UNIVERSITAT
ROVIRA I VIRGILI

Escola Tècnica Superior d'Enginyeria Química
Departament d'Enginyeria Química

Environmental Diagnosis of Process Plants by Life Cycle Techniques

Memoria presentada por
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para optar al Título de Doctor en Ingeniería Química
Tarragona, 2006

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ISBN: 978-84-691-2429-1 /D.L:T.218-2009

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Resumen

El diseño y la optimización de procesos industriales se basan en aspectos técnicos y económicos. No obstante, también deben considerarse los aspectos ambientales, tanto en el diseño preliminar del proceso como cuando éste se está llevando a cabo.

El objetivo de la investigación es desarrollar una herramienta que relacione aspectos de simulación, optimización, evaluación ambiental y análisis de sensibilidad. Para lo cual se estableció una metodología que consta de cinco niveles: Simulación de proceso, Inventario, Evaluación de impactos ambientales, análisis económico y análisis de sensibilidad.

La metodología desarrollada describe las variables relacionadas con el proceso (entradas y salidas de flujos de materia y energía), así como los impactos asociados a cada una de sus etapas, la viabilidad económica del proceso (mediante la determinación de cinco indicadores económicos), e identifica las etapas de proceso con el mayor impacto ambiental (mediante el análisis de sensibilidad).

Para la simulación de procesos se empleó el simulador ASPEN Hysys®. Mediante este programa, es posible obtener la caracterización de las corrientes de materia y energía del proceso industrial que se estudia, introduciendo las condiciones iniciales de operación del proceso. El inventario, la evaluación de impactos y el análisis económico se lleva a cabo en hojas de cálculo de forma automática, mediante la ejecución de macros.

La obtención del inventario de efectos ambientales y la evaluación de los correspondientes impactos se realizan siguiendo la metodología de ciclo de vida, por lo que se consideran las cargas ambientales asociadas a las materias primas, la generación de electricidad y utilidades. Para obtener el inventario se construyó una base de datos que contiene la información ambiental asociada a varios procesos industriales que se relacionan indirectamente al proceso bajo estudio. Similarmente, se incluyó una base de datos con los factores de caracterización de las categorías de impacto más importantes. Esta base de datos incluye categorías *mid* y *end point*, así como diversos horizontes de tiempo.

La validación de la metodología y de la herramienta desarrollada se ha llevado a cabo mediante tres procesos industriales: polietileno de baja densidad (LDPE), óxido de etileno (EO) y biodiesel. Para cada proceso se han evaluado diferentes configuraciones para poder determinar cual de ellas es la mejor opción desde el punto de vista ambiental y económico.

En el caso del LDPE, el cambio de configuración se ha enfocado en el origen de la electricidad, la cual puede ser proveniente de la Red Nacional Española o de una unidad de cogeneración. Los resultados indican que la mejor configuración corresponde al proceso que emplea electricidad proveniente de la unidad de cogeneración, puesto que en esta configuración se obtiene vapor como sub-producto y se evitan las emisiones asociadas a la generación de electricidad, lo que se refleja en una importante reducción de los impactos asociados a este proceso.

En el segundo proceso analizado, referente a la producción de oxido de etileno, se han evaluado cuatro configuraciones, empleando aire u oxígeno como materia prima y electricidad de la Red Española o produciéndola mediante cogeneración. En relación al origen de la electricidad, al emplear la

cogeneración, el comportamiento ambiental del proceso mejora considerablemente. En cuanto a la importancia de la materia prima empleada (aire u oxígeno), al emplear oxígeno se obtiene un mejor rendimiento en la etapa de reacción, con lo cual se compensa los costes asociados a la materia prima con la productividad del proceso.

Finalmente, se ha llevado a cabo la evaluación del proceso de producción de biodiesel, para la cual se comparó el comportamiento ambiental del proceso empleando un catalizador ácido y un catalizador básico. La mejor configuración corresponde al proceso empleando un catalizador ácido. En el proceso ácido se generan menores impactos ambientales. De forma similar, ésta configuración tiene un mejor perfil económico ya que los costes asociados a la producción son menores y no se requiere ninguna unidad de pretratamiento, la cual es necesaria que en el proceso alcalino.

Mediante la herramienta desarrollada, la información inicial puede modificarse en cualquier momento con el fin de obtener los valores correspondientes a las nuevas condiciones. Uno de los aspectos más importantes es el que la herramienta se adapta fácilmente a cualquier proceso con el mínimo de variaciones. Las bases de datos que se incluyen en las hojas de cálculo pueden ser actualizadas por el usuario en cualquier momento o ajustarse a las necesidades específicas de cada proceso. Todo el análisis se lleva a cabo de forma automática, una vez introducida la información inicial del proceso e información económica.

La herramienta desarrollada es capaz de realizar la simulación, el diagnóstico ambiental, la evaluación económica y el análisis de sensibilidad, introduciendo las condiciones iniciales de operación del proceso.

Abstract

The design and the optimization of industrial processes are based on technical and economic aspects. However, the environmental aspects must be considered, both in the preliminary design of the process and as well as it is running.

The objective of this work is to develop a tool that integrates simulation, optimization, environmental assessment and sensitivity analysis aspects. To support this tool, a methodology consisting of five levels was established. These are: process simulation, Inventory, environmental impacts assessment, economic analysis and sensitivity analysis.

The developed methodology describes the variables related to the process (mass and energy inputs and outputs), as well as the impacts associated to each stages, the economic viability of the process (through the calculation of five economic indicators), and the process stages with the highest environmental impact (by means of the sensitivity analysis).

ASPEN Hysys® is the chosen software for the simulation of processes. The energy and mass flows involved in the process under study can be characterized by means of this software, introducing the initial operation conditions. The inventory, impact assessment and the economic analysis are automatically obtained in spreadsheets, by means of macros execution.

The inventory and the impacts assessment are performed following the Life Cycle methodology. Therefore, the environmental loads of the raw materials, electricity generation and utilities are considered. In order to generate the inventory, a data base was constructed; it contains the environmental information associated to industrial processes that are indirectly related to the process under study. Similarly, a data base with the characterization factors of the most important impact categories was included in the tool. This database comprises mid and end point categories, as well as diverse time horizons for selected categories.

The validation of the methodology and the developed tool has been accomplished by their application to three industrial processes: low density polyethylene (LDPE), ethylene oxide (EO) and biodiesel production. Different configurations have been evaluated for each process to determine the best option from the environmental and economic point of view.

For the LDPE process, the configuration change has focused in the origin of the electricity, which can be supplied by the Spanish National Network or a cogeneration unit. Based on our results, the best configuration corresponds to the process employing electricity by cogeneration, since steam is obtained as by-product and the emissions associated to the electricity generation are eliminated. These facts are reflected in an important reduction of the overall impacts associated to this process.

In the second analyzed process, referring to the production of ethylene oxide, four configurations have been evaluated: using air or oxygen as raw material and electricity from the Spanish Network or produced by cogeneration. Related to the origin of the electricity, using cogeneration, a better environmental profile is obtained. On the other hand, the oxygen as raw material is better than air due to the best yield of ethylene oxide in the reaction stage. Due to the better selectivity of the oxygen in the reaction, the costs of O_2 as raw material are compensated by high production.

Finally, the process evaluation of the biodiesel production has been carried out. In this case, an acid and a basic catalyst were compared. The best configuration corresponds to the process using an acid catalyst. In the acid process lower environmental impacts are generated. Furthermore, this configuration has a better economical profile since the costs associated to the production are smaller and a pre-treatment unit is not required, as in the alkaline process.

The initial information can be modified at any time to obtain the profile associated to the new conditions by means of the developed tool. Also, the tool can be adapted to any process in an easy way. The included database can be updated or adjusted by the user at any time to personalize them to the specific necessities of each process. Once the initial information is introduced, the analysis is executed automatically.

The developed tool is able to make the simulation, its environmental diagnosis, economic evaluation and the sensitivity analysis of any industrial process, introducing the initial operation conditions.

Resum

El disseny i l'optimització de processos industrials es basen en aspectes tècnics i econòmics. No obstant això, també han de considerar-se els aspectes ambientals, tant en el disseny preliminar del procés com quan aquest s'està portant a terme.

L'objectiu de la investigació és desenvolupar una eina que relacioni aspectes de simulació, optimització, avaluació ambiental i anàlisi de sensibilitat. Per a això es va establir una metodologia que consta de cinc nivells: Simulació de procés, Inventari, Avaluació d'impactes ambientals, anàlisi econòmica i anàlisi de sensibilitat.

La metodologia desenvolupada descriu les variables relacionades amb el procés (entrades i sortides de fluxos de matèria i energia), així com els impactes associats a cadascuna de les seves etapes, la viabilitat econòmica del procés (mitjançant la determinació de cinc indicadors econòmics), i identifica les etapes de procés amb el major impacte ambiental (mitjançant l'anàlisi de sensibilitat).

Per a la simulació de processos es va emprar el simulador ASPEN Hysys®. Mitjançant aquest programa, és possible obtenir la caracterització dels corrents de matèria i energia del procés industrial que s'estudia, introduint les condicions inicials d'operació del procés. L'inventari, l'avaluació d'impactes i l'anàlisi econòmica es porta a terme en fulls de càlcul de forma automàtica, mitjançant l'execució de macros.

L'obtenció de l'inventari i l'avaluació d'impactes es realitzen seguint la metodologia de cicle de vida, pel que es consideren les càrregues ambientals associades a les matèries primeres, la generació d'electricitat i utilitats. Per a obtenir l'inventari es va construir una base de dades que conté la informació ambiental associada a diversos processos industrials que es relacionen indirectament al procés sota estudi. Similarment, es va incloure una base de dades amb els factors de caracterització de les categories d'impacte més importants. Aquesta base de dades inclou categories mid i end point, diversos horitzons de temps.

La validació de la metodologia i de l'eina desenvolupada s'ha portat a terme mitjançant tres processos industrials: polietilè de baixa densitat (LDPE), òxid d'etilè (EO) i biodiesel. Per a cada procés s'han avaluat diferents configuracions per a poder determinar com d'elles és la millor opció des del punt de vista ambiental i econòmic.

En el cas del LDPE, el canvi de configuració s'ha enfocat en l'origen de l'electricitat, la qual pot ser provinent de la Xarxa Nacional Espanyola o d'una unitat de cogeneració. Els resultats indiquen que la millor configuració correspon al procés que empra electricitat provinent de la unitat de cogeneració, ja que en aquesta configuració s'obté vapor com subproducte i s'eviten les emissions associades a la generació d'electricitat, el que es reflecteix en una important reducció dels impactes associats a aquest procés.

En el segon procés analitzat, referent a la producció de óxid d'etilè, s'han avaluat quatre configuracions, emprant aire o oxigen com matèria primera i electricitat de la Xarxa Espanyola o produint-la mitjançant generació. En relació a l'origen de l'electricitat, a l'emprar la cogeneració, el comportament ambiental del procés millora considerablement. Quant a la importància de la matèria primera empleada (aire o oxigen), a l'emprar oxigen s'obté un millor rendiment en l'etapa de reacció, amb la qual cosa es compensa els costos associats a la matèria primera amb la productivitat del procés.

Finalment, s'ha portat a terme l'avaluació del procés de producció de biodiesel, per a la qual es va comparar el comportament ambiental del procés emprant un catalitzador àcid i un catalitzador bàsic. La millor configuració correspon al procés emprant un catalitzador àcid. En el procés àcid es generen menors impactes ambientals. De forma similar, aquesta configuració té un millor perfil econòmic ja que els costos associats a la producció són menors i no es requereix cap unitat de pretractament, la qual és necessària que en el procés alcalí.

Mitjançant l'eina desenvolupada, la informació inicial pot modificar-se en qualsevol moment amb la finalitat d'obtenir els valors corresponents a les noves condicions. Un dels aspectes més importants és el qual l'eina s'adapta fàcilment a qualsevol procés amb el mínim de variacions. Les bases de dades que s'inclouen en les fulls de càlcul poden ser actualitzades per l'usuari en qualsevol moment o ajustar-se a les necessitats específiques de cada procés. Tot l'anàlisi es porta a terme de forma automàtica, una vegada introduïda la informació inicial del procés i informació econòmica. L'eina desenvolupada és capaç de realitzar la simulació, el diagnòstic ambiental, l'avaluació econòmica i l'anàlisi de sensibilitat, introduint les condicions inicials d'operació del procés.

2. Introduction

In recent years, systems for processing environmental information have changed from research and development systems to practical applications. A broad range of uses in environmental protection is covered by these systems, including monitoring and control, conventional information management, computation and analysis, as well as planning and decision support. New disciplines are emerging, which combines research fields such as data base systems, modeling and simulation, user interfaces, knowledge processing, and systems integration (Radermacher et al., 1994).

The international agreements to decrease the pollutants emitted by industrial processes makes necessary to consider different alternatives of processes and products design. One of these alternatives refers to the identification and quantification of the impacts generated in the process. The achievement of this goal requires a multidisciplinary design team to evaluate simultaneously different aspects (Gradael, 2000).

Design methods in the development phases require diverse criteria and methods to characterize the environmental performance of different process alternatives for comparison and identification of critical process steps (Heinzle et al., 1998).

One of the most used methods for this purpose is the Life Cycle Assessment. LCA is a systematic approach to estimate environmental impacts associated with products, processes and services. It is described as a process to evaluate environmental burdens by identifying and quantifying energy and materials used and wastes released into the environment, and to identify and evaluate opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity covering extraction and processing of raw materials, manufacturing, transportation and distribution, use, recycle, and final disposal (Fava et al., 1999; EPA, 1995; Tucker, 2000).

LCA is generally designed to provide information on the environmental releases, burdens or impacts of the system under study in a general frame, including other non-environmental issues (Consoli, 1993). For this reason, the results of LCA must be interpreted in combination with social, economic and political considerations to enable more balanced decisions (Boustead, 1995). According to Huppes (1996), a current goal should be to "broaden the domain of application of LCA, aimed at optimization of decision-making, through integration of environmental decision support with non-environmental information". This is an important aspect in the industrial process design, because, the decision-making step would be based on the information generated by different perspectives, by the combination of environmental and non-environmental information, giving a most accurate idea about the system under study. This is derived from the fact that the design of a process plant requires the satisfaction of economic, environmental and social objectives (Alexander et al., 2000).

Previous studies evidenced the importance of the process modelling and environmental analysis tool integration, because, the results obtained in the process modeling could be used to carry out the application of the environmental analysis (Herrera et al., 2002). The idea of developing a tool which integrates environmental and economic information is not new in our group, previous work on establishing the base of such a tool being done by Herrera (2004). In his thesis he dealt with the theoretical issues of process analysis from environmental and economic points of view and thought of a way to put together the information. Due to use of specific economic or environmental software to assess the performance of a process, his method lacks from transparency and clarity of calculations. Therefore, based on his experience, in this work we propose a more complete methodology to assess environmentally and economically an industrial process. Furthermore, to avoid the errors introduced by the use of different pieces of software for performing each level of the methodology, this work proposes a unique tool that integrates environmental information from a process simulator with economic information calculated by the tool itself based on the information introduced by the user.

Thus, a methodology combining standard process simulation software with an environmental assessment methodology, and including economical and sensitivity analysis will be useful to evaluate several alternatives of any industrial process.

2.1. Hypothesis

2.1.1. General Hypothesis

The environmental profile of any intrustrial product could be evaluated, in an easy and practical way, by means of a methodology that integrates process simulation (e.g. ASPEN Hysys®), economical and environmental assessment tools, through the identification of all the variables, associated to the streams or process stages (separation, synthesis, purification). These variables are: used raw material, generated emissions or releases, energetic requirements, reaction yield, among others. This methodology would facilitate the obtention of environmental and economical information for any process, showing the results in a precise form to the industry.

2.1.2. Specific Hypothesis

Once the above-mentioned variables are identified, the necessary information about the process could be obtained (input/output streams process characterization, as mass fraction, total mass flow, temperature, pressure), allowing the implementation of new conditions or process stages with higher benefits, economical as well as environmental.

In addition to the environmental benefits, the process optimization including LCA will help to reduce the cost by means of the minimization and use of raw material and energy.

2.2. Objectives

2.2.1. General Objective

Development and description of a process analysis methodology to design a decision-making tool, based on environmental and economic criteria, starting from the process simulation step, and including a sensitivity analysis.

2.2.2. Specific Objectives

- Conception and description of the methodology stages.
- Construction of a tool to validate the methodology, integrating simulation and environmental assessment
- Creation of an environmental database, through the selection of the impact categories, models, receiving environment, and common sub-processes.
- Integration of economical aspects, including a general balance and the economical viability of the process.

- Incorporation of sensitivity analysis.
- Validation of each step by applying the tool to three different processes:
    - Low-density polyethylene process: to familiarize with the Life Cycle Assessment nomenclature.
    - Ethylene oxide process: validation of the simulation, environmental assessment and economical evaluation.
    - Biodiesel process: application of the methodology and the final tool.

3. Fundamentals

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3.1. Life Cycle Analysis (LCA)

LCA is an analytical environmental management tool used in decision-making to assess the environmental impact to determine the environmental burden of a product, process or activity over its entire life cycle, starting with raw material extraction and ending with final waste disposal (a cradle-to-grave assessment approach) (Chevalier and Meunier, 2005). LCA may be carried out under different conditions, but it is mostly based on a careful accounting of all energy and material flows associated within a system or a process (Khan et al., 2005).

The LCA basically consists of four steps shown in Figure 1 and outlined below:

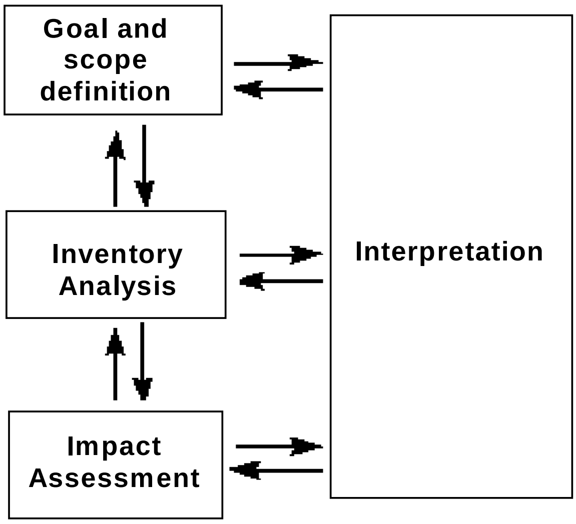

Figure 1 Life Cycle Analysis Methodology according to ISO 14040

3.1.1. Goal and scope definition

This is the decisive step to manage and coordinate a life-cycle study by getting together the LCA information needed to make a decision and an understanding of the reliability and representativeness of the LCA (Barnthouse et al., 1997). At the beginning of the LCA evaluation, the use of the results must be clearly identified. The scope describes the system under study and marks which information is necessary, in what categories, and the level of detail and quality (Curran, 2000).

One approach to boundary setting is the process-based model developed by the Society of Environmental Toxicology and Chemistry (SETAC) and the US Environmental Protection Agency (EPA) (Curran, 1997; Fava et al., 1993). This approach divides each product into individual process flows, identifying and quantifying environmental impacts.

In the goal and scope definition step, the process system boundary is defined to include processes from raw materials extraction, energy generation, and disposal, for a specific unit (for example: 1 MWh of electricity, 1 kg of product, etc.) As shown in Figure 2, this requires backtracking from the conventional process system. The definition of the process system boundary as an expanded “global” system has the main advantage of quantifying the input burdens with their respective route and the output emissions, forming an aggregated vector of the overall burdens of the process (Khan et al., 2005).

