. Used solvents having one particular ink colour can be used to make up the solvent content of new or waste inks of the same colour (US EPA, 1990, 1995). This is a preparing for re-use technique that involves mixing waste solvent with residual or fresh inks. The recycling option is solvent distillation (European Commission, 2007c). It hardly releases any atmospheric pollutant and produces a distilled solvent with the same quality as the fresh one (European Commission, 2006c). When the solvent is not too polluted, it can be just filtered. The most typical recovery option is energy recovery. If accurate control is applied, waste solvents or dirty wipes can be used in clinker kilns, where temperatures are high enough to destroy the hazardous components (European Commission, 2001b).
- Dirty wipes. Waste solvents not only arrive to the waste transfer station as a liquid effluent, but also soaking dirty wipes. These wipes can be centrifuged, so that the wipe can be re-used and the separated solvent can be distilled and recovered (European Commission, 2007c).

- Spent developer. The life of developer baths can be extended by adding specific chemicals which control the pH of the solution (US EPA, 1995) and make up the developer for its re-use. On the other hand, ion exchange resins can be used to remove halide ions and regenerate spent developer (Bober et al., 2007).
- Spent fixer. Fixer can be regenerated by electrolysis, to reduce silver concentration, followed by the addition of make-up chemicals (Bober et al., 2007). Fixer is the main source of silver among the printing waste. The most common techniques to recover it are metallic replacement and electrolytic recovery. They reduce the hazardousness of the effluent by removing the silver ions, which can be used for different purposes (Bober et al., 2007; US EPA, 1990).
- Polluted water. Ion exchange is applied to recover dampening solutions. This technique reduces the amount of water used in washing operations (European Commission, 2007c). Additionally, nanofiltration is an efficient technique to remove most pollutants from washes. It enables recycling up to 80% of the water used in washing operations (Bober et al., 2007).
- Ink residues. Inks can be re-used by mixing waste inks of different colours together to get black ink. The reformulated black ink is comparable to some lower quality new black inks, such as newspaper ink (US EPA, 1990). Other possibility is making-up the solvent content of ink residues by mixing them with waste solvents. Water-based inks can be recovered if they are not too diluted or contaminated with cleaning agents. The wastewater is captured by ultrafiltration, and the recovered ink can be used as an additive to black ink. If the residue is captured separately from each single unit, the different colours can be re-used in the same cartridge (European Commission, 2007c).
- Empty cartridges. If kept in good condition, cartridges can be recharged with toner or ink to be re-used at the printing sites. When they get out specifications, they can be treated at plastic or metal recycling installations, depending on the type of cartridge.
- Used containers. As long as they comply with the requisites for containing hazardous substances, they can be cleaned and re-used (European Commission, 2007c). Once they get out specifications, they can be recycled at plastic or metal recycling installations, according to the nature of the container.

4.7. Implementation

Some of the elements proposed have been selected for implementation in the system, to evaluate the potential benefits of the methodology.

4.7.1. Improvements in the printing plant

There have been selected 12 BEP concerning prevention and 6 concerning preparation for re-use (highlighted in italics in table 6.5). Consequently, the activity at the printing plant is modified as it follows:

- The conventional plate preparation stage is replaced by the CTP process. This process does not need any printing product, so spent developer and fixer are not generated anymore. Odours and VOC emissions are also reduced.
- Sizing and planning printing projects. They have been included as two new stages in the printing module of the offset process.

- Segregation of every waste stream, as a new stage affecting the whole process.
- Re-usable wipes for cleaning, as they could be easily prepared for being re-used at the waste transfer station.
- Re-utilization of used materials, such as paper, ink or cleaning agents.

4.7.2. Improvements in the waste transfer station

A new processing module is suggested to complement the typical activities of a waste transfer station. There have been selected five treatment alternatives aiming to enhance four IF, according to the WMH.