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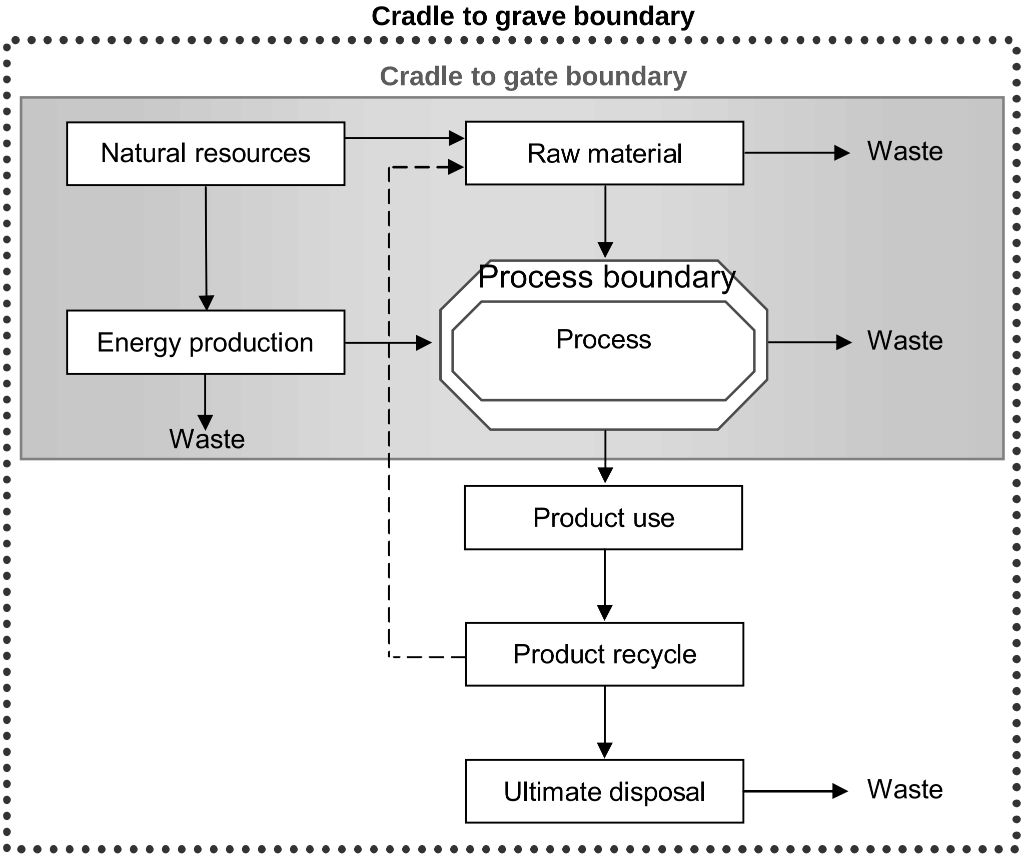


Figure 2.Definition of life cycle boundaries

3.1.2. Inventory analysis

The inventory is obtained through a flow diagram, describing the energy and material inputs, wastes and emissions data in order to associate them to a specific environmental load (EL) (EPA, 2001). This is accomplished by performing material and energy balances for each operation within the system and for the entire life cycle of the system. Inventory analysis has to be comprehensive in order to provide the necessary data to make the final decision (Stavros et al., 2003). All the assumptions and considerations must be clearly noted. Data quality varies depending on its source; therefore, extreme care must be taken to ensure that the used information is in the best available form and from updated sources.

All the environmental loads are assigned to each process stream and its corresponding balance by means of an eco-vector (e_v), which contains all the information about the contaminants (Castells et al., 1995; Sonneman, 2000). Generally, the vector is expressed in environmental load (kg of pollutant or environmental load) per functional unit (FU, kg of product or energy unit). Eq. 1 shows an ecovector in which the loads are grouped by type of environmental impacts.

$$e_v = \begin{bmatrix} \text{kg / FU or EL / FU} \\ \text{Raw material} \\ \text{Air emissions} \\ \text{Liquid discharges} \\ \text{other environmental loads} \end{bmatrix} \quad \text{Eq. 1}$$

From each part of the process, an eco-vector can be calculated, the total environmental impact is obtained adding them (Sonneman et al., 2003). Another approach to attain an environmental assessment consists of an analysis of the impacts related to each process. In order to express this method, the eco-vector has to be transformed into an eco- matrix E_M, in which there are M columns for M linear processes, and N rows for the N environmental loads represented in the eco-vector (Figure 3)

$$\begin{array}{ccccc} \text{Process 1} & \text{Process 2} & \text{Process 3} & h & \text{Process M} \\ e_{v1} = \begin{pmatrix} CO_2 \\ SO_2 \\ NH_3 \\ j \\ X_N \end{pmatrix} & e_{v2} = \begin{pmatrix} CO_2 \\ SO_2 \\ NH_3 \\ j \\ X_N \end{pmatrix} & e_{v3} = \begin{pmatrix} CO_2 \\ SO_2 \\ NH_3 \\ j \\ X_N \end{pmatrix} & i \; i & e_{vm} = \begin{pmatrix} CO_2 \\ SO_2 \\ NH_3 \\ j \\ X_N \end{pmatrix} \end{array}$$

$$E_M = \begin{pmatrix} CO_2 & CO_2 & CO_2 & i \; i & CO_2 \\ SO_2 & SO_2 & SO_2 & i \; i & SO_2 \\ NH_3 & NH_3 & NH_3 & i \; i & NH_3 \\ j & j & j & & j \\ X_N & X_N & X_N & i \; i & X_N \end{pmatrix}$$

Figure 3 Graphic representation of eco-matrix

The eco-matrix can be multiplied by another matrix (W_M, weighting or damage matrix), containing the fate analysis, the characterization factors or the final weighting. This matrix assigns to each process the damage indicator caused by one environmental load. There are N columns for the N environmental loads, and M rows for the M linear processes. In this way a new matrix is obtained, the weighted eco-matrix W_{EM} (Eq. 2)

$$W_{EM} = W_M * E_M \qquad \text{Eq. 2}$$

The matrix provides important information from the process and it is very useful to formulate different tools in a life cycle perspective.

3.1.3. Impact Assessment

This step examines the potential and real environmental and human health effects derived from the environmental loads assigned to the product, the use of resources (energy and materials) and environmental releases. Figure 4 presents the emissions or releases associated to an industrial process that need to be considered in the impact assessment step.

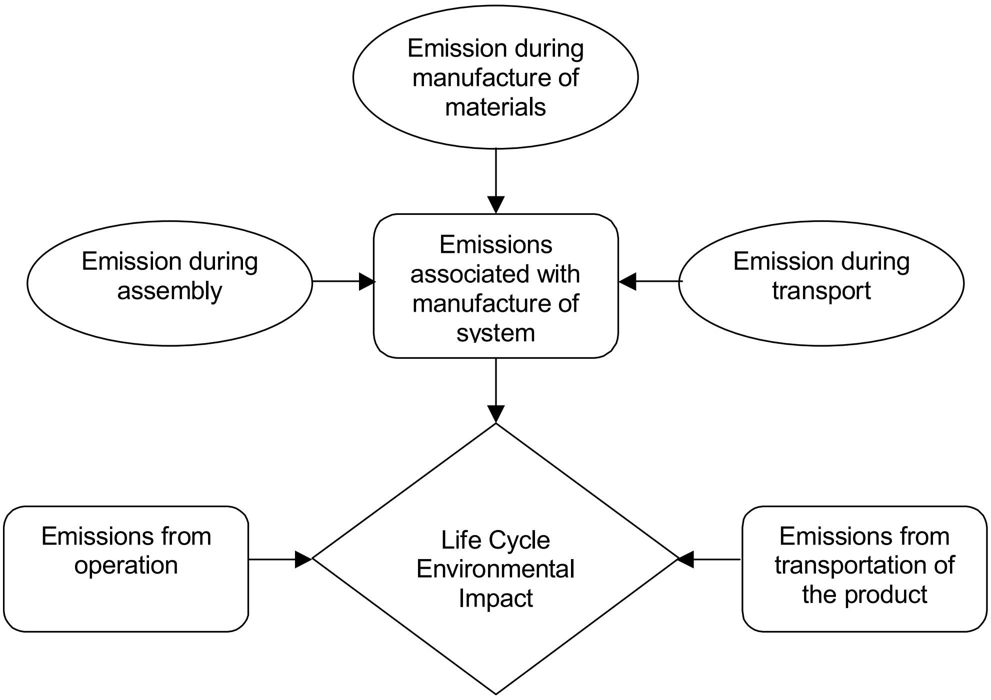


Figure 4 Impact Assessment in the LCA methodology adapted from Khan et al., 2005

A Life Cycle Impact Assessment (LCIA) is divided in two phases. The first one, classification, is the process of assignation and aggregation of the results from the inventory into impact categories (explained in more detail below). The characterization (second phase) assesses the magnitude of the impact for each category to facilitate the conversion of the inventory analysis data into category indicator (Bovea and Gallardo, 2006).

3.1.4. Interpretation and Improvement assessment

Finally, according to ISO 14040 (Figure 1), the results of the inventory analysis and impact assessment are combined for evaluation. In addition to the environmental impacts assessment, this step also identifies areas where impacts could be reduced and compares with other processes offering a similar utility.

3.2. Life Cycle Impact Assessment (LCIA)

One of the most important concepts in impact assessment is the impact category. The environmental mechanism of each category takes into consideration all physical processes and variables starting from extractions, emissions or other types of interaction between the system and the environment, which are related to a given impact category (ISO 14042, 1998). In that way, several environmental processes constitute the environmental mechanism, which is related to the following concepts:

- *Environmental inputs and outputs*, these are the particular extractions from or emissions into the environment and other variables at the boundary of the product system and the environment;
- *Category midpoints,* variables in the environmental mechanism of an impact category between the environmental interventions and the category endpoints;
- *Category endpoints or damage level*, variables which are directly related to the society, such as human life span or incidence of illnesses, natural resources, valuable ecosystems or species, fossil fuels and mineral ores, monuments and landscapes, man-made materials, etc.
- *Areas of protection*, classes of endpoints which have some recognizable value for society, four areas of protection can be distinguished: human

health, natural resources, natural environment and man-made environment (ISO/DIS 14042, SETAC).

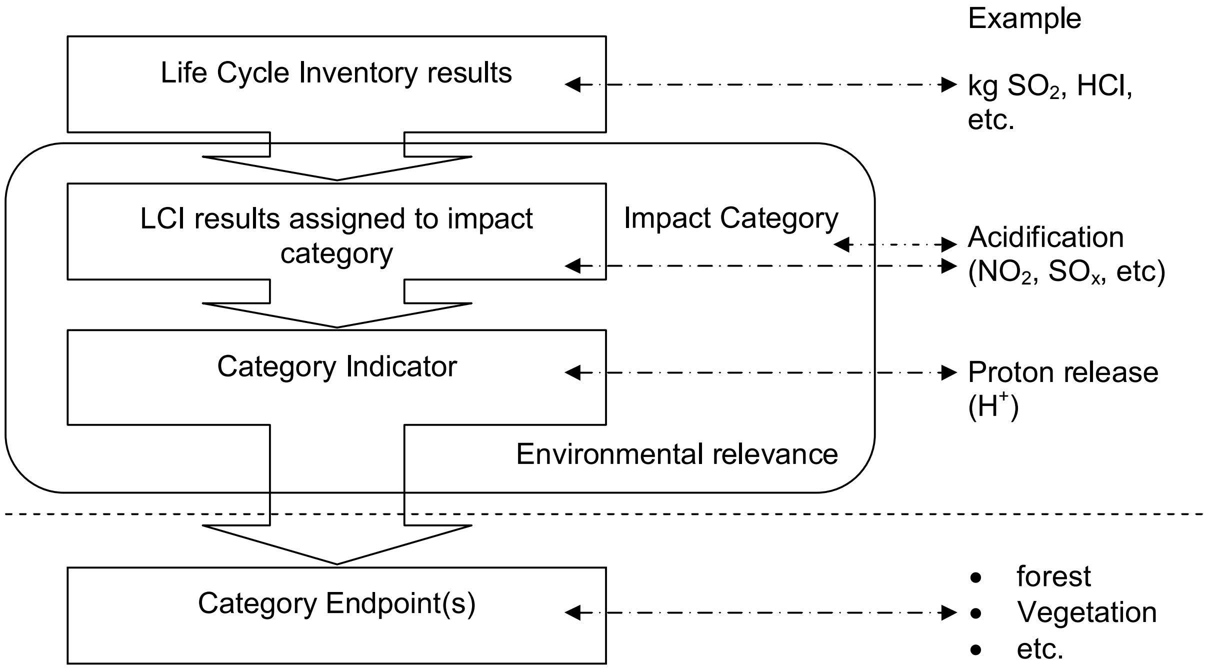


Figure 5 Concept of indicators (ISO 14042)

Given the total environmental mechanism, a category indicator can be identified, and correspond to a quantifiable representation of an impact category. In order to categorize the impact categories, several methods are followed. These methods can be problem-oriented (midpoints) or damage-oriented (endpoints). This work is focused in three impact assessment methods: CML, Eco-indicator 99 and IMPACT 2002+.

The CML method was developed in 1992 by the Center of Environmental Science of the Leiden University (Heijungs et al., 1992). In 2001, CML published a new “operational guide to the ISO standards”.This method summarizes the LCI results into a set of environmental impact categories, which describes the environmental profile of the analyzed product or process, employing the problem-oriented (midpoint) approach covering all emission- and resource-related impacts, for which practical and acceptable characterization methods are available. The different ISO elements and requirements are made operational to be `best available practice' for each step. For most impact categories a baseline and a number of alternative characterization methods is recommended and for these methods comprehensive lists of characterization and also normalization factors are supplied (Guinée et al., 2002).

The EcoIndicator is a damage-oriented method developed in 1995 (Goedkoop, 1995). The steps of life cycle inventory analysis and life cycle impact assessment are based on the CML method. An idea in this method is the consistent management of subjective choices using the concept of cultural perspectives: Egalitarian, Individualist and the Hierarchist. This method considers that the valuation of the emissions or the effects on an environmental theme is the most controversial step in a LCA procedure (Goedkoop et al., 2000).

The IMPACT 2002+ method was developed by the Industrial Ecology & Life Cycle Systems Group (GECOS) in the Swiss Federal Institute of Technology Lausanne (EPFL). This method proposes an implementation of a combined midpoint/endpoint approach. For IMPACT 2002+ new concepts and methods have been developed, especially for the comparative assessment of human toxicity and eco-toxicity. Some midpoint categories are adapted from existing characterizing methods (Eco-indicator 99 and CML) (Jolliet et al., 2003).

3.2.1. Life Cycle Impact Assessment steps

In order to obtain an LCIA, several steps have to be followed to convert the inventory results into indicators results. These steps are:

1. Selection and Definition of Impact Categories - identifying relevant environmental impact categories (e.g., global warming, acidification, terrestrial toxicity).
2. Classification - assigning LCI results to the impact categories (e.g., classifying CO_2 emissions to global warming).
3. Characterization - modeling LCI impacts within impact categories using science-based conversion factors. (e.g., modeling the potential impact of CO_2 and methane on global warming).
4. Normalization - expressing potential impacts in ways that can be compared (e.g. comparing the global warming impact of CO_2 and methane for the two options).
5. Grouping - sorting or ranking the indicators (e.g. sorting the indicators by location: local, regional, and global).
6. Weighting - emphasizing the most important potential impacts.
7. Evaluating and reporting LCIA results - gaining a better understanding of the reliability of the LCIA results.

The International Organization of Standardization (ISO) developed a standard for conducting an impact assessment entitled ISO 14042, Life Cycle Impact Assessment, which states that steps 1, 2, 3 and 7 are obligatory for an LCIA. The other steps are optional depending on the goal and scope of the study.

3.2.1.1. Selection and definition of Impact Categories

This step should be completed as part of the initial goal and scope definition phase to guide the LCI data collection process and requires reconsideration following the data collection phase.

For a LCIA, impacts are defined as the consequences caused by the input and output streams of a system on human health, plants and animals, or the future availability of natural resources. A description of the most significant impact categories is presented in section 4.3. In this step, the relevant impact categories ought to be identified. The CML method provides a list of impact assessment categories, sorted by their significance in a LCA, in order to facilitate their classification. Each group considers several impact categories, detailed in Table 1. These impact categories groups are sorted in three sets:

- Group A: Baseline impact categories, comprise the categories used in most LCA studies,
- Group B: Study-specific impact categories, comprises categories that may merit inclusion, depending the goal and scope of the LCA study and whether appropriate data are available,
- Group C: Other impact categories, comprises several categories for which alternative characterization methods may be available.

Table 1 Impact Categories groups proposed in the CML method

Group	Impact category	
A. Baseline	Depletion of abiotic resources	
	Impact of land use	
		Land competition
	Climate change	
	Stratospheric ozone depletion	
	Human Toxicity	
	Ecotoxicity	
		Freshwater aquatic ecotoxicity
		Marine aquatic ecotoxicity
		Terrestrial ecotoxicity
	Photo-oxidant formation	
	Acidification	
	Eutrophication	
B. Study-specific	Impacts of land use	
		Loss of life support function
		Loss of biodiversity
	Ecotoxicity	
		Freshwater sediment ecotoxicity
		Marine sediment ecotoxicity
	Impacts of ionising radiation	
	Odour	
		Malodourous air
	Noise	
	Waste heat	
	Casualities	
C. Other	Depletion of biotic resources	
	Desiccation	
	Odour	
		Malodourous water

3.2.1.2. Classification

The main goal of this step is the organization and combination of the Life Cycle Inventory results in order to evaluate the impact categories. For LCI items that only contribute to one impact category, the procedure is an easy assignment. A rule is established for classification if the item contributes to more than one impact category. In this case, there are two ways:

- When the effects are independent of each other, all LCI results are assigned to all impact categories to which they contribute.
- The allocation of a representative portion of the LCI results to the correspondent impact categories contribution, allowed when the effects depend on each other. The allocation proportionally distributes the environmental burdens, such as resource depletion, emissions to air and water and solid waste, to each functional input or output of a multiple-function system. The most common method is to allocate on the basis of mass, but allocation based on other properties such as volume, energy content, number of moles, or economic value may also be used (ISO 14042, 1998).

According to Ekvall and Finnveden (2001), the allocation of environmental burdens can be applicable to three types of multiple-function systems:

- Multiple-input systems (waste treatment processes),
- Multiple-output systems (co-production), and
- Multiple-use or “cascaded use” systems (“open-loop recycling”).

In multiple-input systems, a number of different materials are treated in the same system. These input materials have different composition and therefore properties which determine the total environmental burdens from the system. The main problem in these systems is to allocate the burdens between different inputs into the system. Similar problems occur in multiple-output systems, which produce more than one functional output. The problem of allocation is to find a procedure to assign to each product only those environmental burdens which each product generates. The last type, the multiple-use system, is even more complicated, because the products can be reprocessed and reused in other systems; in LCA, this is termed “open-loop recycling”. (Azapig et al., 1999).

3.2.1.3. Characterization

This step provides a way to directly compare the LCI results within each impact category. The total environmental interventions in an impact category are shown in the units of the category indicator (i.e. kg_{eq} of CO_2 in the Global Potential Warming). This total is obtained by multiplying each environmental intervention by a value called characterization factor or equivalency factors (Eq. 3), used to convert the LCI results into representative indicators of impacts to human and ecological health. In other words, characterization factors translate different inventory outputs into directly comparable impact indicators.

$$\text{Impact category indicator}_i = \sum_j \left(e_j \text{ or } r_j\right) * CF_{i,j} \qquad \text{Eq. 3}$$

where:

Impact category indicator$_i$ - indicator value per functional unit for impact category *i;*

e_j or r_j - release of emission *j* or consumption of resource *j* per functional unit,

$CF_{i,j}$ - characterization factor for emission *j* in category *i*.

The use of the appropriate characterization factor is fundamental in the impact characterization. The source of each characterization factor is documented in the LCIA step, to ensure that they are relevant to the goal and scope of the study.

3.2.1.4. Normalization

LCIA tool is used to express impact indicator data in a way that can be compared among impact categories, dividing the indicator results by a selected reference value. The goal and scope of the LCA may influence the choice of an appropriate reference value. Normalized data can only be compared within an impact category (ISO, 2000). There are numerous methods of selecting a reference value:

- Total emissions or resource use for a given area that may be global, regional or local.
- Total emissions or resource use for a given area on a per capita basis.
- The ratio of two alternatives.
- The highest value among all options.

3.2.1.5. Grouping

The assignation of the impact categories into one or more sets is performed in this step, in order to facilitate the interpretation of the results into specific areas of concern. Typically grouping involves sorting or ranking indicators. The following are two possible ways to group LCIA data (ISO 14042, 1998):

- Sorting of indicators by characteristics such as emissions or location.
- Sorting of indicators by a ranking system, such as high, low, or medium priority.

3.2.1.6. Weighting

Also referred as valuation step, it assigns weights or relative values to the different impact categories based on their importance or relevance. Weighted data could be combined across impact categories, but the weighting procedure has to be explicitly referenced. In general, weighting includes the following activities (Soares et al., 2005):

- Identifying the underlying values of stakeholders.
- Determining weights to place on impacts.
- Applying weights to impact indicators.

3.2.1.7. Evaluation and documentation of the results

Once the impact potential for each category has been calculated, it is necessary to confirm the results. This step checks the accuracy of the results and verifies if the goal and scope have been achieved. All the assumptions considered in the analysis and the methodology followed must be described in the results. At this level, several premises are took into account, in order to make a better analysis of the results, such as: space considered in the analysis (an industry, a city, a country, etc.), time (days, months, years, etc.), compounds groups (VOC, metals, etc.), among others.

This work is aims at in the evaluation of any type of industrial processes. All the compounds groups are considered at the beginning of the assessment step, depending on the elements associated in the process under study the groups could be reduced. Following the ISO standard, the four mandatory steps are considered in this work. Normalization, grouping and weighting are not considered in the developed methodology.

3.3. Economical Analysis

Engineers and technicians need tools to take economic decisions. These tools can be applied to independent project to determine if it is possible or not to invest, or they can be applied to several projects in order to determine which one should be implemented (Biezma and Cristóbal, 2004).

Several evaluation methods and techniques provide the investor with valuable tools for determining which projects can be accepted or rejected. The typical steps of an economic evaluation of a project are (Au and Au, 1992; Canada and Sullivan, 1989; Newman, 1991):

- Define a set of investment projects to considerate.
- Establish the analysis period for economic study.
- Estimate the cash flow profile for each project.
- Specify the minimum attractive rate of return.
- Examine the objective and establish criteria to measure effectiveness.
- Apply the project evaluation technique(s).
- Compare each project proposal for preliminary acceptance or rejection.
- Accept or reject a proposal on the basis of the established criteria.

In order to obtain a project evaluation, many different techniques are used. The most common methods, from the industrial point of view, are the Net Present Value (NPV), the Rate of Return, and Payback period (PP).

3.3.1. Net present value method

This method can be divided into four time analysis periods: present worth method, future worth method, annual worth method, and capitalized worth method (Park, 1993).

The present worth method examines the cash flows of a project over a given time period and solves them to an equivalent present date cash flow through the use of economic factors (Newman, 1991; Park and Sharp-Bette, 1990).

The future worth method, determines the present consequences of an investment, solving the cash flows to one equivalent at a future date, in order to determine the present consequences of an investment. This method is also known as the future value method (Grant et al., 1990), future worth analysis (Newman, 1991), or future worth-cost (Canada and White, 1980). The annual worth method examines the cash flows of a project, but does not solve them to a cash flow at one date; it solves all cash flows to an equivalent series of equal, usually annual cash flows over a specified number of years in any analysis period. Finally, the capitalized worth method is an annual worth method evaluated over an infinite time period from any starting date (Park, 1993).

In any of these economical methods all cash flows are reinvested at the same fixed rate used to calculate the equivalent worth: rate of return, that is the rate used in the economic factors. Only one method is needed to judge the profitability of a project, since they use the same economic factors; they yield the same results when used to evaluate a project. Therefore, only one of the four methods is needed to judge the profitability of a project. Thus, the use of the term net present value encompasses all of the equivalent methods. In general, a project is accepted if the NPV is positive and rejected if it is negative. (Blank and Tarquin, 2005; Jelen and Black, 1983).

3.3.2. Rate of return methods

The rate of return methods includes three subtopics: internal rate of return (IRR), external rate of return (ERR), and growth rate of return (GRR). To apply these methods, a positive present worth is necessary. A project is selected if its rate of return is higher than the minimum attractive rate of return (Blank and Tarquin, 2005).

The first one, the IRR is the rate of interest that equates the NPV of the cash flow payments to zero. The external or modified rate of return (MIIR) is a variation of the internal rate of return method; it assumes that all cash flows are reinvested at another rate (Canada and White, 1980).

Finally, the GRR method determines a rate of return at any moment during the life of the project. Specify a year is necessary to apply this method, and two cash flows are calculated; one represents the present worth for the period previous to the selected year. The second corresponds to the value of the following years (Remer and Nieto, 1995).

3.3.3. Payback period method

Two variations of the payback methods are considered, the payback period (PP), and the project balance (PB). Like in the previous methods, a positive NPV is indispensable to apply any of these methods.

The PP method evaluates the number of years required for project investment recovery (Blank and Tarquin, 2005). The procedure to evaluate this method is similar to the used in the internal rate of return calculation. The differences are: the unknown variable is the time, not the rate of interest, and all future cash flows do not need to be considered. Two types of PP method are used, the conventional and the discounted. The first one assumes an interest of 100%, the discounted PP method usually uses the minimum attractive rate of return. Generally, the project with the lowest PP is preferred when more than one project are evaluated (Au and Au, 1992). The main advantage of this method is that it determines the risk of a project based in the length of the PP, making easier the understanding by people without economics background (Jelen and Black, 1983).

The second variation, PB method, calculates the future worth of cash flows at every time period using the minimum attractive rate of return. This method determines the amount of positive or negative total receipts at the end of each period (Remer and Nieto, 1995).

Five economic indicators are considered in the proposed methodology in order to determine the viability of the industrial process under study. These indicators are: Net Present Value, Internal Rate of Return, Modified Internal Rate of Return, Payback Period and Discounted Payback period.

3.4. Tools integration in environmental assessment field

According to Jones (1999), environmental assessment has four objectives: preserving natural resources, minimizing or eliminating pollution, reducing waste generation and saving energy. These aspects have environmental and commercial sense, however new tools have to be developed to show their economical benefits in an easy and practical way.

Environmental simulation is one of these, and can be used to evaluate environmental implications of new policies or specific measurements before the implementation; at same time can be useful for decision-making to determine about handling resources, urban or regional development, and waste or pollution administration, among others.

Environmental simulation is a technology used to study the effects of process or activities on the environment and vice versa. It can predict the consequences of various choices and analyze the impact of one decision over another. The main information obtained from an environmental simulation model includes (Fatta and Moll, 2003):

- Waste generation from production process, products use, urban or regional development, specific policies of implementation;
- Environmental impacts originated by waste generation and their contribution to global environmental problems (acid rain, global warming, etc.)
- Evaluation of alternative scenarios in terms of their environmental, economic and social impacts;
- Costs and benefits, both environmental and economic for the implementation of a project;
- Optimal level of recycling, compost, incineration, etc.

Benefits and restrictions can be mentioned using these models. Some benefits are the capacity to show the current situation and to estimate the future one, link the economy and the environmental, geographical flexibility, evaluation of several scenarios permitting to find the best solution.

As limitations can be mentioned: inconveniences related to compilation of information (e.g. required a big amount of data, availability, format, etc.), adjustment and constant modifications are necessary, there cannot be considered all the parameters, use of software is generally required, etc.

Some methods developed in several research groups have been reviewed to know the current situation on environmental simulation, a brief description is presented below.

3.4.1. GEM-E3 model

The General Equilibrium Model for Energy-Economy-Environment is a model developed by a consortium involving National Technical University of Athens, the Catholic University of Leuven, University Mannheim and the Centre for European Economic Research.

This model considers the interactions between the economy, the energetic systems and the environmental, determining the optimum balance for energy and emissions. It includes some modules focused in diverse aspects as environment, market imperfections, and engineering representation of energy, among others.

Focusing on the environmental module, the main goal is to represent the effect of the environmental policy in the regional economy and on the state of the environment. The inclusion of the environmental module is with the purpose of improving the analysis in the following directions:

- Integrated analysis of environmental and energy objectives on a European scale;
- Representation of a set of environmental policy instruments at different levels: standards, taxes, tradable permits, international, national;
- Integrated analysis of different environmental problems: simultaneous analysis of impact categories;
- Comparative evaluation of source and receptor oriented.

The environmental part makes a cost-effectiveness and cost-benefit analysis and can be used as an assessment of policy tool (NTUA, 1997).

3.4.2. European Environment Agency (EEA) model

It is focused in the waste generation in the EU, estimating future trends. This model considers municipal waste, glass and paper waste, end-of-life vehicles, using assumptions and equations to relate residues generation with the most important economic activities. These equations consider the raw material consumption that generates waste, and they have coefficients to relate waste to economic parameters (EEA, 1999).

The required information necessary to estimate the coefficients and use the equations includes:

- Private consumption, disaggregated into the relevant consumer expenditure items;
- Waste generation (household/municipal, glass, paper, cardboard);
- Future trends on private consumption, disaggregated into the relevant consumer expenditure items;
- Gross domestic product by kind of activity;
- Other macroeconomic parameters (exchange rate, population, etc.).

A different approach is taken for end-of-life vehicles. The required information to make the projections includes the car fleet, an initial age distribution and a calculated life-time function describing the probability of finding a car of a certain age on the market (EEA, 1999).

3.4.3. STOAT model

The Sewage Treatment and Operation over Time is a computerized model developed by the European Topic Centre on Water. This model simulates in a dynamic way the wastewater treatment and sewage production from an industrial perspective. The software can be used to simulate individual treatment processes or the whole treatment plants, including sludge treatment processes, septic tank imports and recycles. It allows the user to optimize the processes in terms of sludge and effluent quality, efficiency of treatment plants design and operation, risk minimization and costs. The user is able to calculate the sewage sludge production and quality for different wastewater treatment processes and evaluate and assess the response of multiple changes with respect to the influent loads, works capacity or process operating conditions, etc. The STOAT model is capable of comparing the performance of alternative scenarios and determining the best one for wastewater management in terms of sludge production or effluent quality or the most efficient technique for sludge management. Through the alternative scenarios evaluation, it is possible to make future predictions regarding, among others, the sludge production, quality and treatment (Stokes et al., 1997; WRc plc, 1990)

3.4.4. MARKAL model

The IEA-Markal model was developed by Brookhaven Laboratory and Kernforschunganlage under the support of the International Energy Agency. MARKAL, acronym for MARKet ALlocation, is a model used for energy and material systems analysis, representing the economy of a region and modeling the processes and the monetary, energy and material flows between them, during the generation of a product. This model shows the associated environmental impact related to all of these flows. The most important aspect in this model is that their basic components are specific types of energy and emission control technologies, represented by a set of performance and cost characteristics (Gielen et al., 1998; Seebregts et al., 2001).

This model can be used to determine the optimum configuration system, considering energy, materials and products demand, with the minimum environmental and economical cost. It provides a comprehensive methodology to decide the most efficient waste-management strategies, which promote energy and material recovery and reduce the environmental impacts of waste-management processes (Seebregts et al., 2001).

The methods described above perform environmental evaluations, considering environmental, economic and optimization aspects, but they are limited to specific products. Therefore, a methodology able to analyze any industrial process will be useful. This work was focus on this aspect; a methodology and a tool were created in order to obtain a complete analysis of any process.

3.5. Process Simulation

The process simulation is a tool used to reproduce in a detailed and accurate way the behavior of processes for its analysis and optimization. The simulations perform the energy and mass balance, predicting operation conditions and stream compositions of the process. Since the results obtained in the simulation are predictions, it is necessary to validate them with experimental data. The process simulation considers the following aspects:

- Definition of thermodynamic and physico-chemical properties
- Description of the involved compounds, reactions and equipment
- Specification of the product or products
- Description of the process by a flow chart

- Equipment sizing

3.5.1. ASPEN Hysys® process simulator

ASPEN Hysys® is a user-friendly computer software package developed by Aspentech. It is a process modeling tool for steady state simulation, design, performance monitoring, and optimization of industrial processes. The package combines comprehensive data regression, thermodynamic database access to enable the design and analysis of systems (Aspen Technology, 2005).

An interactive simulation of industrial processes can be created using this tool. It ensures accurate calculation of physical properties, transport properties, and phase behavior; and contains an extensive component database with the ability to add user components. Also, Aspen HYSYS® provides a graphical representation of the process flow sheet that describes the mass and energy streams, and the equipment associated to the simulated process.

This software can be connected to Microsoft Excel by programming in Visual Basic. This link allows the integration of the process simulator results with other data concerned to the process, i. e. economical or environmental information.

4. Methodology

A methodology has been developed to obtain an overall analysis, including simulation, environmental and economic aspects of any industrial process. In order to reach this evaluation, five levels described in Figure 6 must be accomplished, these are:

- Level I: Process Simulation
- Level II: Inventory
- Level III: Impact Assessment
- Level IV: Economical Analysis
- Level V: Sensitivity Analysis

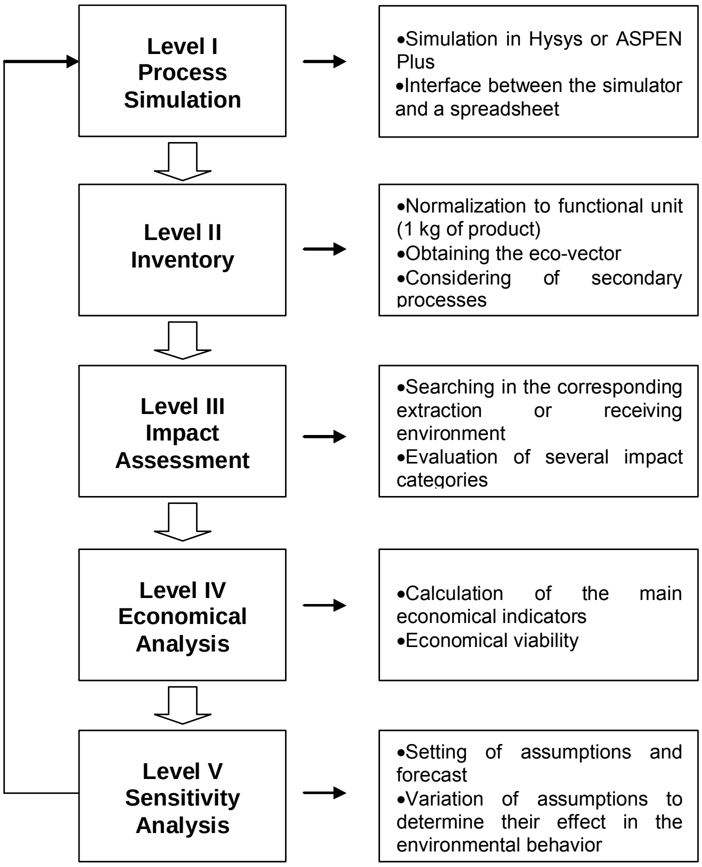


Figure 6 Methodology diagram

4.1. Level I: Process Simulation

Process simulation is known as the modelization of a process plant by means of a set of algorithms to determine the operation conditions and to characterize the output streams as a function of input variables. Once the validity of a model is tested, it can be used to predict or simulate the plant operation under other working variables.

Process simulation is usually done by the assistance of appropriate software. We have chosen the ASPEN Hysys® simulator for modeling the case studies (Chapter 5).

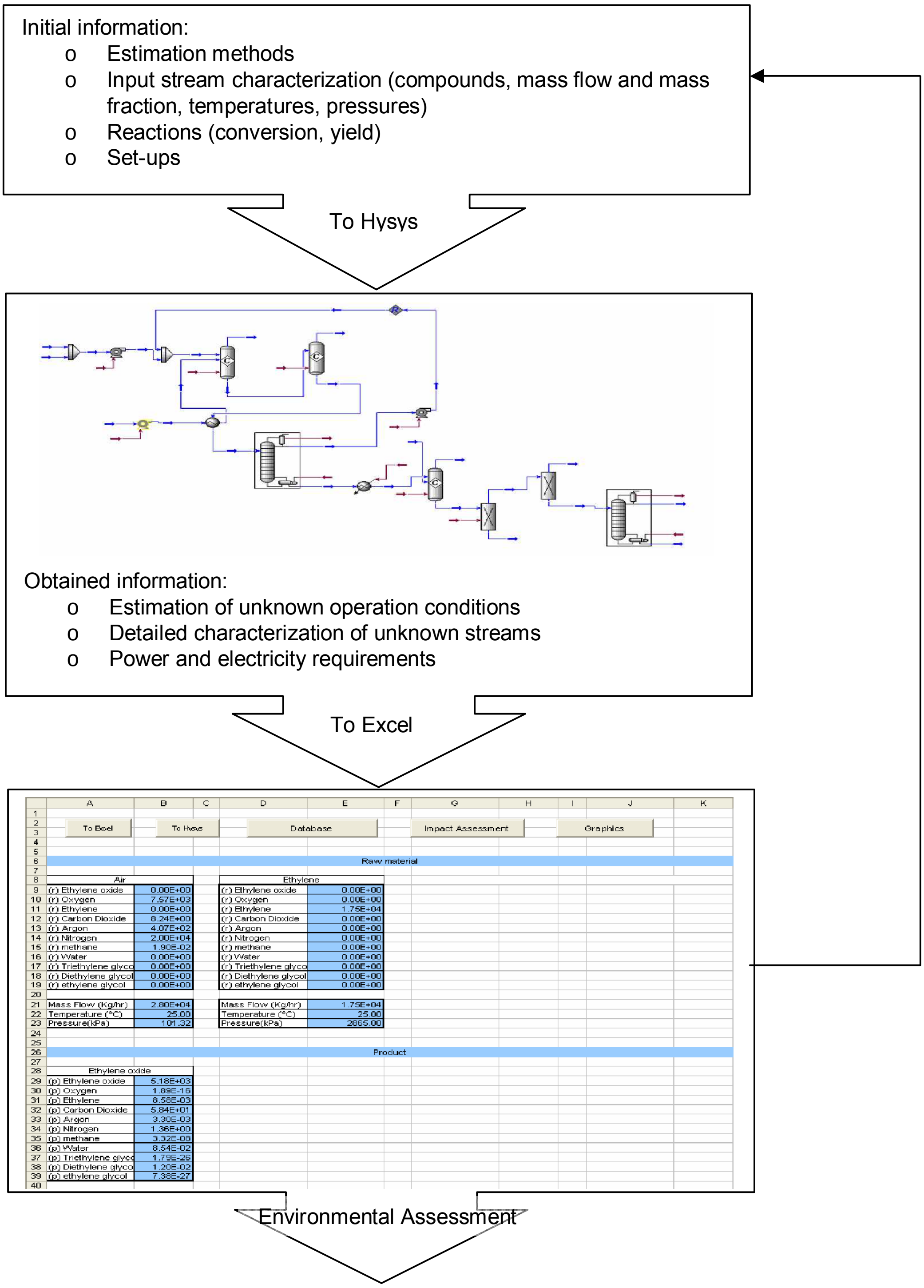
The design of a process is performed in this step, and it includes the development of specifications, synthesis, analysis, construction, tests and evaluation of the selected process. The design is based on the definition of the following aspects:

- Initial information: definition of units (SI, metric), properties (estimation methods, state equations), and compounds.
- Definition of the process type (batch or continuous)
- Description of inputs and outputs: stream characterization (temperature, pressure, composition, mass flow, etc.).
- Energetic requirements.
- Recycles or sub-products.
- System description: separation, reaction or heating systems.
- Construction of process flow diagram (PFD)

All these aspects are introduced in the ASPEN Hysys® simulator to obtain a complete characterization of a process, and thus, all the necessary information to achieve an evaluation is generated (unknown mass and energy streams, required equipment, reaction profile, etc.). The information can be sent from the simulator to the worksheet "Hysys" in Excel® or in the inverse way by using an interface developed in Visual Basic.

Visual Basic was used for programming the automatically linked spreadsheet that imports and exports process data between ASPEN Hysys® model and Microsoft® Excel. In Figure 7 is presented a scheme of the information flow between ASPEN Hysys® simulator and Excel worksheet *"Hysys"*. The worksheet was automatically linked to a running ASPEN HYSYS® simulation case with two different functions:

- The macro reads all the necessary flowsheet data from a running ASPEN Hysys® application and updates the active Excel worksheet. The following data is retrieved: mass flow, temperatures, pressures, compositions of the streams (mass flow fractions), and energy requirements.
- To read data from Excel and update ASPEN Hysys® simulation case, the same data than the previous function can be updated in the simulator, whenever the information have been introduced by the user. ASPEN Hysys® do not allow to change information from Excel to the simulator when the value was previously calculated in the simulator.