- Waste solvent. Distillation, which recovers 70% of the original waste solvent. The remaining 30% is a distillation waste integrated by wastewater, oil sludge and traces of other products typical from the sector.
- Dirty wipes. Centrifugation to prepare them for being re-used at the printing plant. They contain, on average, 40% of waste solvent that, after centrifugation, is recycled by distillation.
- Ink residues. Mixing ink residues to obtain low-quality black ink. It is estimated that almost 50% of the ink residues can be recovered by this techniques.
- Empty cartridges. Recharging with the recovered ink.

4.7.3. Comparing the improved system with the base case

Figure 6.5 represents the system after applying all the modifications listed above. The comparison between the improved system (Figure 6.5) and the original one (Figure 6.4) shows that the IF have been reduced and the symbiosis between both actors has been improved.

In the improved system a symbiotic relationship between both actors has been established. Some of the flows are re-used in the proper printing process, and others are fed-back after recovery in the intermediate waste manager plant. The main consequence is the reduction of the hazardous waste flows in the system and the recovery of an important part of them (Table 6.7).

When replacing the conventional plate preparation process by the CTP process, two waste streams (spent developer and spent fixer) disappear. Therefore, the amount of hazardous waste managed by the intermediate waste manager is reduced (from 193.5 to 133.8 t/year). In addition, the treatments applied in the waste transfer station recover 74 t/year of waste, which is fed back to the printing process. Consequently the amount of waste transferred to the final waste manager is reduced from 193.5 to 59.8 t/year.

Respecting the original system, the consumption of resources is also reduced, as almost all solvent and re-usable wipes are recovered, and 50% of the ink residue and the empty cartridges are fed back to the process. Furthermore, the re-utilization of residual streams such as used paper, ink residues, polluted water or waste solvent in the process itself contributes to reduce the consumption of resources, though it is difficult to estimate at what extent.

Another relevant consequence of the implementation of these measures is segregation. The proper classification of all the wastes involved facilitates their management by an appropriate waste manager.

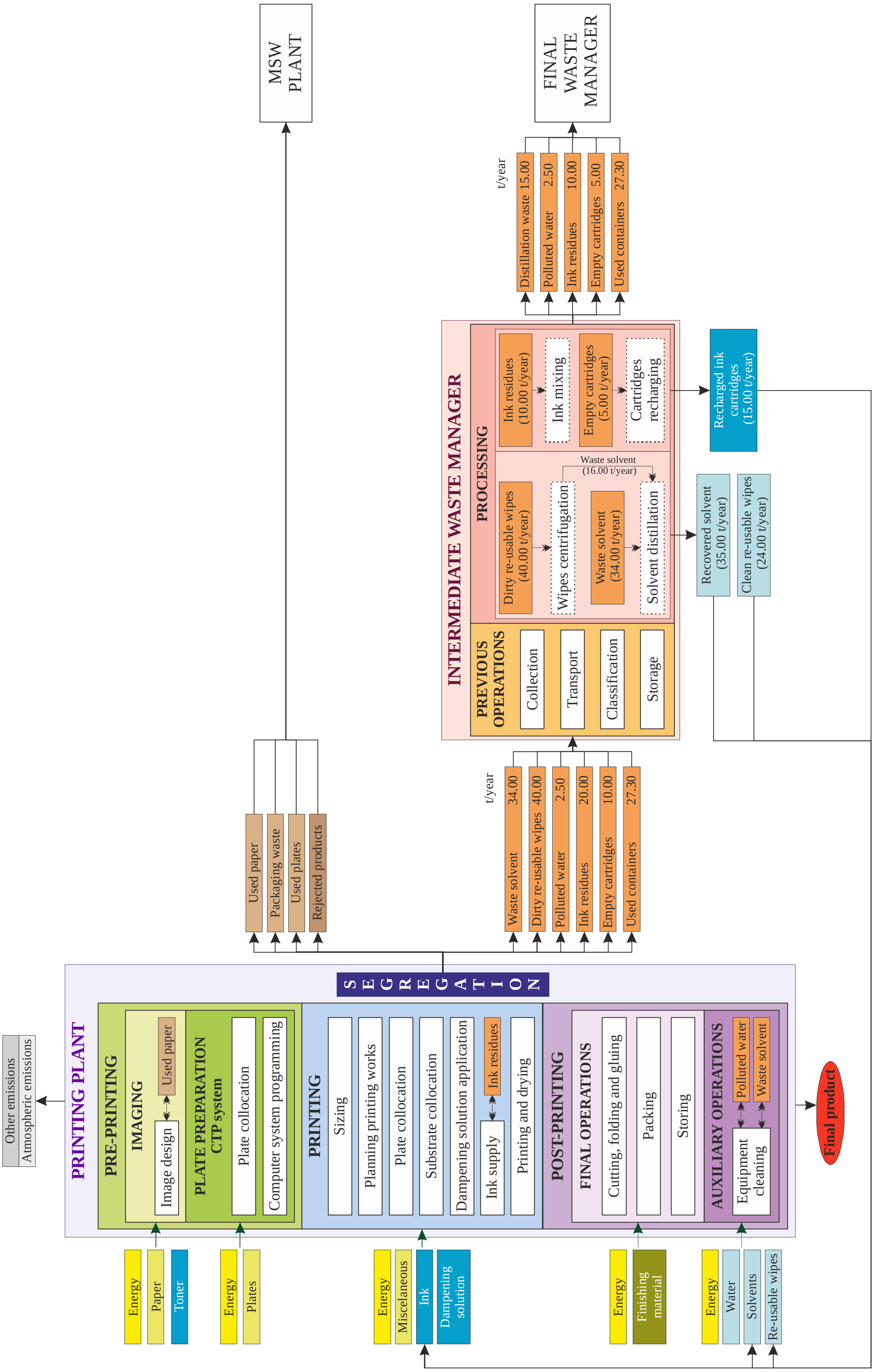


Figure 6.5: Improved system, after implementing the selected management options (Cristóbal Andrade et al., 2012)

Table 6.7: Comparing hazardous waste management between the original and the improved system

Managed waste	Units	Original system	Improved system
Hazardous waste to the intermediate waste manager	t/year	193.5	133.8
Recovered waste	t/year	0	74.0
Hazardous waste to the final waste manager	t/year	193.5	59.8

5. Results and discussion

This chapter has presented a methodology to get sustainable hazardous waste management in industrial systems integrated by SME. It applies qualitative and quantitative analysis to identify the IF of the system, which are enhanced by implementing alternatives from technical inventories developed regarding the WMH and the IPPC philosophy. The methodology has been developed considering the particularities of sectors mainly integrated by SME.

The implementation of the methodology in a real system has provided an integrated waste management scheme for the actors involved. By the application of selected good practices, the waste producer is able to avoid the generation of two types of hazardous waste and reduces some waste streams by re-using in-situ some products. On the other hand, the intermediate waste manager, which originally simply collected, transported and stored waste, is now applying preparing for re-use and recycling techniques. Hence, the system applies the IPPC principle of preventing or, where not practicable, reducing waste generation, as well as the priority order for waste management set by the WMH.

The combination of two of the actors involved in the whole waste production and management network is crucial for the success of the proposed methodology. As evidenced by literature, although synergies emerge from spontaneous collaboration between industries, it is important to have a context that triggers these collaborations (Costa and Ferrão, 2010). This context is provided by the methodology, which proposes an improved waste management scheme intertwining the actions of both actors. Industrial symbiosis is established in a system that originally did not have it, integrating geographically proximate plants in a network of material exchange (Karlsson and Wolf, 2008). The intermediate waste manager is the boost that encourages the SME sector, typically reluctant to environment-driven changes and normally operational rather than strategic in their decision-making (Redmond et al., 2008), to apply preparing for re-use good practices that improve management. In turn, the SME sector demands recovered and recycled products to the intermediate waste manager, creating new business opportunities. Both actors benefit from the methodology, preventing and controlling pollution in an integrated manner.