Raw material

Air		Ethylene	
(r) Ethylene oxide	0.00E+00	(r) Ethylene oxide	0.00E+00
(r) Oxygen	7.57E+03	(r) Oxygen	0.00E+00
(r) Ethylene	0.00E+00	(r) Ethylene	1.75E+04
(r) Carbon Dioxide	8.24E+00	(r) Carbon Dioxide	0.00E+00
(r) Argon	4.07E+02	(r) Argon	0.00E+00
(r) Nitrogen	2.00E+04	(r) Nitrogen	0.00E+00
(r) methane	1.90E-02	(r) methane	0.00E+00
(r) Water	0.00E+00	(r) Water	0.00E+00
(r) Triethylene glyco	0.00E+00	(r) Triethylene glyco	0.00E+00
(r) Diethylene glycol	0.00E+00	(r) Diethylene glycol	0.00E+00
(r) ethylene glycol	0.00E+00	(r) ethylene glycol	0.00E+00
Mass Flow (Kg/hr)	2.80E+04	Mass Flow (Kg/hr)	1.75E+04
Temperature (°C)	25.00	Temperature (°C)	25.00
Pressure(kPa)	101.32	Pressure(kPa)	2865.00

Product

Ethylene oxide	
(p) Ethylene oxide	5.18E+03
(p) Oxygen	1.89E-16
(p) Ethylene	8.58E-03
(p) Carbon Dioxide	5.84E+01
(p) Argon	3.30E-03
(p) Nitrogen	1.36E+00
(p) methane	3.32E-08
(p) Water	8.54E-02
(p) Triethylene glyco	1.79E-26
(p) Diethylene glyco	1.20E-02
(p) ethylene glycol	7.38E-27

Figure 7 ASPEN Hysys® and Excel connection diagram

All the assumptions ought to be documented and considered in the overall analysis, since the final results are strongly related to this level.

To execute a process simulated in ASPEN Hysys® in our methodology, it will be necessary to copy the corresponding code segment in Visual Basic, change the item name and the destiny cell in Excel®. This procedure reduces programming problems and makes easy the information transfer.

The structure of the developed code was adapted from Kulay, et al 2003. The basic programming code is presented in Annex I. The data transfer of a new process can be performed copying the basic code, changing the names and the parameters like number of compounds, cells number to write the information, stream name, etc.

The information displacement from Excel® to ASPEN Hysys® must be carried out regarding the configuration and units used in the original worksheet due to the developed macros, if the format is changed, the code should be modified.

Some processes cannot be simulated; in this case, it is possible to write the process information directly in Excel. The next levels of the proposed methodology can be executed without any modification to the worksheets.

Once the information is sent to Excel® in the worksheet *"Hysys"*, the user should write the components names by it selection from the included list, because the simulator only transfers the numeric information of the stream characterization, but it is not possible to write the components names, thus, the user should complete these data.

The information showed in the *"Hysys"* worksheet is the characterization of the raw material streams, product and by-product streams, emission and releases, energy streams (as energy or electricity). Also, information related to the product or raw material transportation can be written in this part.

The process simulated in ASPEN Hysys® is defined as the *"primary process"*, since the functional unit is modeled there. Following the LCA approach, in the considered process, there are several inputs streams; each one of them is a product of their respective manufacturing process. We call them "secondary processes", and they correspond to the raw material production, electricity generation, and utilities, among others

4.2. Level II: Inventory

At this step, an ecovector (Eq. 1) is assigned to each mass or energy input stream. As it was previously described (see section 3.1.2), it is possible to calculate the ecovector associated to the functional unit (1 kg of product), by an environmental load balance. A programming code in Visual Basic was developed in order to automatically generate the inventory associated to the process under study (this code is not included in this thesis).

In this work, several *"secondary processes"* are incorporated to the worksheet database, with a detailed description of the emissions, liquid and solid releases. The secondary processes considered in the case studies analyzed in this work are:

- Natural gas production,
- Sodium hydroxide production,
- Methanol production,
- Ethylene production,

- Sulphuric acid production,
- Electricity generation in Spain,
- Calcium Oxide production,
- Glycerol production,
- Steam production,
- Deionized water

Only these were included in the Excel® file used to validate the developed tool. A list of secondary processes incorporated in the final version of the software is presented in Annex II.

The *"secondary processes"* are selected from a list and added trough the button *"Database"*; the program search the raw material associated to the process, depending on the information displayed in the worksheet *"Hysys"*, and the related compounds are integrated to the inventory.

Any other process can be added at any time; just it is necessary to use the same format than in the other *"secondary processes"* worksheet to facilitate the automatic search. The substances are designated by their names preceded by an (a), (w), and (s) respectively, and corresponding to emissions to air, releases to water and solid wastes (Figure 8). The raw material is indicated with a (r) before the correspondent name. It is important to remark that in the sub processes database, just one raw material is possible for each *"secondary process"* worksheet. The substances associated to natural resources and landscape are specified by their names preceded by an (o). The compounds are identified by name, due to the "*compounds groups*" (as VOC), do not have an associated identification number (as CAS).

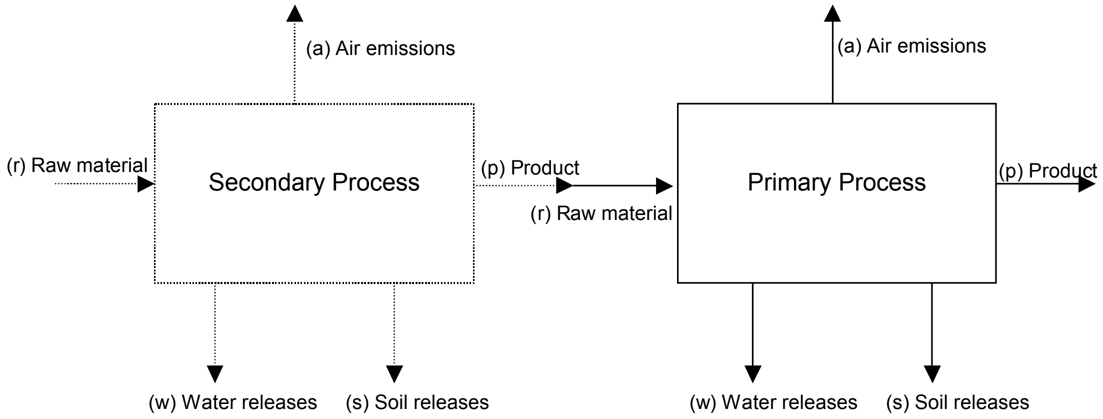


Figure 8 Stream designation in secondary and primary processes

Thus, based in LCA, the final inventory describes the compounds referred to the simulation (*Hysys* worksheet), and also specifies the emissions, releases, raw material use, natural resources and energy consumption related in an indirect way to the process (see section 3.1.2)

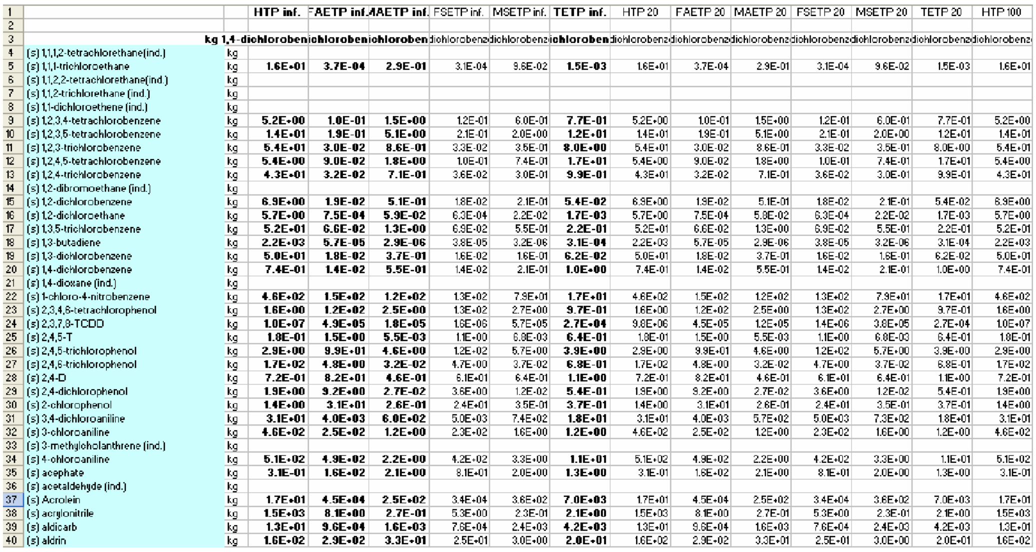
4.3. Level III: Impact Assessment

As in the *"Inventory Level"*, the evaluation is carried out by means of an automatic search in three different receiving environments: air, soil and water. Also, the impacts associated to natural resources and landscape have been included. A modifiable database was constructed with the characterization factors related to several impact categories, including mid and end point categories. Table 2 shows the categories incorporated to the developed tool. This level is automatically performed by means of the developed programming code in Visual Basic.

The identification is through the combination of the extraction or receiving environment label, air (a), water (w), soil (s), and natural resources (o) and the name of each compound. The contribution of each item to the corresponding impact category is through the assignation of the LCI result to each impact categories in an independent way.

4.3.1. Impact categories

Several compounds or groups have been considered for each one of the four extraction or receiving environments: 709 for air, 241 for water, 209 for soil and 66 for resources and landscape. The impact categories include diverse methods database (CML, Eco-indicator 99, Impact 2002+), different time horizon for selected categories (5, 10, 15, 20, 25, 30, 40, 100, 500 years), mid and endpoints units. Like in the previous level, the impact assessment comprises the compounds related in a direct and indirect way (primary and secondary processes). Figure 9 shows part of the constructed characterization factor worksheet associated to soil releases.



1			HTP inf.	FAETP inf.	MAETP inf.	FSETP inf.	MSETP inf.	TETP inf.	HTP 20	FAETP 20	MAETP 20	FSETP 20	MSETP 20	TETP 20	HTP 100
2															
3			kg 1,4-dichloroben	ichloroben	ichloroben	dichlorobenz	dichlorobenz	ichloroben	dichlorobenz	dichlorobenz	dichlorobenz	dichlorobenz	dichlorobenz	dichlorobenz	dichlorobenz
4	(s) 1,1,1,2-tetrachlorethane(ind.)	kg													
5	(s) 1,1,1-trichloroethane	kg	1.6E+01	3.7E-04	2.9E-01	3.1E-04	9.6E-02	1.5E-03	1.6E+01	3.7E-04	2.9E-01	3.1E-04	9.6E-02	1.5E-03	1.6E+01
6	(s) 1,1,2,2-tetrachlorethane(ind.)	kg													
7	(s) 1,1,2-trichlorethane (ind.)	kg													
8	(s) 1,1-dichloroethene (ind.)	kg													
9	(s) 1,2,3,4-tetrachlorobenzene	kg	5.2E+00	1.0E-01	1.5E+00	1.2E-01	6.0E-01	7.7E-01	5.2E+00	1.0E-01	1.5E+00	1.2E-01	6.0E-01	7.7E-01	5.2E+00
10	(s) 1,2,3,5-tetrachlorobenzene	kg	1.4E+01	1.9E-01	5.1E+00	2.1E-01	2.0E+00	1.2E+01	1.4E+01	1.9E-01	5.1E+00	2.1E-01	2.0E+00	1.2E+01	1.4E+01
11	(s) 1,2,3-trichlorobenzene	kg	5.4E+01	3.0E-02	8.6E-01	3.3E-02	3.5E-01	8.0E+00	5.4E+01	3.0E-02	8.6E-01	3.3E-02	3.5E-01	8.0E+00	5.4E+01
12	(s) 1,2,4,5-tetrachlorobenzene	kg	5.4E+00	9.0E-02	1.8E+00	1.0E-01	7.4E-01	1.7E+01	5.4E+00	9.0E-02	1.8E+00	1.0E-01	7.4E-01	1.7E+01	5.4E+00
13	(s) 1,2,4-trichlorobenzene	kg	4.3E+01	3.2E-02	7.1E-01	3.6E-02	3.0E-01	9.9E-01	4.3E+01	3.2E-02	7.1E-01	3.6E-02	3.0E-01	9.9E-01	4.3E+01
14	(s) 1,2-dibromoethane (ind.)	kg													
15	(s) 1,2-dichlorobenzene	kg	6.9E+00	1.9E-02	5.1E-01	1.8E-02	2.1E-01	5.4E-02	6.9E+00	1.9E-02	5.1E-01	1.8E-02	2.1E-01	5.4E-02	6.9E+00
16	(s) 1,2-dichloroethane	kg	5.7E+00	7.5E-04	5.9E-02	6.3E-04	2.2E-02	1.7E-03	5.7E+00	7.5E-04	5.8E-02	6.3E-04	2.2E-02	1.7E-03	5.7E+00
17	(s) 1,3,5-trichlorobenzene	kg	5.2E+01	6.6E-02	1.3E+00	6.9E-02	5.5E-01	2.2E-01	5.2E+01	6.6E-02	1.3E+00	6.9E-02	5.5E-01	2.2E-01	5.2E+01
18	(s) 1,3-butadiene	kg	2.2E+03	5.7E-05	2.9E-06	3.8E-05	3.2E-06	3.1E-04	2.2E+03	5.7E-05	2.9E-06	3.8E-05	3.2E-06	3.1E-04	2.2E+03
19	(s) 1,3-dichlorobenzene	kg	5.0E+01	1.8E-02	3.7E-01	1.6E-02	1.6E-01	6.2E-02	5.0E+01	1.8E-02	3.7E-01	1.6E-02	1.6E-01	6.2E-02	5.0E+01
20	(s) 1,4-dichlorobenzene	kg	7.4E-01	1.4E-02	5.5E-01	1.4E-02	2.1E-01	1.0E+00	7.4E-01	1.4E-02	5.5E-01	1.4E-02	2.1E-01	1.0E+00	7.4E-01
21	(s) 1,4-dioxane (ind.)	kg													
22	(s) 1-chloro-4-nitrobenzene	kg	4.6E+02	1.5E+02	1.2E+02	1.3E+02	7.9E+01	1.7E+01	4.6E+02	1.5E+02	1.2E+02	1.3E+02	7.9E+01	1.7E+01	4.6E+02
23	(s) 2,3,4,6-tetrachlorophenol	kg	1.6E+00	1.2E+02	2.5E+00	1.3E+02	2.7E+00	9.7E-01	1.6E+00	1.2E+02	2.5E+00	1.3E+02	2.7E+00	9.7E-01	1.6E+00
24	(s) 2,3,7,8-TCDD	kg	1.0E+07	4.9E+05	1.8E+05	1.6E+06	5.7E+05	2.7E+04	9.8E+06	4.5E+05	1.2E+05	1.4E+06	3.8E+05	2.7E+04	1.0E+07
25	(s) 2,4,5-T	kg	1.8E-01	1.5E+00	5.5E-03	1.1E+00	6.8E-03	6.4E-01	1.8E-01	1.5E+00	5.5E-03	1.1E+00	6.8E-03	6.4E-01	1.8E-01
26	(s) 2,4,5-trichlorophenol	kg	2.9E+00	9.9E+01	4.6E+00	1.2E+02	5.7E+00	3.9E+00	2.9E+00	9.9E+01	4.6E+00	1.2E+02	5.7E+00	3.9E+00	2.9E+00
27	(s) 2,4,6-trichlorophenol	kg	1.7E+02	4.8E+00	3.2E-02	4.7E+00	3.7E-02	6.8E-01	1.7E+02	4.8E+00	3.2E-02	4.7E+00	3.7E-02	6.8E-01	1.7E+02
28	(s) 2,4-D	kg	7.2E-01	8.2E+01	4.6E-01	6.1E+01	6.4E-01	1.1E+00	7.2E-01	8.2E+01	4.6E-01	6.1E+01	6.4E-01	1.1E+00	7.2E-01
29	(s) 2,4-dichlorophenol	kg	1.9E+00	9.2E+00	2.7E-02	3.6E+00	1.2E-02	5.4E-01	1.9E+00	9.2E+00	2.7E-02	3.6E+00	1.2E-02	5.4E-01	1.9E+00
30	(s) 2-chlorophenol	kg	1.4E+00	3.1E+01	2.6E-01	2.4E+01	3.5E-01	3.7E-01	1.4E+00	3.1E+01	2.6E-01	2.4E+01	3.5E-01	3.7E-01	1.4E+00
31	(s) 3,4-dichloroaniline	kg	3.1E+01	4.0E+03	6.0E+02	5.0E+03	7.4E+02	1.8E+01	3.1E+01	4.0E+03	5.7E+02	5.0E+03	7.3E+02	1.8E+01	3.1E+01
32	(s) 3-chloroaniline	kg	4.6E+02	2.5E+02	1.2E+00	2.3E+02	1.6E+00	1.2E+00	4.6E+02	2.5E+02	1.2E+00	2.3E+02	1.6E+00	1.2E+00	4.6E+02
33	(s) 3-methylcholanthrene (ind.)	kg													
34	(s) 4-chloroaniline	kg	5.1E+02	4.9E+02	2.2E+00	4.2E+02	3.3E+00	1.1E+01	5.1E+02	4.9E+02	2.2E+00	4.2E+02	3.3E+00	1.1E+01	5.1E+02
35	(s) acephate	kg	3.1E-01	1.6E+02	2.1E+00	8.1E+01	2.0E+00	1.3E+00	3.1E-01	1.6E+02	2.1E+00	8.1E+01	2.0E+00	1.3E+00	3.1E-01
36	(s) acetaldehyde (ind.)	kg													
37	(s) Acrolein	kg	1.7E+01	4.5E+04	2.5E+02	3.4E+04	3.6E+02	7.0E+03	1.7E+01	4.5E+04	2.5E+02	3.4E+04	3.6E+02	7.0E+03	1.7E+01
38	(s) acrylonitrile	kg	1.5E+03	8.1E+00	2.7E-01	5.3E+00	2.3E-01	2.1E+00	1.5E+03	8.1E+00	2.7E-01	5.3E+00	2.3E-01	2.1E+00	1.5E+03
39	(s) aldicarb	kg	1.3E+01	9.6E+04	1.6E+03	7.6E+04	2.4E+03	4.2E+03	1.3E+01	9.6E+04	1.6E+03	7.6E+04	2.4E+03	4.2E+03	1.3E+01
40	(s) aldrin	kg	1.6E+02	2.9E+02	3.3E+01	2.5E+01	3.0E+00	2.0E+01	1.6E+02	2.9E+02	3.3E+01	2.5E+01	3.0E+00	2.0E+01	1.6E+02

Figure 9 Characterization factor worksheet

The receiving environment air worksheet comprises 26 categories, and tacking into account the preceding considerations, there are 96 in total. In similar way, releases to water are evaluated through 17 categories (48 in total), 15 for soil (42 in total), and 9 for natural resources and lanscape (21 in total). Further information about the included impact categories is in Annex III.

The Kg_{eq} of the reference substance is the unit employed in the midpoint categories, expressing the reference substance amount that is equivalent to the impact of the considered contaminant.

The damage level units are the DALY (Disability Adjusted Life Years), $PDF \cdot m^2 \cdot yr$ (Potentially Disappeared Fraction of species per m^2 per year), and MJ. The DALY corresponds to human health damage category, and it characterizes the disease severity, considering both mortality, Years of Life Lost (YOLL) and Years Lived Disabled (YLD). Health effects leading to death are described using the YO/LL indicator; it includes all fatal health effects due to respiratory health effects. On the other hand, YLD express the morbidity in years, it describes those health effects that do not lead to immediate death or to a shorter period of life, but which account for a life quality decrease and for pain and suffering (Murray and Lopez, 1996). Therefore, the DALY indicator is the addition of both indicators (Eq. 4).

$$\mathrm{DALY} = \mathrm{YOLL} + \mathrm{YLD} \qquad \text{Eq. 4}$$

$PDF \cdot m^2 \cdot yr$ is related to ecosystem quality damage category, and it represents the fraction of species disappeared per m^2 of earth during one year.