Another effective element of the methodology is the recommendation of visiting the involved plants and contacting associations that represent the SME sector. When dealing with SME, these initiatives are a useful method to obtain data and information about the material flows and the processes performed, as SME normally do not have resources enough to provide such information themselves (Laner and Rechberger, 2009).

The real system is currently implementing some of the proposed measures. The most active is the waste transfer plant, which has applied solvent distillation to recover used solvents and recycle them to the printing plants. It is also considering wipes centrifugation for the near future, whereas the other two treatments, ink mixing and cartridges recharging, will be considered afterwards. The implementation in the printing plants is more difficult to analyse, as each plant applies the measures considered appropriate, so there is no uniform implementation.

The degree of implementation of the methodology in the printing sector is highly affected by the nature and actual situation of the sector. The printing market, traditionally quite steady and not really dynamic (Intergraf, 2007), is nowadays facing a period of crisis, mainly due to intense competition and low investment in key technological advances (Glykas, 2004). In fact, between the beginning of 2008 and the middle of 2009, the production of European printing industry fell by 11% (Intergraf, 2011a), mainly as a consequence of the changing customer behaviour and the shift to web and other e-solutions (Intergraf, 2011b). Accordingly, the printing industry must evolve into a sector devoted to the newly rising industry featured with digital content, digital production and networking communication (Liu, 2008). But no only the products demanded are evolving, but also the technologies applied, turning the traditional techniques into modern technologies. The introduction of digital printing technology involves substantial changes in the overall printing process (Glykas, 2004), ranging from technological updating to diversification into new areas, as web design or other services within the communication industry (Intergraf, 2011a). The unstoppable evolution of the sector increases the need to modernise the sector by implementing new technologies, which can be a future driving force for the considered plants to implement the suggested measures.

Besides changes in the technologies applied, the printing industry is facing important changes in the way some typical products are consumed, due to the Internet and the emerging technologies (Jiang and Katsamakas, 2010). E-books, a new information technology product that facilitates reading and acquisition of information (Kang et al., 2009), are actually having quite an impact on the publishing and book markets. As an example, according to the American Association of Publishers, e-books have grown from 0.6% of the total trade market share in 2008 to 6.4% in 2010 (AAP, 2012), reaching $113 million in 2008 in the US (Jiang and Katsamakas, 2010). Though impactful for the book publishing industry, these data are not that impactful when the global printing industry is considered, let alone small and medium sized plants. According to the *AEAGG*, book publishing only accounts for 9% of the products produced by the printing sector. Therefore, the total impact of this new technology over the whole sector is not as relevant as it could seem, and the sector can be easily adapted to enhance other products and overcome the possible impact of e-books in the production of traditional printing books.

The symbiotic relationship established could be highly enhanced by the development of a proper market structure for the printing waste of the region. The already existing attempts of developing such a network of materials should be improved to optimise symbiosis. Besides the considered waste transfer plant, there are some plants collecting used paper for recycling, some enterprises that recover silver from used photographic liquids and even a new plant for preparing used wipes for re-use, though it is not being as successful as expected owing to its high prices. This latent structure could be strengthen by a proper resource management plan based on the proposed symbiotic system and involving, at least, the printing plants, the association *AEAGG* and the waste managers. One initiative that could be included in this plan would be a deposit/refund system to incentivize waste minimization. Such initiative could be quite effective for refillable containers, as toner, ink cartridges and solvent containers.

6. Conclusions

The proposed methodology integrates the WMH together with the IPPC philosophy, adapting both of them to sectors integrated by atomised SME in order to get a sustainable industrial system creating a symbiotic relationship between the actors involved. The methodology has been successfully validated on a system integrated by the printing plants from a regional association (all of them SME) and a waste transfer plant. Several techniques from inventories developed regarding the WMH and the IPPC have been proposed to enhance the IF of the system.

The methodology involves a series of consecutive steps, all of them relevant to get a successful optimisation of the process in terms of sustainability. In the first steps, the evaluation of the Galician printing sector has shown that it is integrated by atomised small enterprises spread across the region, with limited resources and generating small amounts of a great variety of hazardous wastes. The offset process is the most applied one, being the main activity of more than 63% of the enterprises from *AEAGG*. A reference printing plant was selected. An intermediate manager, represented by a local waste transfer station, has been pointed out as the most appropriate actor to deal with the waste from such a sector. It can collect, transport, classify and store waste from the small and atomised plants, and it can easily implement the WMH thanks to its close relationship with the waste producers.

The qualitative analysis of the printing process defines and limits its stages and flows, so that its potential pollutant flows can be identified. Consequently, the pollutant flows collected by the intermediate waste manager can be classified and quantified. Furthermore, the analysis of the specific properties of the actors involved facilitates the identification of the IF of the system, all of them hazardous waste. Thus, alternatives to enhance the management of the selected IF are proposed.

An inventory of good practices has been developed for the printing industry. It joins 29 practices concerning prevention and 14 focused on preparing for re-use. On the other hand, a series of management alternatives have been proposed for treating the IF at the waste transfer station. Some of these alternatives have been applied to the system.

The printing process has been modified by replacing the conventional plate preparation by the CTP process. Consequently two printing products, developer and fixer, are not needed anymore, so the corresponding waste flows, spent developer and spent fixer, are not generated. This technique results in reducing more than 30% the total amount of waste generated by the printing process. Three new stages (sizing, planning printing projects and segregation) have been introduced. Waste streams are re-used in the process itself (used paper, ink residues, polluted water and waste solvent), and re-usable wipes have replaced the original ones. On the other hand, the activity of the intermediate waste manager has been extended with a new processing module. It includes treatments aiming to recover waste solvent, dirty re-usable wipes, ink residues and empty cartridges.

The comparison between the original system and the improved one shows that the symbiosis between the involved actors has been improved. The modifications in the printing process directly affect the intermediate waste manager, who receives a smaller amount of a segregated waste. The amount of hazardous waste managed at the waste transfer station has been reduced, 30.85% less than in the original system. Moreover the transfer station is now recovering 55.3% of the materials, which are fed back to the printing process, while in the original system all waste was simply delivered to a final waste manager. In fact, with the new configuration, only 47.85% of the waste is delivered to the final waste manager, meaning a reduction of almost 70% regarding the original system.

This chapter points out the relevance of analysing and integrating two of the actors involved in waste management from atomised SME: the waste producer, as a printing reference plant, and the intermediate manager, as a local waste transfer station. The analysis of both actors, the identification of the IF, and the application of the selected measures has resulted in a system where symbiosis between actors has been favoured. Therefore it is concluded that enhancing symbiotic relations between the actors involved in waste management improves the exploitation of the resources involved.

Owing to the positive results obtained after applying this methodology, it can be recommended for application in other sectors or even in bigger and more complex systems. Iterations between sectors make it necessary to implement waste management strategies that consider all the involved elements to achieve the proper implementation of the WMH together with the IPPC principles.

CHAPTER 7

CONCLUSIONS

The objective of this thesis was to develop and apply methodologies to get sustainable industrial systems based on technical inventories and flow identification tools, used to detect the so-called Improvable Flows of the system.

Technical inventories were proposed regarding two different criteria derived from European environmental policies: the integrated pollution prevention and control philosophy and the waste management hierarchy. An IPPC-based methodology was proposed in chapter 2 to develop inventories of techniques candidate to be BAT, BAT Analysis. This method was validated in the Galician heavy ceramics manufacture industry, resulting in a deep qualitative analysis of the system that led to an inventory of candidate techniques. As techniques were selected regarding the IPPC principles, BAT Analysis was found to be a suitable tool not only to improve the sustainability of industrial processes but also to help applicants of IPPC environmental permits, as it provides information about techniques available to meet the ELV set by the Directive.