Table 2 Impact categories considered in the methodology

Impact category	Initial emission or extraction				
	Air	**Water**	**Soil**	**Resources**	**Lanscape**
Depletion of abiotic resources				*	
Impact of land use					*
Climate change	*				
Stratospheric ozone depletion	*				
Human toxicity	*	*	*		
Ecotoxicity					
Freshwater aquatic ecotoxicity	*	*	*		
Marine aquatic ecotoxicity	*	*	*		
Terrestrial ecotoxicity	*	*	*		
Freshwater sediment ecotoxicity	*	*	*		
Marine sediment ecotoxicity	*	*	*		
Photo-oxidant formation	*		*		
Acidification	*	*	*		
Eutrophication	*	*	*		
Radiation	*	*			
Odour	*	*			

The main idea in this level is to connect the Life Cycle Inventory with the Life Cycle Impact Assessment. The contribution of each compound to a specific impact category is calculated with Eq. 3 (see Section3.2.1.3). A similar process has been employed to calculate the associated damage for selected categories. The results are presented in the correspondent extraction or receiving environment worksheet (“Air_Results”, “Soil_Results”, “Water_Results”, “Resources&Lanscape_Results”). The evaluation can be made for the four extraction or receiving environments at same time or one of them by clicking in the macro button “Impact Assessment” in “Hysys” worksheet. The contribution from each compound are showed in the results worksheets, at the same time as the related processes (primary or secondary). A brief description of some of the analyzed impact categories that correspond to the Group A: “Baseline Impact Categories” of the CML method is presented on following (see section 3.2.1.1).

4.3.1.1. Depletion of abiotic resources

"Abiotic resources" are natural resources (including energy resources) such as iron ore, crude oil and wind energy, which are regarded as non-living. Abiotic resources depletion is one of the most frequently discussed impact categories and there is consequently a wide variety of methods available for characterizing contributions to this category. To a large extent, these different methodologies reflect differences in problem definition. Depending on the definition, this impact category includes only natural resources, or natural resources, human health and the natural among its areas of protection (Guinée, 2002).

4.3.1.2. Impacts of Land use

This category covers a range of consequences of human land use. A distinction has been made between use of land with impacts on the resources aspects and use of land with impacts on biodiversity, life support functions, etc. The subcategory "Land competition" is concerned with the loss of land as a resource, in the sense of being temporarily unavailable. The areas of protection are natural resources and man-made environment (Guinée, 2002).

4.3.1.3. Climate change

Energy from the sun drives the earth weather and climate, and heats the earth surface; in turn, the earth radiates energy back into space. Atmospheric greenhouse gases (water vapor, carbon dioxide, methane, and other gases), trap some of the outgoing energy, retaining heat like the panels of a greenhouse (IPCC, 2001).

The earth average temperature is more hospitable due to greenhouse gases. However, problems may arise when the atmospheric concentration of greenhouse gases increases. Atmospheric concentrations of these gases have increased due to the human activity (IPCC, 2001).

This impact category affects three areas of protection: human health, natural environment and man-made environment. The characterization factors database constructed in this work evaluates:

- Three time horizon (20, 100 and 500 years).
- Air as the analyzed receiving environment.

4.3.1.4. Stratospheric ozone depletion

Depletion of the stratospheric ozone layer leads to an increase of UV-B intensity at the surface of the earth, causing a number of radiation impacts (Guinée et al., 2002). This impact category affects four areas of protection: human health, natural environment, man-made environment and natural resources. The characterization factor database includes:

- Time horizon of 5, 10, 15, 20, 25, 30, 40 years and infinite.
- Air as the analyzed receiving environment.

4.3.1.5. Human Toxicity

This impact category covers the impacts on human health of toxic substances present in the environment. The area of protection for this impact category is human health.

- Carcinogenic, non-carcinogenic and total effect can be evaluated.
- Time horizon of 20, 100, 500 years and infinite.
- Air, soil and water are the analyzed receiving environment.

4.3.1.6. Ecotoxicity

This impact category covers the impacts of toxic substances on aquatic and terrestrial ecosystems. The area of protection is the natural environment and natural resources (Guinée et al., 2002). The constructed data base includes:

- Time horizon of 20, 100 , 500 years and infinite
- Air, water and soil are the analyzed receiving environments.

4.3.1.7. Photo-oxidant formation

Under the influence of the solar radiation, the nitrogen oxides, NO_x, react with the volatile organic compounds (VOC), to produce ozone tropospheric. Also, the presence of carbon monoxide can contribute to the formation of ozone (Udo de Haes et al., 1999b). These oxidizers can be risky for the human health, the ecosystems and the agriculture, affecting therefore the four areas of protection: human health, natural environment, man-made environment and natural resources. Characterization factors associated to air as receiving environment are included in the worksheet.

4.3.1.8. Acidification

Acidification is the process whereby air pollution, mainly NH_3, SO_2 NO_x, is converted into acid substances. This 'acid rain' is best known for the damage it causes to forests and lakes. Acidifying substances cause a large diversity of impacts on soil, plants, animals and materials (Udo de Haes et al., 1999b).

This impact category affects four areas of protection: human health, natural environment, man-made environment and natural resources. Air, water and soil are the analyzed receiving environments.

4.3.1.9. Eutrophication

Eutrophication covers all potential impacts of excessively high environmental levels of macronutrients, the most important of which are nitrogen and phosphorus. Nutrient enrichment may cause an undesirable shift in species composition and elevated biomass production in both aquatic and terrestrial ecosystems. In addition, high nutrient concentrations may also render surface waters unacceptable as a source of drinking water. In aquatic ecosystems increased biomass production may lead to a depressed oxygen levels, because of the additional consumption of oxygen in biomass decomposition (measured as BOD, biological oxygen demand). As emissions of degradable organic matter have a similar impact, such emissions are also treated under the impact category "eutrophication". The areas of protection are the natural environment, natural resources and the man-made environment (Guinée et al., 2002). The constructed data base includes Air, water and soil as receiving environments.

4.4. Level IV: Economical Analysis

The economic evaluation of the process has been carried out on the basis of the total capital investment, total operating costs, and revenues from sale of produced compound. All these terms have a significant relevance from the industry point of view. Total capital investment has been evaluated as the sum of all direct costs, including purchased equipment costs and their installation cost, site preparation and building, and indirect cost comprising engineering, star-up, and contractor fees.

Total operating cost includes equipment operating cost, maintenance costs, operating labor (workers, salary), raw material (purchase and transport), disposal costs and overheads.

Some information has to be introduced in the worksheet “Economical Evaluation” in order to carry out the analysis:

- Operating costs.
- Number of employees, salary and working days.
- The plant life period,
- The annual interest rate, *k*.

The analysis is presented in the worksheet, and it shows four parts:

- Production cost, the calculations are based in the production amount, considering costs, human labor, depreciation and amortization during the analyzed period.
- Selling Program, it estimates the income correspondent to each year, based in the sale price and production per year.
- Equilibrium point, total costs, total production and total income for the entire life of the project are calculated.
- Cash Flows, this part summarizes the data calculated in the previous parts in order to calculate five economic indicators that show the viability of each process.

Net Present Value (NPV), Payback Period (PP), Discounted Payback Period (DPP), Internal Rate of Return (IRR) and Modified Internal Rate of Return (MIIR) are the selected indicators (described in section 3.3). They can be used to evaluate the feasibility of one process or to compare it within several configurations, giving to the industry a clear idea of the economical benefits associated to each option. Table 3 shows the criteria to select or refuse a project (adapted from Blank et al., 2005).

Table 3 Proposed standards used in economical analysis

Indicator	Single Project	Multiple Project
NPV	NPV > 0	greater NPV
IRR	IRR > k	greater IRR
MIRR	MIRR > k	greater MIRR
PP	less than the half life of the project	lesser PP
DPP	less than the half life of the project	lesser DPP

The NPV indicator is calculated as the sum of the net cash flow at the end of each year (Eq. 5, Park et al., 1990).

$$\mathrm{NPV} = \sum_{t=0}^{N} \frac{F_t}{(1+k)^t} \qquad \text{Eq. 5}$$

where:
N is the plant life,
F_t is the net cash flow at the end of the period *t*,
k corresponds to the annual interest rate.

The net cash flows (NCF) are estimated as de difference between the input cash flows (incomes) and the output cash flows (expenditures).

The IRR is defined as the interest rate value that makes null the NPV value, therefore the IRR is obtained by the substitution of the *k* value in Eq. 5 (Canada and White, 1980).

$$\mathrm{NPV} = 0 = \sum_{t=0}^{N} \frac{F_t}{(1+\mathrm{IRR})^t} \qquad \text{Eq. 6}$$

The modified internal rate of return is evaluated using Eq. 7 (Canada and White, 1980):

$$\mathrm{MIRR} = \sqrt[N]{\frac{\sum_{t=0}^{N} CF_{(+)t}(1+k)^{N-1}}{\sum_{t=0}^{N}\left|\frac{CF_{(-)t}}{(1+k)^{t}}\right|}} - 1 \quad \text{Eq. 7}$$

where:

$CF_{(+)t}$ is the positive cash flow in period *t*, during the analyzed period N,

$CF_{(-)t}$ is the negative cash flow correspondent to the period *t*, and

k corresponds to the annual interest rate.

The payback period is obtained from Eq. 8 (Blank and Tarquin, 2005), using information from the net cash flow table,

$$PP = Y_{ACF} - 1 + \frac{ACF_{Y-1}}{NCF_{(Y)}} \quad \text{Eq. 8}$$

where:

Y_{ACF} - year when the accumulative cash flow become positive

ACF_{Y-1} – Accumulative cash flow in the year Y-1

NCF_{Y} – Net Cash flow in year Y

The ACF is the sum of the accumulative cash flow in the period "*t-1*", and the cash flow in the period "*t*". When a project starts, the ACF is equal to the cash flow.

The DPP (Eq. 9) is obtained like PP, but using the discounted cash flow chart. The discounted cash flow (DCF) is calculated using a discount rate, d, during the discounting period t (Eq. 10). This rate is the risk factor, or the time value of money (Au and Au, 1992).

$$PP = Y_{DACF} - 1 + \frac{DACF_{Y-1}}{DCF_{(Y)}} \quad \text{Eq. 9}$$

$$DCF = \frac{F_t}{(1+d)^t} \qquad \text{Eq. 10}$$

where:
Y - year when the discounted accumulative cash flow become positive
$DACF_{Y-1}$ – Discounted accumulative cash flow in the year Y-1
DCF_Y – Discounted Cash flow in year Y

Similarly to the ACF, the DACF is the sum of the discounted accumulative cash flow in the period "*t-1*", and the discounted cash flow in the period "*t*".

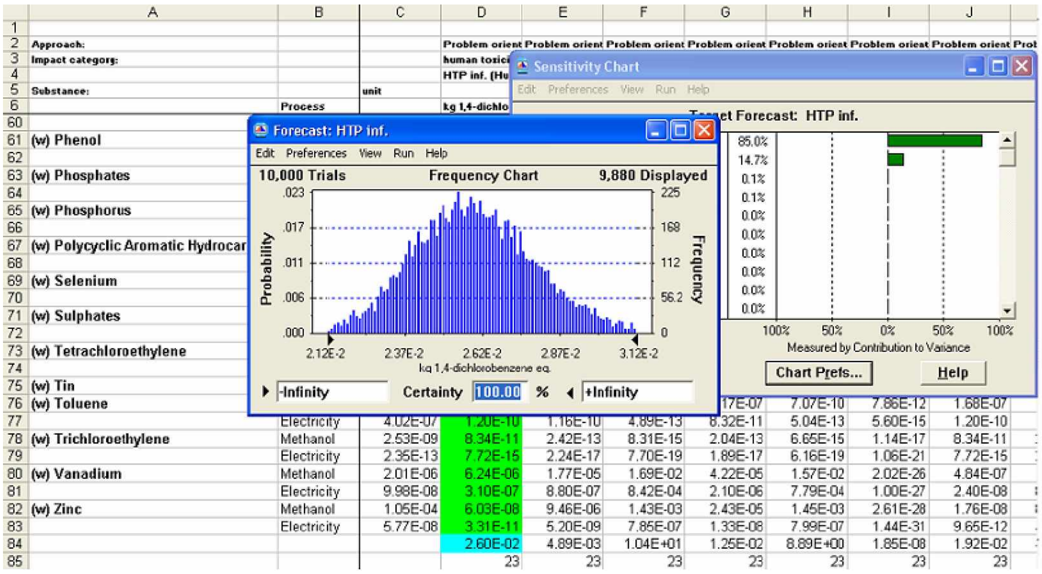
4.5. *Level V: Sensitivity Analysis*

A sensitivity analysis is carried out by means of the determination of the process variables with the higher contribution to each impact category. The Monte Carlo (MC) method has been chosen as stochastic simulation model to characterize the sensitivity of the LCIA results. The software Crystal Ball Version 5.2 from Decisioneering is the simulation program used to perform the sensitivity analysis.

The first step is to fit each impact category in the correspondent result worksheet ("Air_Results", "Soil_Results", "Water_Results", and "Resources&Lanscape_Results"), as *"objective function"*. Then, each compound related to this category, is defined as *"variables"*. This analysis is employed to know the overall effect produced in the objective function, as result of the modification of these variables.

The probability distribution, mean and standard deviation have to be specified for each *variable*, in order to perform a MC simulation. The Crystal Ball software changes all these *variables* at random. The variation is restricted by the given probability distribution. Repeated calculations produce a distribution of the *objective function*, reflecting the sensitivity.

This analysis shows the influence of each *variable* on the results, centering in this variables to change it and to improve the process. Figure 10 shows an example of the Crystal Ball screenshot with the activated cells of an Excel worksheet, the result of a sensitivity analysis and the final provision. The green cells correspond to each *variable* associated to the *objective function* (blue cell), in this case the Human Toxicity category. As the results are presented by process (primary or secondary), we can see in the sensitivity chart which is the compound and the process with the higher contribution to each impact category and therefore, it will be able to determine the way to reduce it.



10,000 Trials

9,880 Displayed

-Infinity Certainty 100.00 % +Infinity

Target Forecast: HTP inf.

	A	B	C	D	E	F	G	H	I	J
1										
2	**Approach:**			**Problem orient**	**Problem orient**	**Problem orient**	**Problem orient**	**Problem orient**	**Problem orient**	**Problem orient**
3	**Impact category:**			**human toxici**						
4				**HTP inf. (Hu**						
5	**Substance:**		**unit**							
6		**Process**		**kg 1,4-dichlo**						
60										
61	**(w) Phenol**									
62										
63	**(w) Phosphates**									
64										
65	**(w) Phosphorus**									
66										
67	**(w) Polycyclic Aromatic Hydrocar**									
68										
69	**(w) Selenium**									
70										
71	**(w) Sulphates**									
72										
73	**(w) Tetrachloroethylene**									
74										
75	**(w) Tin**									
76	**(w) Toluene**						17E-07	7.07E-10	7.86E-12	1.68E-07
77		Electricity	4.02E-07	1.20E-10	1.16E-10	4.89E-13	8.32E-11	5.04E-13	5.60E-15	1.20E-10
78	**(w) Trichloroethylene**	Methanol	2.53E-09	8.34E-11	2.42E-13	8.31E-15	2.04E-13	6.65E-15	1.14E-17	8.34E-11
79		Electricity	2.35E-13	7.72E-15	2.24E-17	7.70E-19	1.89E-17	6.16E-19	1.06E-21	7.72E-15
80	**(w) Vanadium**	Methanol	2.01E-06	6.24E-06	1.77E-05	1.69E-02	4.22E-05	1.57E-02	2.02E-26	4.84E-07
81		Electricity	9.98E-08	3.10E-07	8.80E-07	8.42E-04	2.10E-06	7.79E-04	1.00E-27	2.40E-08
82	**(w) Zinc**	Methanol	1.05E-04	6.03E-08	9.46E-06	1.43E-03	2.43E-05	1.45E-03	2.61E-28	1.76E-08
83		Electricity	5.77E-08	3.31E-11	5.20E-09	7.85E-07	1.33E-08	7.99E-07	1.44E-31	9.65E-12
84				2.60E-02	4.89E-03	1.04E+01	1.25E-02	8.89E+00	1.85E-08	1.92E-02
85				23	23	23	23	23	23	23

Figure 10 Crystal Ball screenshot

In order to perform the Monte Carlo simulation, the necessary elements have to be identified. These include the compilation and classification of the necessary data, and the identification of probability distribution (obtained from literature). Many environmental impacts follow the lognormal or normal models, therefore, these were the probability distributions assigned in the case studies. Probability distribution, means and standard deviations values of the *variables* (compounds) were taken from literature.

At the end of this level, a new and better configuration can be established using the results obtained in the overall analysis (e. g. emissions/releases to be reduced, alternative process stages or raw materials). A new assessment can be started in order to generate the profile of the improved process.

5. Case Studies

Once the methodology was developed, three different case studies correspond to different level of development:

- Low Density Polyethylene (LDPE),
- Ethylene oxide (EO), and
- Biodiesel processes.

We have started with a preliminary application used to introduce the methodology: the abbreviated environmental assessment of the LDPE. This case comprises the mass and energy balance using worksheets in Excel and an abbreviated environmental profile employing commercial environmental software. The process information was obtained from Dow Chemical in Tarragona, Spain. Also, a future alternative using cogeneration was evaluated, in order to compare the environmental behavior of the current configuration plant and the proposed implementation. At the end of this case, the main concepts about LCA methodology were understood, the relation between emissions and releases with their correspondent impact categories and the importance of the environmental profile development were established.

The second process used to validate the methodology is the ethylene oxide (EO) production. The tested alternatives are using air or oxygen as raw material and electricity coming from cogeneration or the national network. The information about mass and energy streams, and process conditions were obtained with the simulator ASPEN Hysys®. A database of the characterization factors related to the considered impact categories (see Annex III), and the *secondary processes* was constructed. A basic economical analysis worksheet was constructed, and an environmental evaluation was validated through this industrial process. A programming code was developed to perform the Level II and III, specifically for this process.

The last assessment considers a standard biodiesel plant, by means of the simultaneous analysis of two plant configurations: acid and alkali catalyzed. In both cases, the process characterization was obtained using the simulator ASPEN Hysys®. The environmental and economical assessments were evaluated with the developed tool. A sensitivity analysis was carried out to know the influence of the streams or stages in the environmental behavior. At this point, the final *secondary processes* database was accomplished; the created software was generalized to any industrial process, it is not necessary to modified the programming code, excepting for the information transfer from ASPEN Hysys® to Excel because this code depends on the input/output streams name. Also, the graphical presentation of the results was modified in order to personalize them, the user can represent all the associated interventions for a given impact categories or restrict them for the higher values. The final version of the tool is able to search automatically all the necessary parameters to execute the overall analysis, without the user intervention.

5.1 Case 1: Low Density Polyethylene Process

5.1.1 Mass and energy balances

The balances of LDPE were obtained using the information provided from DOW Chemical in Tarragona. Detailed mass balance is presented in Annex IV. The process was divided in 4 stages:

1. Steam generation in boiler (using natural gas),
2. LDPE production,
3. Steam production, and
4. Electricity generation (from Spanish network).

The general diagram is presented in Figure 11, it includes the polymerization process (detailed in Figure 12), steam generation and electricity production. The steam production stage and the electricity generation by cogeneration were simulated by ASPEN Hysys®. The assumptions considered in the process are:

- The ratio between the steam generated in the LDPE process and the steam produced in boiler is 2:1,
- The starters and the additives do not have an important environmental load,
- The starters are not involved in the reaction step; the input flow is equal to the output.

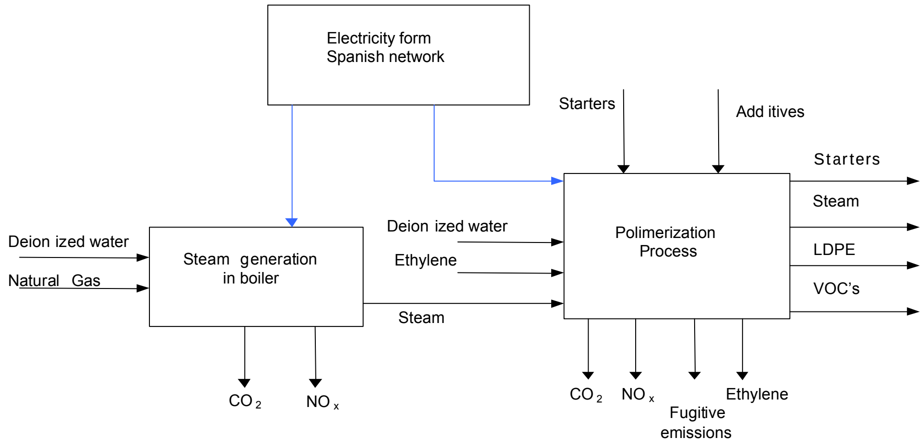


Figure 11 Diagram of the LDPE production

The evaluation considers the LDPE as the main product and the steam, as by-product. The electricity was employed in the LDPE production (compressor, extrusor, pumps and silo), and in the steam production.

The steam generation in boiler is used to start the LDPE process, and it was calculated through the mass balance. Under normal conditions, the LDPE unit generates more steam than the stoichiometrically necessary in the reaction; therefore, the plant can export this steam to other units in the same plant or to another plant, avoiding the conventional generation in a boiler and the energy consumption.

This fact derives in an avoided environmental load, as the reduction in the environmental assessment related to the LDPE process. Figure 12 shows the scheme of the DOW polymerization process, including the LDPE and steam production (stage 2 and 3), the mass balance is detailed in Annex IV.

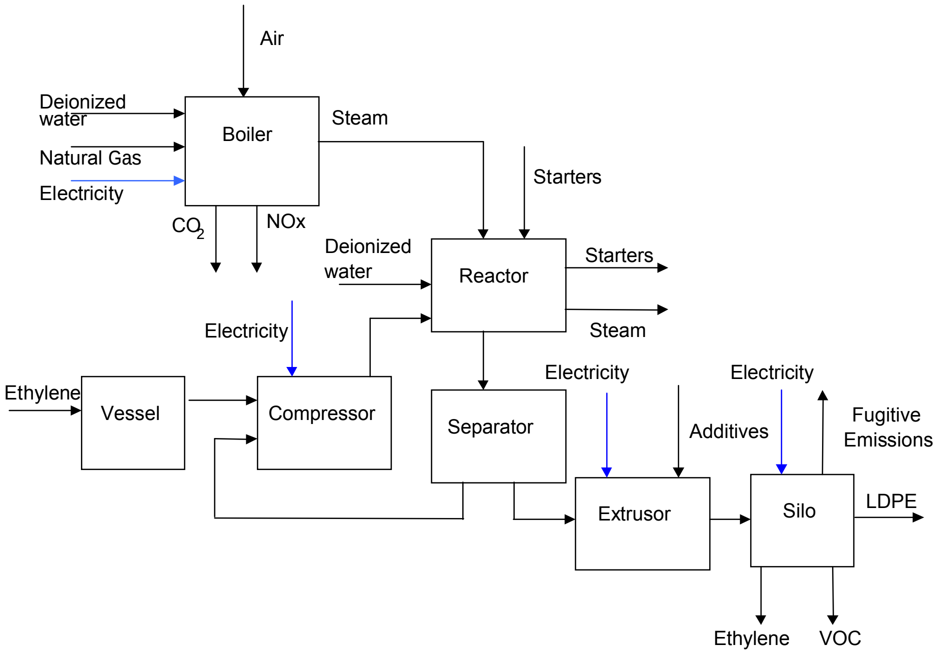


Figure 12 Polymerization process diagram

5.1.2 Life Cycle Inventory and Environmental assessment

The Life Cycle Inventory was generated from the information obtained by TEAM^{TM} (Tools for Environmental Analysis and Management). This software estimates the emissions and releases associated to 1 kg of LDPE. In this level, the avoided environmental loads are considered in order to reduce the overall environmental impact.

Each part of the process has an associated ecovector. The abbreviated ecovector (Table 4) is composed of: CO_2, CO, NO_x, VOC (the organic compounds form the data base, propane and ethane), ethylene and N_2O (as CO_2 equivalent). However, the study is focused in this compounds due to these are the emissions quantified in the DOW pplant. It is important to remark than it shows the most representative elements of the ecovector, because the final inventory includes more than these elements.

Table 4 Ecovector associated to LDPE process

	Steam production kg/LDPE kg	Electricity Producion kg/LDPE kg	Polimerization process kg/LDPE kg	Steam generation kg/LDPE kg	Total kg/LDPE kg
CO_2	1.12E-02	7.68E-01	8.22E-04	-5.15E-02	7.28E-01
CO	9.69E-03	2.64E-04	0.00E+00	-5.52E-05	9.90E-03
VOC	1.94E-06	5.79E-05	3.18E-05	0.00E+00	9.16E-05
NO_x	2.30E-05	4.12E-04	0.00E+00	-3.68E-04	6.63E-05
N_2O	4.89E-05	6.80E-04	0.00E+00	0.00E+00	7.29E-04
SO_x	5.97E-06	2.48E-03	0.00E+00	-5.52E-04	1.93E-03
C_2H_4	1.10E-06	1.91E-04	2.01E-04	0.00E+00	3.93E-04

Figure 13 to Figure 16 represent the environmental loads distribution in the four stages of the process. Since the magnitude of the values changes considerably, the details are presented in Table 4 because apparently some stages do not contribute to the burdens.

As can be seen, the avoided load produces the minimization of some burdens. The process improvements were focused in the electricity generation stage, due to the main contributions correspond to this phase.

In order to know, from the environmental point of view, if the process operates under optimal conditions, the results were compared with information obtained from Association of Plastics Manufacturers in Europe (APME), for 1997 and 1993. These values correspond to the average generation of emissions from several polymerization industries in Europe. As can be seen in Table 5, the CO emissions are higher than the average values from APME; however, the value is very small. A reduction (~6%), is obtained for CO_2 and

SO_x due to the avoided environmental load and the electricity requirements in DOW.

Table 5 Comparison of emissions associated to LDPE process

Emission	DOW Kg/kg LDPE	$APME_{1997}$ Kg/kg LDPE	$APME_{1993}$ Kg/kg LDPE
CO	0.0099	0.0009	0.0013
CO_2	0.728	1.25	2.6
SO_x	0.00193	0.009	0.015

The electricity from Spanish network is the stage with the highest contribution for almost all the analyzed emissions. Only the ethylene emission is mainly generated in the polimerization process.

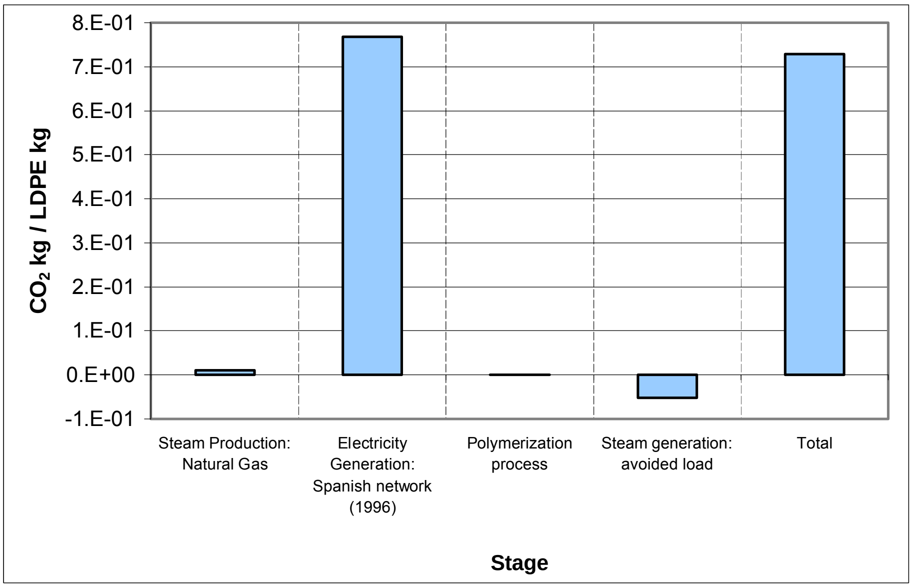


Figure 13 CO_2 emissions associated to the LDPE process

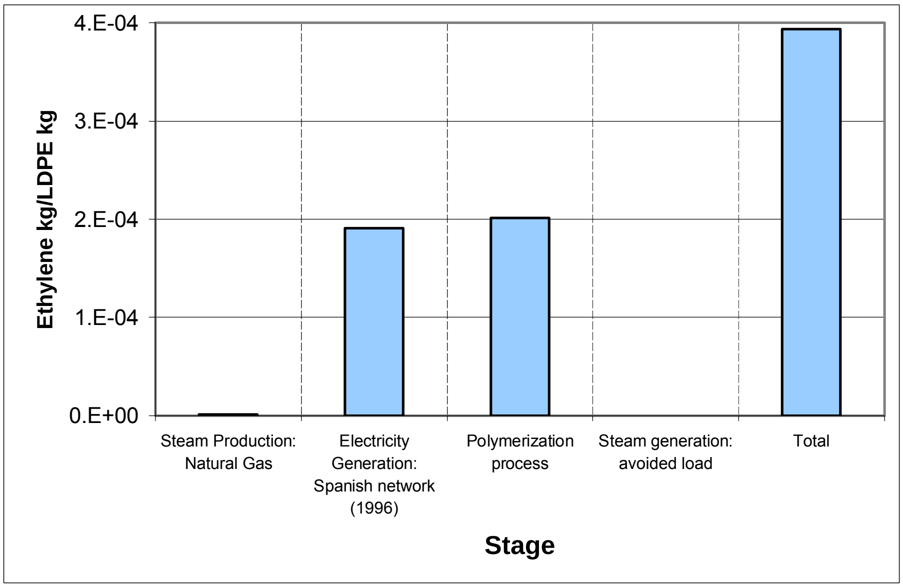


Figure 14. Ethylene emissions associated to the LDPE process

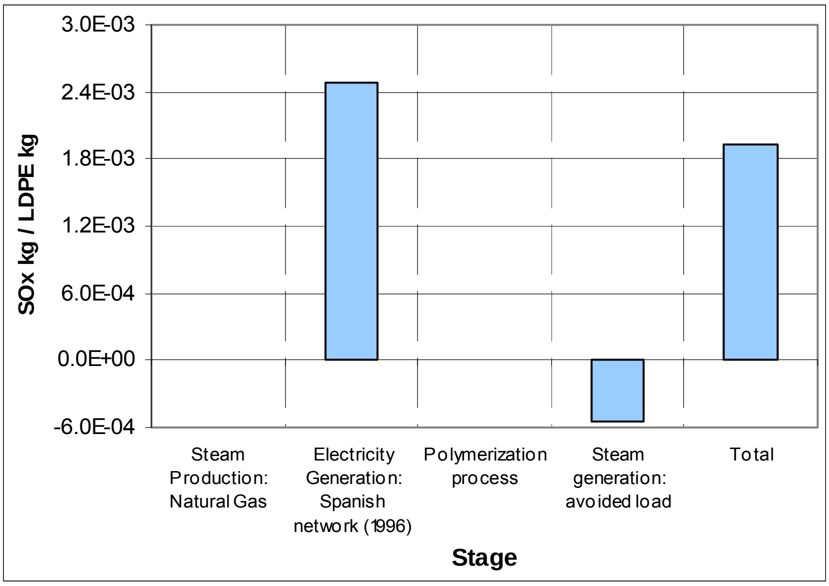


Figure 15. SO_x emissions associated to the LDPE process

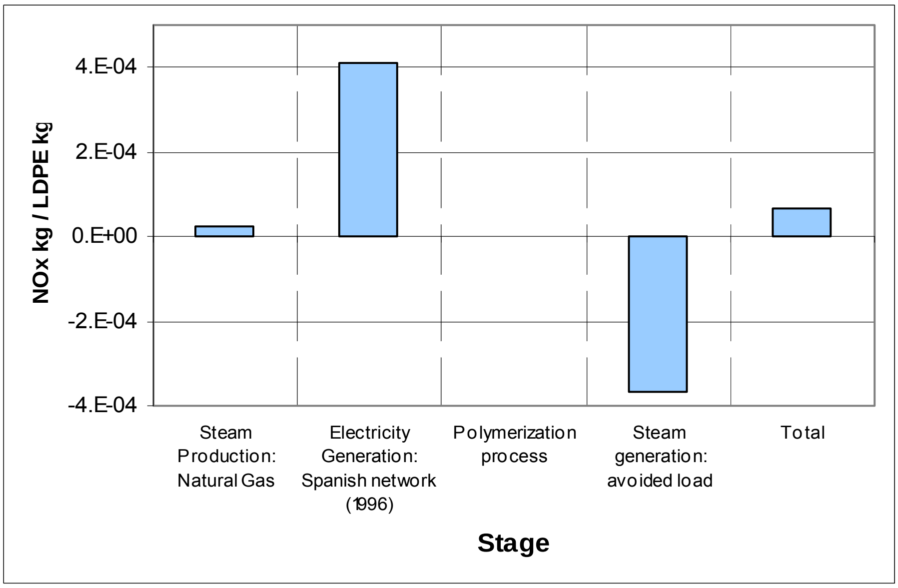


Figure 16. NO_x emissions associated to the LDPE process

5.1.3 Future alternative

Currently, the LDPE plant use electricity form Spanish network and produce steam in a boiler; therefore, a cogeneration unit could be implemented in order to optimize the process. This process was simulated in ASPEN Hysys®, considering the required steam for the process. Figure 17 corresponds to the PFD generated in the simulator (detailed in Annex V). The necessary input information is the natural gas mass flow.

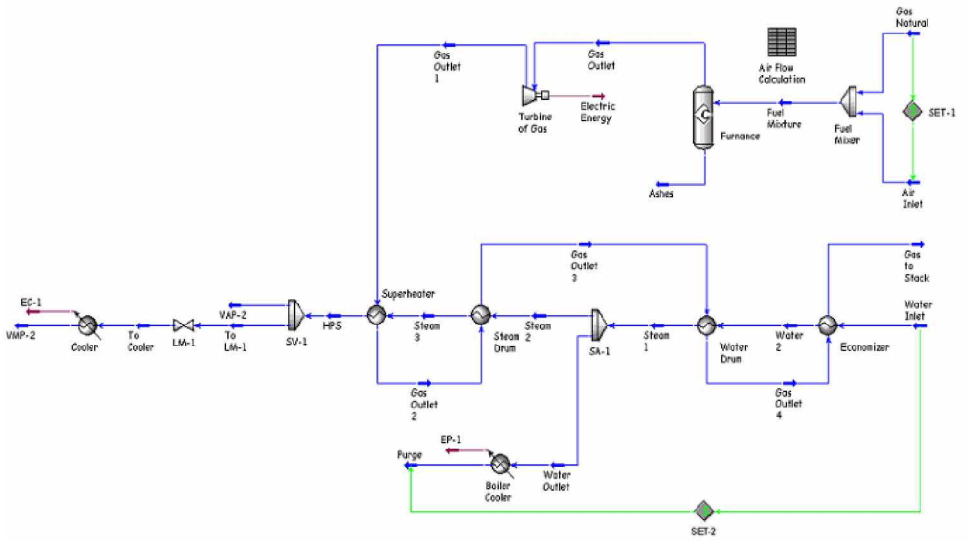


Figure 17 Cogeneration process flow diagram generated in ASPEN Hysys®

2610 kg/hr of Natural gas is required in order to produce 7.44 MW, and 961.24 kg/hr of steam at 157ºC and 559 KPa. However, the plant needs 10.45 MW, thus the difference must be covered with electricity from the national network, nevertheless, the emissions are reduced in 60% using this option, especially in the negative values that implies an important reduction in the generated environmental impact. As in the previous configuration analysis (current conditions), Table 6 shows the new profile and the graphical representations are presented in Figure 18 to Figure 21.

Table 6. Ecovector associated to LDPE process using cogeneration

	Cogeneration kg/LDPE kg	Electricity Producion kg/LDPE kg	Polimerization process kg/LDPE kg	Steam generation kg/LDPE kg	Total kg/LDPE kg
CO_2	1.72E-01	2.13E-01	8.22E-04	-5.15E-02	3.34E-01
CO	0.00E+00	7.31E-05	0.00E+00	-5.52E-05	1.79E-05
VOC	0.00E+00	1.60E-05	3.18E-05	0.00E+00	4.79E-05
NO_x	9.21E-05	1.14E-04	0.00E+00	-3.68E-04	-1.62E-04
N_2O	0.00E+00	1.89E-04	0.00E+00	0.00E+00	1.89E-04
SO_x	0.00E+00	6.88E-04	0.00E+00	-5.52E-04	1.36E-04
C_2H_4	0.00E+00	5.30E-05	2.01E-04	0.00E+00	2.54E-04

Only the required amount of steam was considered in this evaluation, nevertheless, the real production in the boiler is bigger. Given that the electricity produced by cogeneration is proportional to the generated steam, the total electricity will be enough to cover the energy requirements of the plant, and electricity from the Spanish network won't be necessary, the emissions will reduce still more, since this is the stage with the bigger contribution to them. The distribution of the environmental loads to each stage can be observed in the next graphs:

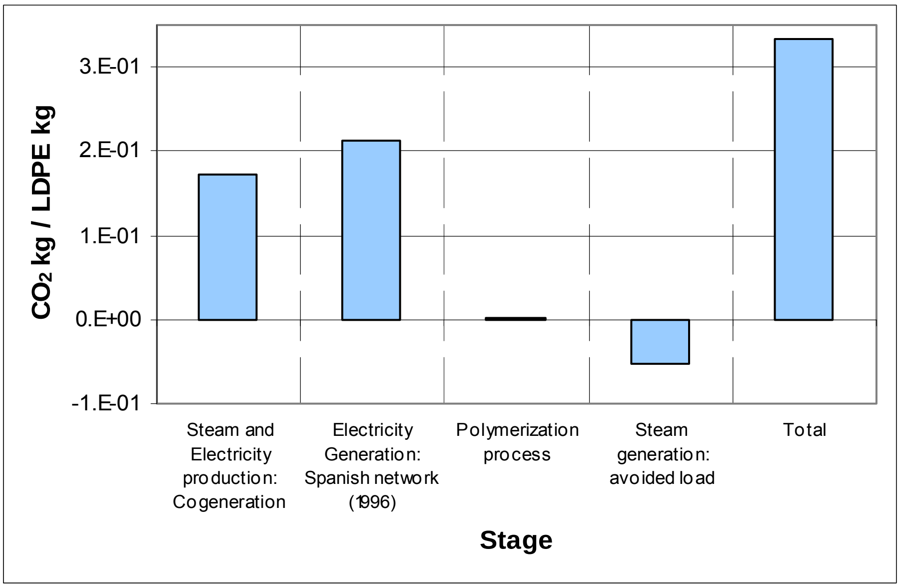


Figure 18 CO_2 emissions generated in the LDPE process using cogeneration

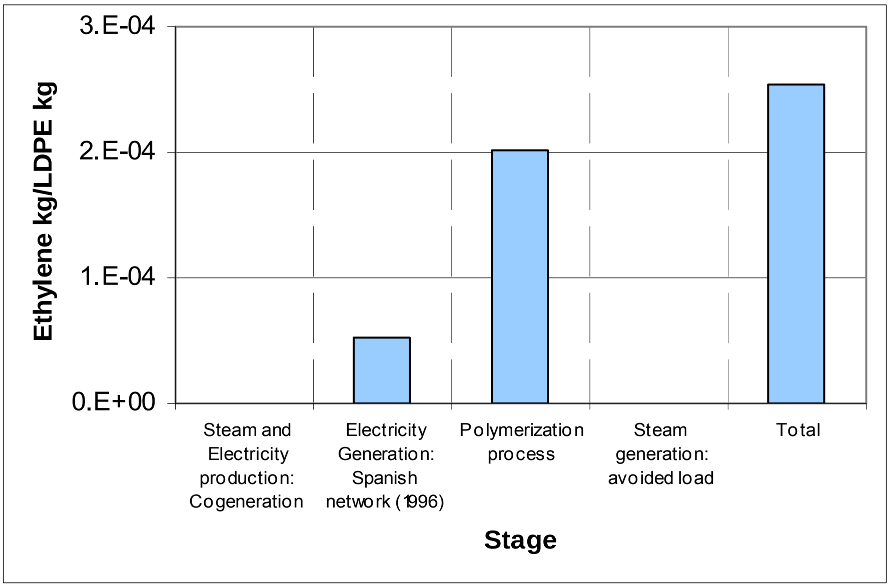


Figure 19 Ethylene emissions generated in the LDPE process using cogeneration

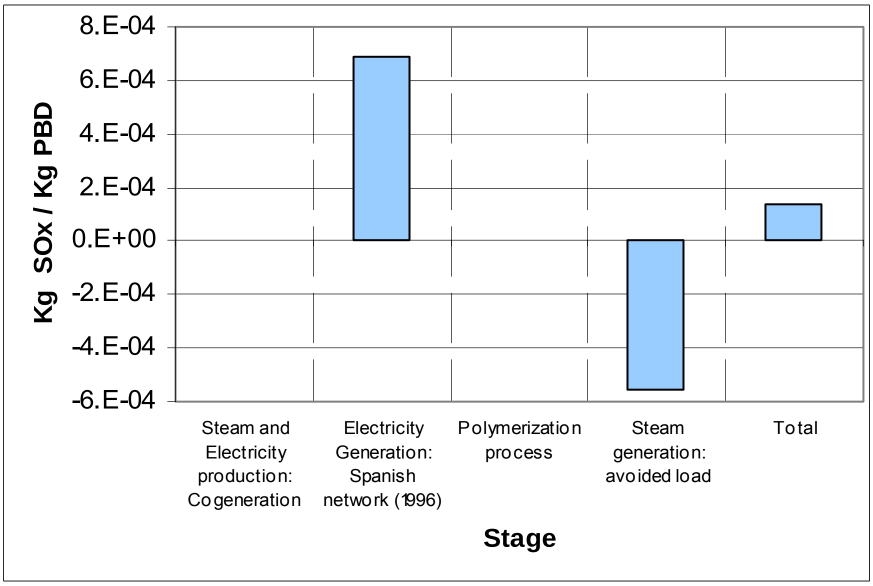


Figure 20 SO_x emissions generated in the LDPE process using cogeneration

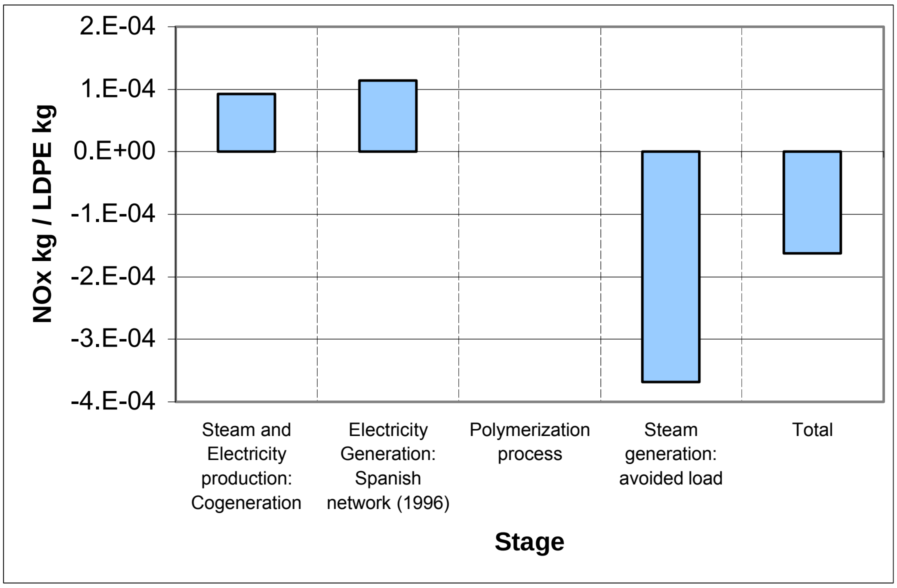


Figure 21 NO_x emissions generated in the LDPE process using cogeneration

This case study was useful to know the required information to obtain an environmental assessment, to familiarize with the LCA methodology and to evaluate the LDPE impact in the environment. At the end of this evaluation, several improvements can be implemented to the process, like conditions modifications and alternative processes.

This analysis demonstrates the importance of the quantity and origin of the energy. For example in the Global Warming Potential (Table 7), the electricity from the Spanish network generates 0.769 kg of CO_2 eq./kg LDPE, a reduction of ~70% is obtained using cogeneration. In similar way, the emissions of NO_x are reduced from 0.000412 kg to 0.0002061 kg. This diminution is very important since the NO_x and the SO_x are related to the acidification impact category.

Table 7 Global Warming Potential obtained in the LDPE process

	Steam production (Natural Gas/Cogeneration) kg/LDPE kg	Electricity Producion (Spanish kg/LDPE kg	Polimerization process kg/LDPE kg	Steam generation (avoided load) kg/LDPE kg	Total kg/LDPE kg
$GWP_{(Natural\ gas)}$	1.13E-02	7.69E-01	8.22E-04	-5.15E-02	7.81E-01
$GWP_{(Cogeneration)}$	1.72E-01	2.13E-01	8.22E-04	-5.15E-02	3.34E-01

When steam is exported to other units and the concept of avoided environmental load is taken into account, it is important to consider which type of steam is taken as reference value. The most common is to consider steam form steam boiler operating with natural gas, but other scheme could be considered.

When the cogeneration unit is incorporated to the LDPE plant, the exported electricity has, in general, a better environmental profile, compared to the electricity for national network. The Emissions N_2O, CO, VOC, SO_x and ethylene decrease between a 35 and 74%.

71% of the required electricity is obtained using cogeneration, therefore electricity from National network should be used to cover the energetic requirements of the process, however, mixing both alternatives, the emissions decreases, so this alternative is the most favorable.

The LDPE analysis is useful to show the importance of the developed methodology in this work, because if additional software is employed, mistakes and/or variations in the results can be produced when the user transfer information “manually”. Also, the chosen software (TEAM®) is just focused in environmental assessment; thence a more deeply evaluation considering other aspects is necessary in order to help the decision-making step.

5.2 Case 2: Ethylene Oxide Process

According to the methodology described in the preliminary application with the LDPE process, a simplified environmental assessment was presented in this case study. The example of an ethylene oxide (EO) plant was selected to compare different process alternatives from the economical an environmental point of view.

Ethylene oxide was produced commercially by two basic routes: the ethylene chlorohydrin and direct oxidation processes. In the first case, the process involves the reaction of ethylene with hypochlorous acid followed by dehydrochlorination of the resulting chlorohydrin with lime to produce ethylene oxide and calcium chloride. This process is not economically competitive, thus it was replaced by the direct oxidation process as the dominant technology.

The direct oxidation technology uses the catalytic oxidation of ethylene with oxygen over a silver-based catalyst to yield ethylene oxide. Depending on the source of the oxidizing agent the process can be divided into two categories: the air-based process and the oxygen-based process. In the first, air or enriched air is fed directly to the system. In the second, a high purity oxygen stream from an air separation unit is employed as the source of the oxidizing agent.

Nowadays, all the ethylene oxide production in the world is obtained by the direct oxidation process. The ethylene oxide plants that have been built during the last years were oxygen-based processes, and a number of existing ethylene oxide plants were converted from the air to the oxygen-based process. Nevertheless to show the capabilities of the decision tool, the EO with air feed is presented in this work as an alternative to this process (Kirk-Othmer Encyclopedia of Chemical Technology, 2004).

5.2.1 Process simulation

Four alternatives are tested, using air or oxygen as raw material and electricity coming from cogeneration or the national network. The cogeneration process was modeled as an independent process like in the previous case (Figure 17, see Annexes VII and IX). Table 8 shows the operation conditions considered in the different configurations. Hysys® (previous version of ASPEN Hysys®), was the simulator chosen to obtain the streams characterization. The process conditions were taken from the literature (Ullmann's Encyclopedia of Industrial Chemistry, 1985; Kirk-Othmer Encyclopedia of Chemical Technology, 2004).

Table 8 Operation conditions of the ethylene oxide process

Stream	% mol
Ethylene feed	> 98
Oxygen feed	> 97 - 99
Ethylene oxide product	99.50

Unit	Pressure (kPa)
Reaction	1500
Absorption	1100
Desorption	800
Distillation	100

The ethylene oxide process is based on the main reaction:

$$C_2H_4 \quad + \quad \frac{1}{2}O_2 \quad \rightarrow \quad C_2H_4O$$

The significant by-products are carbon dioxide and water, which are formed either by complete combustion of ethylene or by oxidation of ethylene oxide:

$$C_2H_4 + 3\,O_2 \rightarrow 2CO_2 + H_2O$$

$$C_2H_4O + 2\frac{1}{2}\,O_2 \rightarrow 2CO_2 + 2H_2O$$

The main disadvantage of the direct oxidation process is the lower yield or selectivity of ethylene oxide per unit of ethylene consumed. In order to promote the oxidation of ethylene oxide, the ethylene conversion of the commercial processes is typically between 10 and 20%.

The process has been divided into three primary stages: reaction system, oxide recovery, and oxide purification. In the first section, compressed air is filtered, purified and fed separately with ethylene into a gas stream. This stream feeds reactors operated in parallel. The ethylene is oxidized to ethylene oxide, carbon dioxide, and water in the converters reactors and the heat of reaction is removed. The general conditions ranges suggested by literature for the reaction stage are summarized in Table 9 (Ullmann's Encyclopedia of Industrial Chemistry, 1985).

Table 9 Ranges of reaction variables in the Ethylene Oxide process

Variable	Air Oxidation	Oxygen oxidation
Ethylene (mol %)	2 -10	20 –35
Oxygen (mol %)	4 – 8	4 – 8
Carbon dioxide (mol%)	5 – 10	5 – 10
Ethane (mol%)	0 – 1	0 – 1
Temperature, C	220 – 277	220 – 235
Pressure, kPa	1000 – 3000	2000 – 4500
Selectivity or yield (mol basis %)	63 - 75	75 - 82

The second step, where the ethylene oxide is recovered, is accomplished in an absorber by scrubbing with cold water. The produced ethylene oxide is dissolved in the water with some nitrogen and carbon dioxide, and traces of ethylene, and ethane. The aqueous stream is removed from the base of the absorber and sent to a desorber.

In the oxide purification section, the water streams rich in ethylene oxide are fed to the top section of a desorber. The concentrated ethylene oxide vapor is fed to a stripper for further purification. The ethylene oxide recovered in the desorber contains some carbon dioxide, nitrogen, and traces of ethylene and ethane. In the stripper the light gases are separated overhead and vented, and the partially purified ethylene oxide is sent from the bottom of the stripper to a final refining column.

The flow diagram of the air-based ethylene oxide process developed in ASPEN Hysys® is shown in Figure 22. A detailed PFD including mass balance is presented in Annex VI.

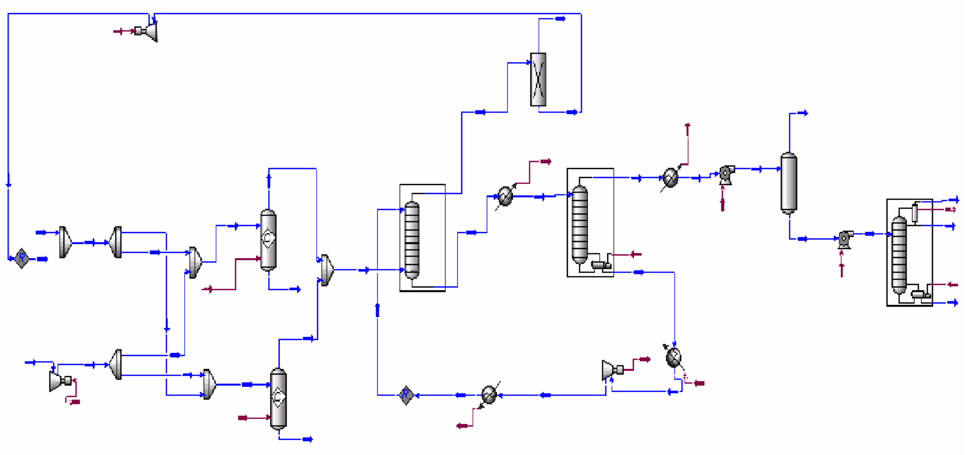


Figure 22 Air-based direct oxidation process diagram for EO production

There are important differences between air and oxygen-based processes, although the fundamental reaction and the final results are the same. The differences occur from the change in the oxidizing agent from air to pure oxygen (> 97%mol). The air process requires a purge stream, due to the low conversion, the need for complete removal of ethylene oxide by absorption, and the accumulation of nitrogen in the cycle. Since the oxygen-based process uses substantially pure oxygen, inert gases are reduced considerably, and thus a complete recycle of the unconverted ethylene is needed, eliminating the purge. When pure oxygen is fed to the reactor, the conversion to ethylene oxide is substantially higher than when the reactor receives air as reactant. Thus, the amount of ethylene and energy input required in the plant per unit of product (EO), is consequently lower using pure oxygen. Figure 23 shows the schematic diagram of an oxygen-based process obtained in ASPEN Hysys® (detailed in Annex VIII).

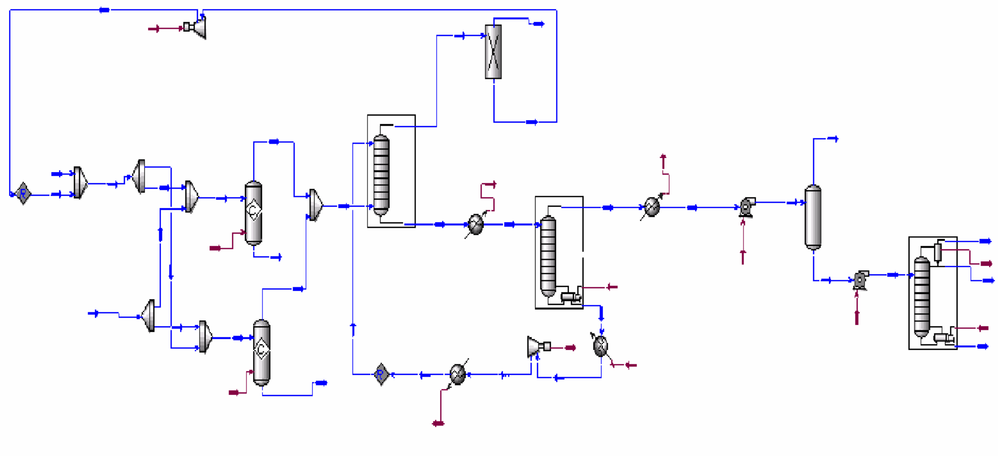


Figure 23 Oxygen-based direct oxidation process diagram for EO production

5.2.2 Life Cycle Inventory and Impact assessment

The final environmental loads associated to the process result from the balance between the environmental loads of associated raw material and the output compounds (including product, emissions, etc.). 1 kg of produced ethylene oxide is the functional unit. The considered secondary processes in this case study are:

- Ethylene Production
- Electricity generation in Spain
- Natural gas production
- Steam production by Natural Gas
- Deionized water

We have only taken into account the contribution of electricity associated to the manufacturing of oxygen to consider the environmental load corresponding to it production in a typical separation column. The steam production by natural gas corresponds to the by-product obtained in the cogeneration unit.

Table 10 shows the most representatives environmental loads included in the eco-vector for each configuration. As can be seen, the raw material and the origin of the energy have an important effect in the emissions and releases generated. In general, the lower values correspond to the configuration using oxygen and cogeneration. There are a lot of compounds that are not related to the *primary process*, as was mentioned in chapter 4, following the LC approach, the final inventory contain the elements from the *primary* and the *secondary* processes.

The processes configuration that use electricity produced by cogeneration include more secondary processes than the configuration using electricity by National network (natural gas, deionized water and steam processes), however, the steam is a by-product, and therefore its environmental loads are consider as avoided load, compensating the emissions generated in the cogeneration unit. This fact results in negative values for most of the burdens presented in Table 10. All the electricity is provided from the cogeneration unit and the generated steam can be used somewhere else in the plant or it can be sold obtaining economical benefits.

Table 10 Abbreviated ecovector for the ethylene oxide process

Compartment	Compound (Kg/Kg EO)	Process			
		Ox (Electricity)	Ox (Cogeneration)	Air (Electricity)	Air (Cogeneration)
Air	Ammonia	2.57E-08	-2.83E-09	1.08E-07	-3.80E-09
	Benzene	2.96E-07	-1.06E-06	1.24E-06	-1.42E-06
	Carbon Dioxide	1.08E+00	9.32E-01	2.24E+00	2.42E+00
	Carbon Monoxide	3.70E-04	1.48E-04	1.64E-03	1.00E-03
	Ethylene	2.91E-02	1.83E-01	1.63E-01	1.40E-04
	Methane	1.63E-03	1.40E-03	7.52E-03	8.17E-03
	Nitrogen Oxides	2.18E-03	2.10E-03	1.01E-02	1.15E-02
	Sulphur Oxides	2.09E-03	1.94E-03	9.63E-03	1.06E-02
Soil	Arsenic	4.76E-12	-5.45E-10	2.00E-11	-7.31E-10
	Cadmium	2.16E-15	-2.47E-13	9.07E-15	-3.31E-13
	Chromium	5.96E-11	-6.83E-09	2.51E-10	-9.15E-09
	Mercury	3.97E-16	-4.55E-14	1.67E-15	-6.09E-14
	Nickel	1.64E-14	-1.88E-12	6.91E-14	-2.52E-12
	Phosphorus	5.96E-10	-6.83E-08	2.51E-09	-9.15E-08
	Zinc	1.79E-10	-2.05E-08	7.53E-10	-2.75E-08
Water	Benzene	1.59E-08	-1.52E-08	6.68E-08	-2.03E-08
	Biochemical Oxygen Demand	9.03E-06	8.95E-06	4.19E-05	4.83E-05
	Lead	8.87E-09	-8.86E-09	3.73E-08	-1.19E-08
	Manganese	3.59E-08	-1.58E-08	1.51E-07	-2.12E-08
	Nitrates	3.70E-07	3.22E-07	1.70E-06	1.78E-06
	Sulphates	4.33E-05	1.38E-05	1.88E-04	1.03E-04
	Toluene	1.32E-08	-1.37E-08	5.55E-08	-1.83E-08

For each configuration, an independent inventory and analysis was carried out, and the results worksheets show the related compounds to a specific receiving environment and the process (primary or secondary), which generates this element. As can be seen in Figure 24 the main contribution corresponds to the ethylene production and the EO process plant (obtained from simulation in ASPEN Hysys®). The associated values are detailed in Table 11.

The processes using air as raw material employ more ethylene than the oxygen processes due to the lower yield in the reaction step. On the other hand, the emissions generated in EO process plant mainly correspond to the secondary reaction (see section 5.2.1), where the main product is CO_2.