However BAT Analysis had an important limitation. Though quite useful to elaborate technical inventories, it failed to identify which technique or set of techniques were required in every specific situation. BAT Analysis required a new element that helped detecting the needs of the industrial systems so that techniques from the inventories could be accurately selected.

Industry is known to determine flows of materials and energy through the human economy. Thus, material and energy flows seem like the most appropriate indicator of the needs of an industrial system. They were pointed out as easily quantifiable and locatable by available tools, and so a new concept was defined as an indicator of the unsustainabilities of industrial systems: the Improvable Flows.

IF were defined as quantitatively (or even qualitatively) relevant flows in an industrial system which could be improved if properly managed by applying preventive or corrective measures. These flows are quantified and allocated regarding the industrial system they represent, so techniques from an inventory (as the ones provided by BAT Analysis) can be easily selected and implemented to effectively improve the sustainability of the system. Two process-analysis based tools were proposed as IF identification tools: MEFA (an industrial metabolism derived tool) and process simulation.

Both MEFA and process simulation are quantitative tools able to numerically identify and define all the streams involved in a process, though under different angles. MEFA systematically assesses flows and stocks of materials within a system defined in space and time. It is quite useful to identify unsuitable material and energy flows, so that corrective measures can be applied at source. Its suitability as an IF identification tool was successfully validated on chapter 3.1. MEFA was applied to the 'transport and storage of raw materials' stage of an exemplary roof-tile manufacturing plant. This tool provided a complete qualitative and quantitative analysis of the system, identifying 3 IF, which were quantified and allocated in the industrial system. But MEFA also has some limitations, mostly related to the fact that not all the quantitatively relevant flows could be considered as IF, whereas some other flows do require this qualification owing to qualitative features, as their economic value, their environmental impact or their pollution potential, to mention some. Truth is that, though tools and methodologies as MEFA and BAT Analysis provide valuable support, the criteria and expertise of decision-makers plays an essential role on the optimisation of industrial systems.

On the other hand, process simulation is also used to identify malfunctions, although it also has a great potential to evaluate and predict the possible consequences of applying modifications to industrial systems. It was validated in chapter 3.2 as an IF identification tool, in a methodology that combined inventories of waste management alternatives with process simulation to identify the IF of the selected alternative. The methodology was applied to the waste management sector, specifically to the case of the used lubricating oils. It provided an inventory of management alternatives, classified regarding the WMH, and one technique was selected as the most suitable to recycle used lubricating oils. The complete process was simulated and four IF were identified. Therefore, process simulation was proved to allow flow allocation and quantitative estimation of the material and energy flows of an industrial system. It was also validated as a tool with a high potential to evaluate the suitability of alternatives intended to improve production processes.

After validating MEFA and process simulation as suitable tools to identify IF, the suitability of IF as a nexus between methodologies to develop technical inventories (as BAT Analysis) and identification tools was analysed. Three methodologies, each providing a different combination of technical inventories and IF identification tools, were developed, all of them aiming to get sustainable industrial systems.

The first methodology, presented in chapter 4, combined MEFA as an IF identification tool and BAT Analysis to propose enhancement alternatives. It was validated in an exemplary roof-tile manufacturing plant, confirming its effectiveness. 14 IF were identified, most of them concerning the 'thermal treatments' stage, which was pointed out as the most likely to be improved stage. As a result, 7 candidate BAT were proposed, directly affecting 9 of the identified IF. The modelling and simulation of the process by MEFA provided exhaustive information about the material and energy flows of the process, which allowed their quantitative evaluation to select those flows that could be considered as improvable. This methodology allows the quantitative selection of IF, so that the most problematic stages of the process are clearly identified and specific techniques can be proposed.

The second methodology, presented in chapter 5, combined BAT Analysis and process simulation in a more complex procedure. This methodology identifies IF by applying process simulation to the base case. The unsustainable flows are selected by analysing all the material and energy flows involved in the process, and thus candidate techniques from an inventory are proposed. The effectiveness of these techniques is tested by building up new models including these techniques, in different scenarios that analyse all the possibilities. Therefore, the base case can be compared with possible scenarios where the selected alternatives have been implemented. The methodology was validated in a H_2 production plant performing the natural gas steam reforming process. Its application to the base case resulted in an inventory of 17 candidate techniques and on the identification, by process simulation, of 3 IF. Three alternative scenarios, each applying a different technique or set of techniques from the inventory, were suggested and validated by process simulation. The methodology provided not only the proper identification of the IF of the system and the suitable techniques to enhance them, but also a method to predict the behaviour of the suggested techniques, facilitating decision-making. Therefore, this method allows evaluating the improvements expected on the industrial system, specially the effect over the IF, after implementing the selected candidate techniques.

The third methodology, developed and validated on chapter 6, was specially intended for industrial systems integrated by a big number of small plants. It applies the WMH and BAT Analysis to atomised sectors mainly integrated by SME. The objective of this methodology was to improve the sustainability of waste management in industrial systems combining two actors: the waste producers and the intermediate waste manager. The IF between both actors are quantitatively identified by simple material balances. Then, techniques and procedures from inventories developed regarding the WMH and the IPPC philosophy are proposed. The methodology was validated in an industrial system represented by the Galician printing industry and a local waste transfer plant. It has allowed the identification of the IF of the system (raw materials to the printing plants and waste input to the waste transfer plant) and a set of techniques for both actors. The implementation of the techniques has turned the original system into a symbiotic one, where valuable flows are recovered and fed back to the process. Enhancing the symbiosis between the actors involved in waste management schemes highly improves the sustainability of the system. This methodology could be further improved by including an IF identification tool, as MEFA, that facilitates flow quantification and allocation.

Each methodology has its own strengths and weaknesses, and its suitability depends on the specific situation where the method is applied. In all cases qualitative analysis is initially applied to define the industrial system. This step allows stage identification and classification, which facilitates the study and comprehension of the process. It also defines the material and energy flows involved *a priori* in the process, making it easier to identify all the materials expected in each stage and the potential major energy consumers. All this information can be used in the quantitative steps of the methodologies, whether they are based on MEFA, process simulation or simpler material balances. Models are built based on the results of the qualitative part of the method, so that the process structure defined is respected through the whole analysis.

The quantitative analysis is performed using, in each case, a different IF identification tool: MEFA and process simulation, with different results. The method applying MEFA was intended to identify the IF of a process so that candidate techniques could be selected to prevent and reduce those flows. On the other hand, the method applying process simulation was meant to find the sustainable configuration for a given process by comparing the original situation with the potential future situation after applying the selected techniques. The last methodology applied material balances to roughly analyse the improvements expected after implementing the selected techniques.

Improvable Flows have been presented as a suitable indicator representing the unsustainabilities of industrial systems. They are quantifiable and allocable, and easily detected by identification tools based on process analysis. They can be prevented, reduced or enhanced by the application of an accurate selection of candidate techniques mainly defined under the principles of the IPPC philosophy and the WMH. IF have been used in three different methodologies, each combining an IF identification tool and a technical inventory, which have been validated and proved to provide sustainable industrial systems.

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ABBREVIATIONS

AEAGG: Association of Graphics Arts Entrepreneurs of Galicia (from the Spanish *Asociación de Empresarios de Artes Gráficas de Galicia)*;

ATR: Auto-Thermal Reformer;

BAT: Best Available Technique;

BAT-AEL: BAT-Associated Emission Limits;

BEP: Best Environmental Practices;

BREF: Reference Document on BAT;

CBA: Cost-Benefit Analysis;

CTP: Computer-To-Plate;

DEA: Diethanolamine;

DfE: Design for Environment;

EEA: European Environment Agency

ELV: Emission Limit Value;

EIA: Environmental Impact Assessment;

EIPPCB: European IPPC Bureau;

EMS: Environmental Management System;

EPA: Environmental Protection Agency;

EU: European Union;

GHG: Green-House Gases;

GWP: Global Warming Potential;

HTS: High-Temperature Shift;

IE: Industrial Ecology;

IF: Improvable Flow

IEF: Information Exchange Forum;

IPPC: Integrated Pollution Prevention and Control

IPTS: Institute for Prospective Technological Studies;

LCA: Life Cycle Assessment;

LCC: Life Cycle Costing;

LCT: Life Cycle Thinking;

LHV: Low Heating Value;

LTS: Low-Temperature Shift;

MDEA: Methyldiethanolamine;

MEFA: Material and Energy Flow Analysis;

MFA: Material Flow Analysis;

MSW: Municipal Solid Waste;

NACE: Classification of Economic Activities in the European Community;

NBP: Normal Boiling Point;

NMVOC: Non-Methane Volatile Organic Compounds;

NW: North West;

PAH: Polycyclic Aromatic Hydrocarbons;

PCB: Poly-Chlorinated Biphinyl;

PCDD: Polychlorinated dibenzodioxins;

PCDF: Polychlorinated dibenzofurans;

PET: Poly-Ethylene Terephthalate;

PM_{10}: Particulate Matter with an aerodynamic diameter equal to or less than 10 mm;

PM: Particulate Matter;

PSA: Pressure Swing Adsorption;

SLCA: Social Life Cycle Assessment;

SME: Small and Medium-sized Enterprise;

SNCR: Selective Non-Catalytic Reduction;

TWG: Technical Working Group;

VKT: Vehicle Kilometre Travelled;

US: United States;

VOC: Volatile Organic Compounds;

WAR: Waste Reduction;

WMH: Waste Management Hierarchy;

WWTP: WasteWater Treatment Plant;

NOMENCLATURE

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a: empirical constant

b: empirical constant

C: emission factor for exhaust, brake wear and tire wear (g/VKT)

E: CO_2 emissions (kg/h)

E_{np}: particulate emission factor for transport on unpaved roads (g/VKT)

E_p: particulate emission factor for transport on a paved road (g/VKT)

E_s: particulate emission factor for loading, unloading and piles handing (kg/t)

f: emission factor (kg/kJ)

G_i: energy consumption in equipment i (kJ/h)

k_{np}: empirical constant (lb/VMT^3)

k_p: particulate size multiplier (g/VKT)

k_s: particulate size multiplier

M: moisture content (%)

N: total number of days (day)

O_2/C: Oxygen/Carbon (natural gas) ratio

P: gaseous mixture pressure (Pa)

P_c: critic pressure (Pa)

P_L: number of wet days with at least 0.254 mm of precipitation (day)

R: ideal gases universal constant (J/mol·K) s: surface material silt content (%)

S/C: Steam/Carbon (natural gas) ratio

sL: road surface silt loading (g/m^2)

T_c: critic temperature (K)

T: gaseous mixture temperature (K)

U: average wind speed (m/s)

V_m: gaseous mixture molar volume (m^3/mol)

$T_r=T/T_c$: reduced temperature

W: weight (t)

ΔH_0: heat of reaction (kJ/mol)

ΔG_0: Gibb's free energy change (kJ/mol)

ΔP: pressure change (kPa)

ω: acentric factor

DIFFUSION OF RESULTS

Scientific Journals

Torres Rodríguez, M.T., Cristóbal Andrade, L., Bello Bugallo, P.M., Casares Long, J.J. Combining LCT tools for the optimization of an industrial process: Material and Energy Flow Analysis and Best Available Techniques. Journal of Hazardous Materials 192 (2011) 1705-1719.

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