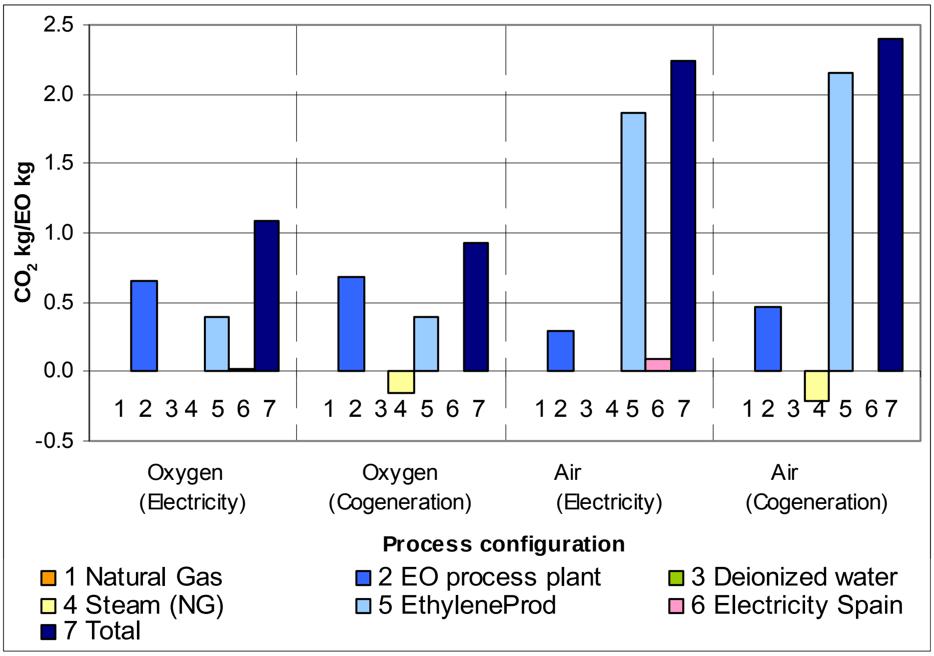


Figure 24 CO_2 emissions related to each configuration per stage

Table 11 CO_2 contribution per process stage in the ethylene oxide process

	Configuration			
	Oxygen		Air	
	Electricity CO_2 kg/EO kg	Cogeneration CO_2 kg/EO kg	Electricity CO_2 kg/EO kg	Cogeneration CO_2 kg/EO kg
Natural Gas Prod.	-	2.78E-03	-	1.17E-02
EO process plant	6.59E-01	6.88E-01	2.94E-01	4.67E-01
Deionized water	-	1.47E-04	-	7.28E-04
Steam (NG)	-	-1.60E-01	-	-2.15E-01
EthyleneProd	4.01E-01	4.01E-01	1.86E+00	2.15E+00
Electricity Spain	2.00E-02	-1.14E-07	8.42E-02	-9.50E-08
Total	1.08E+00	9.32E-01	2.24E+00	2.42E+00

Concerning to the environmental assessment level, all the impact categories were evaluated to validate the tool (automatic search, selection of secondary processes, results presentation). The selection of specific categories depends on the user preferences; this selection can be related to the emissions with higher values (if their have economical importance) and an environmental relevance, raw materials and product losses. The impact categories evaluated correspond to the Group A. "Baseline Impact categories" from the CML method for midpoints, and the associated endpoint categories from Eco-indicator 99 and IMPACT 2002+. Due to the CO_2, ethylene and ethylene oxide are the representative emissions generated in the ASPEN Hysys® simulation, the analysis could be centered in the categories that include these elements.

The lower values correspond to the process using oxygen and cogeneration. On the other hand, the process with the most important contribution corresponds to the air as raw material and electricity from the national network. Table 12, Table 13, Table 14 and Table 15 shows some of the impact categories evaluated for the air, soil and water receiving environments, and the natural resources extraction, respectively. These tables are generated automatically for each configuration process using the created tool. If the user wants to estimate the emissions and releases referred to a specific sub-process, it is possible to evaluate it.

Table 12 Impact categories associated to the emissions to air in the production of 1 kg of ethylene oxide

Method	Impact category	Characteristic	unit	Process configuration			
				Oxygen		Air	
				Electricity	Cogeneration	Electricity	Cogeneration
CML	Global warming	GWP100	kg CO2 eq.	1.12E+00	9.64E-01	2.41E+00	2.60E+00
		GWP20	kg CO2 eq.	1.18E+00	1.02E+00	2.70E+00	2.92E+00
		GWP500	kg CO2 eq.	1.09E+00	9.42E-01	2.29E+00	2.47E+00
	Human toxicity	HTP inf.	kg 1,4-dichlorobenzene eq.	4.10E+00	4.10E+00	2.29E+01	2.29E+01
		HTP 20	kg 1,4-dichlorobenzene eq.	4.10E+00	4.10E+00	2.29E+01	2.29E+01
		HTP 100	kg 1,4-dichlorobenzene eq.	4.10E+00	4.10E+00	2.29E+01	2.29E+01
		HTP 500	kg 1,4-dichlorobenzene eq.	4.10E+00	4.10E+00	2.29E+01	2.29E+01
	Freshwater aquatic ecotoxicity	FAETP inf.	kg 1,4-dichlorobenzene eq.	3.14E-03	-7.39E-06	1.72E-02	1.61E-02
		FAETP 20	kg 1,4-dichlorobenzene eq.	2.89E-03	-1.11E-06	1.61E-02	1.61E-02
		FAETP 100	kg 1,4-dichlorobenzene eq.	2.91E-03	-1.74E-06	1.62E-02	1.61E-02
		FAETP 500	kg 1,4-dichlorobenzene eq.	2.98E-03	-3.37E-06	1.65E-02	1.61E-02
	Marine aquatic ecotoxicity	MAETP inf.	kg 1,4-dichlorobenzene eq.	1.10E+01	-4.47E-01	4.64E+01	-4.60E-01
		MAETP 20	kg 1,4-dichlorobenzene eq.	2.60E-02	-1.85E-05	1.44E-01	1.39E-01
		MAETP 100	kg 1,4-dichlorobenzene eq.	3.06E-02	-1.59E-04	1.63E-01	1.39E-01
		MAETP 500	kg 1,4-dichlorobenzene eq.	5.47E-02	-9.02E-04	2.64E-01	1.38E-01
	Terrestrial ecotoxicity	TETP inf.	kg 1,4-dichlorobenzene eq.	1.84E-04	5.64E-05	8.78E-04	3.88E-04
		TETP 20	kg 1,4-dichlorobenzene eq.	7.55E-05	2.31E-05	4.19E-04	4.10E-04
		TETP 100	kg 1,4-dichlorobenzene eq.	8.26E-05	2.53E-05	4.49E-04	4.08E-04
		TETP 500	kg 1,4-dichlorobenzene eq.	1.10E-04	3.37E-05	5.64E-04	4.01E-04
	Stratospheric ozone depletion	ODP5	kg CFC-11 eq.	2.59E-09	-7.36E-10	1.09E-08	-9.86E-10
		ODP10	kg CFC-11 eq.	2.61E-09	-7.43E-10	1.10E-08	-9.96E-10
		ODP15	kg CFC-11 eq.	2.64E-09	-7.50E-10	1.11E-08	-1.01E-09
		ODP20	kg CFC-11 eq.	2.64E-09	-7.50E-10	1.11E-08	-1.01E-09
		ODP25	kg CFC-11 eq.	2.66E-09	-7.57E-10	1.12E-08	-1.01E-09
		ODP30	kg CFC-11 eq.	2.69E-09	-7.64E-10	1.13E-08	-1.02E-09
		ODP40	kg CFC-11 eq.	2.71E-09	-7.71E-10	1.14E-08	-1.03E-09
	Photo-oxidant formation	POCP (high Nox)	kg ethylene eq.	2.92E-02	1.83E-01	1.63E-01	2.11E-04
		POCP (low Nox)	kg ethylene eq.	2.92E-02	1.83E-01	1.63E-01	2.31E-04
		MIR (very high Nox)	kg formed ozone	6.00E-02	3.75E-01	3.35E-01	1.96E-03
		MOIR (high Nox)	kg formed ozone	6.79E-02	4.22E-01	3.79E-01	3.66E-03
		EBIR (low Nox)	kg formed ozone	7.72E-02	4.79E-01	4.32E-01	5.35E-03
	Acidification	AP	kg SO2 eq.	1.09E-03	1.05E-03	5.04E-03	5.76E-03
	Eutrophication	EP	kg PO4--- eq.	2.10E-03	7.95E-02	8.65E-01	1.19E+00
ECOINDICATOR 99	Carcinogenic effects on humans		DALY	5.33E-06	2.94E-09	2.98E-05	2.98E-05
	Damages to human health caused by climate change		DALY	2.34E-07	2.02E-07	5.03E-07	5.43E-07
	Human health effects caused by ozone layer depletion		DALY	3.17E-12	-9.00E-13	1.33E-11	-1.21E-12
IMPACT 2002+	Global Warming	GWP 500	kg CO2 eq.	1.09E+00	9.42E-01	2.29E+00	2.48E+00
	Human health effects caused by ozone layer depletion		kgeq of CFC-11 into air	3.01E-09	-8.57E-10	1.27E-08	-1.15E-09
	Human health effects caused by ozone layer depletion		DALY	3.17E-12	-9.00E-13	1.33E-11	-1.21E-12
	Human Toxicity (Carcinogenic effects)		kgeq of chloroethylene in air	7.34E-02	3.96E-05	4.09E-01	4.08E-01
	Human Toxicity (Carcinogenic effects)		DALY	2.06E-07	1.11E-10	1.15E-06	1.14E-06
	Human Toxicity (Non-carcinogenic effects)		kgeq of chloroethylene in air	4.93E-05	-1.02E-05	2.08E-04	-1.37E-05
	Human Toxicity (Non-carcinogenic effects)		DALY	1.38E-10	-2.86E-11	5.82E-10	-3.83E-11
	Total Human toxicity effects		kgeq of chloroethylene in air	7.34E-02	2.94E-05	4.10E-01	4.08E-01
	Total Human toxicity effects		DALY	2.06E-07	8.25E-11	1.15E-06	1.14E-06

Table 13 Impact categories associated to releases to soil in the production of 1 kg of ethylene oxide

Method	Impact category	Characteristic	unit	Process configuration			
				Oxygen		Air	
				Electricity	Cogeneration	Electricity	Cogeneration
CML	Human toxicity	HTP inf.	kg 1,4-dichlorobenzene eq.	2.88E-08	-3.30E-06	1.21E-07	-4.42E-06
		HTP 20	kg 1,4-dichlorobenzene eq.	3.22E-11	-3.69E-09	1.36E-10	-4.95E-09
		HTP 100	kg 1,4-dichlorobenzene eq.	1.62E-10	-1.86E-08	6.84E-10	-2.49E-08
		HTP 500	kg 1,4-dichlorobenzene eq.	8.05E-10	-9.21E-08	3.39E-09	-1.23E-07
	Freshwater aquatic ecotoxicity	FAETP inf.	kg 1,4-dichlorobenzene eq.	1.00E-08	-1.15E-06	4.21E-08	-1.54E-06
		FAETP 20	kg 1,4-dichlorobenzene eq.	7.52E-11	-8.61E-09	3.16E-10	-1.15E-08
		FAETP 100	kg 1,4-dichlorobenzene eq.	5.56E-10	-6.37E-08	2.34E-09	-8.54E-08
		FAETP 500	kg 1,4-dichlorobenzene eq.	2.62E-09	-3.00E-07	1.10E-08	-4.02E-07
	Marine aquatic ecotoxicity	MAETP inf.	kg 1,4-dichlorobenzene eq.	1.78E-06	-2.04E-04	7.49E-06	-2.73E-04
		MAETP 20	kg 1,4-dichlorobenzene eq.	1.44E-11	-1.65E-09	6.07E-11	-2.22E-09
		MAETP 100	kg 1,4-dichlorobenzene eq.	7.46E-10	-8.55E-08	3.14E-09	-1.15E-07
		MAETP 500	kg 1,4-dichlorobenzene eq.	2.47E-08	-2.83E-06	1.04E-07	-3.79E-06
	Terrestrial ecotoxicity	TETP inf.	kg 1,4-dichlorobenzene eq.	3.96E-07	-4.54E-05	1.67E-06	-6.08E-05
		TETP 20	kg 1,4-dichlorobenzene eq.	5.30E-10	-6.06E-08	2.23E-09	-8.13E-08
		TETP 100	kg 1,4-dichlorobenzene eq.	2.63E-09	-3.01E-07	1.11E-08	-4.04E-07
		TETP 500	kg 1,4-dichlorobenzene eq.	1.28E-08	-1.47E-06	5.39E-08	-1.97E-06
	Eutrophication	EP	kg PO4--- eq.	1.83E-09	-2.09E-07	7.68E-09	-2.80E-07
ECOINDICATOR 9	Carcinogenic effects on humans		DALY	1.62E-11	-1.86E-09	6.83E-11	-2.49E-09
	Damage to Ecosystem Quality caused by ecotoxic emissions		PDF*m2*yr	7.89E-07	-9.04E-05	3.32E-06	-1.21E-04
IMPACT 2002+	Terrestrial ecotoxicity caused by ecotoxic emissions		kgeq of triethylene glycol in soil	1.07E-03	-1.23E-01	4.50E-03	-1.64E-01
	Terrestrial ecotoxicity caused by ecotoxic emissions		PDF*m2*yr	8.46E-06	-9.69E-04	3.56E-05	-1.30E-03
	Human Toxicity (Carcinogenic effects)		kgeq of chloroethylene in air	4.63E-08	-5.31E-06	1.95E-07	-7.11E-06
	Human Toxicity (Carcinogenic effects)		DALY	1.30E-13	-1.49E-11	5.47E-13	-1.99E-11
	Human Toxicity (Non-carcinogenic effects)		kgeq of chloroethylene in air	4.82E-07	-5.52E-05	2.03E-06	-7.40E-05
	Human Toxicity (Non-carcinogenic effects)		DALY	1.35E-12	-1.55E-10	5.69E-12	-2.07E-10
	Total Human toxicity effects		kgeq of chloroethylene in air	5.28E-07	-6.05E-05	2.22E-06	-8.11E-05
	Total Human toxicity effects		DALY	1.48E-12	-1.70E-10	6.23E-12	-2.27E-10

Table 14 Impact categories associated to releases to water in the production of 1 kg of ethylene oxide

Method	Impact category	Characteristic	unit	Process configuration			
				Oxygen		Air	
				Electricity	Cogeneration	Electricity	Cogeneration
CML	Human toxicity	HTP inf.	kg 1,4-dichlorobenzene eq.	7.47E-04	-1.28E-04	3.14E-03	-1.71E-04
		HTP 20	kg 1,4-dichlorobenzene eq.	4.86E-04	-6.36E-05	2.05E-03	-8.51E-05
		HTP 100	kg 1,4-dichlorobenzene eq.	4.95E-04	-6.44E-05	2.08E-03	-8.61E-05
		HTP 500	kg 1,4-dichlorobenzene eq.	4.96E-04	-6.47E-05	2.09E-03	-8.65E-05
	Freshwater aquatic ecotoxicity	FAETP inf.	kg 1,4-dichlorobenzene eq.	3.13E-04	1.11E-04	1.38E-03	7.96E-04
		FAETP 20	kg 1,4-dichlorobenzene eq.	3.11E-04	1.13E-04	1.37E-03	7.98E-04
		FAETP 100	kg 1,4-dichlorobenzene eq.	3.12E-04	1.12E-04	1.38E-03	7.96E-04
		FAETP 500	kg 1,4-dichlorobenzene eq.	3.12E-04	1.12E-04	1.38E-03	7.96E-04
	Marine aquatic ecotoxicity	MAETP inf.	kg 1,4-dichlorobenzene eq.	3.09E-01	-9.59E-02	1.30E+00	-1.29E-01
		MAETP 20	kg 1,4-dichlorobenzene eq.	6.89E-05	-2.33E-05	2.90E-04	-3.11E-05
		MAETP 100	kg 1,4-dichlorobenzene eq.	3.81E-04	-1.49E-04	1.60E-03	-2.00E-04
		MAETP 500	kg 1,4-dichlorobenzene eq.	1.94E-03	-7.88E-04	8.15E-03	-1.06E-03
	Terrestrial ecotoxicity	TETP inf.	kg 1,4-dichlorobenzene eq.	5.40E-10	9.91E-13	2.27E-09	8.12E-12
		TETP 20	kg 1,4-dichlorobenzene eq.	5.86E-12	1.02E-12	2.53E-11	8.15E-12
		TETP 100	kg 1,4-dichlorobenzene eq.	1.13E-11	9.94E-13	4.81E-11	8.12E-12
		TETP 500	kg 1,4-dichlorobenzene eq.	5.19E-11	9.94E-13	2.19E-10	8.12E-12
ECOINDICATOR 99	Carcinogenic effects on humans		DALY	5.67E-11	-1.97E-10	2.39E-10	-2.65E-10
	Damage to Ecosystem Quality caused by ecotoxic emissions		PDF*m2*yr	3.68E-07	-1.48E-06	1.55E-06	-1.98E-06
IMPACT 2002+	Aquatic ecotoxicity caused by ecotoxic emissions		kgeq of triethylene glycol in water	3.23E-02	-5.07E-02	1.36E-01	-6.53E-02
	Aquatic ecotoxicity caused by ecotoxic emissions		PDF*m2*yr	1.62E-06	-2.55E-06	6.85E-06	-3.28E-06
	Human Toxicity (Carcinogenic effects)		kgeq of chloroethylene in air	3.83E-06	-1.30E-06	1.61E-05	-1.74E-06
	Human Toxicity (Carcinogenic effects)		DALY	5.53E-12	-1.88E-12	2.33E-11	-2.52E-12
	Human Toxicity (Non-carcinogenic effects)		kgeq of chloroethylene in air	1.88E-05	-1.85E-05	7.89E-05	-2.48E-05
	Human Toxicity (Non-carcinogenic effects)		DALY	2.71E-11	-2.68E-11	1.14E-10	-3.59E-11
	Total Human toxicity effects		kgeq of chloroethylene in air	2.26E-05	-1.98E-05	9.51E-05	-2.66E-05
	Total Human toxicity effects		DALY	3.26E-11	-2.86E-11	1.37E-10	-3.84E-11

Table 15 Impact categories associated to natural resources in the production of 1 kg of ethylene oxide

			Process configuration			
Method	**Impact category**	**unit**	**Oxygen**		**Air**	
			Electricity	**Cogeneration**	**Electricity**	**Cogeneration**
CML	Abiotic depletion	kg antimony eq.	3.46E-03	2.47E-03	1.60E-02	1.35E-02
ECOINDICATOR 99	Damage to Resources caused by extraction of minerals	MJ surplus energy	1.11E-04	8.49E-05	5.13E-04	4.61E-04
	Damage to Resources caused by extraction of fossil fuels	MJ surplus energy	1.02E+00	7.26E-01	4.70E+00	3.95E+00
IMPACT 2002+	Mineral extraction	kgeq of iron (in ore)	2.17E-03	1.67E-03	1.01E-02	9.05E-03
	Damage to Resources caused by extraction of minerals	MJ surplus energy	1.11E-04	8.49E-05	5.13E-04	4.61E-04

The highest impact values due to emissions to air (Table 12) are associated to the compounds mentioned above (CO_2, CH_4, NO_x, SO_x, ethylene and ethylene oxide). Special importance has the *Human toxicity, Marine, and Freswater aquatic ecotoxicity* impact categories. For *Human toxicity* and *Freshwater aquatic ecotoxicity*, the ethylene oxide is the main emissions associated to this impact, other process configuration could be centered in its reduction, because joint to the importance from the environment point of view, the ethylene oxide is the main product, therefore its diminution as emission could be translated in higer production. The “Electricity from Spanish Network” is the secondary process which mainly contributes to the Marine ecotoxicity (aquatic and sedimental) categories, due to the generated berilium and hydrogen fluoride emissions; thus, the cogeneration unit considerably reduces these impacts.

The main compounds whose contributes to the *Terrestrial ecotoxicity* are the ethylene oxide (from the EO process plant) and the vanadium (from electricity generation stage) emissions. Similarly, the ethylene is the principal emission that contributes to the *Photo-oxidant formation* category, as in the ethylene oxide case, its reduction will have benefits from the environmental and economic point of view, decreasing the manufacturing costs.

For releases to soil (Table 13), the compounds which have an important contribution to the impact categories are the chromium, zinc and phosphorus released in the "Electricity from Spanish Network" stage. The first one contributes to the *Terrestrial ecotoxicity* and *Human Toxicity* impact categories. The zinc is the main solid release associated to the *Marine* and *Freshwater aquatic ecotoxicy* categories.

The "Electricity generation" and the "Ethylene Production" are the secondary processes which produce the liquid releases associated to the evaluated impact categories (Table 14). The phenol and COD, generated in the "Ethylene Production", have the higher contribution to the *Freshwater aquatic ecotoxicity* and *Eutrophication* impact categories, respectively. On the other hand, the Polycyclic Aromatic Hydrocarbons, barium and mercury are released from the "Electricity generation" stage. These releases correspond to the *Human Toxicity*, *Marine aquatic* and *Terrestrial ecotoxicity* impact categories. Figure 25 shows the total contribution from the three considered receiving environments to the Terrestrial ecotoxicity impact category. Table 16 presents the associated values to this impact per stage of the process, considering emissions to air and releases to soil and water. Finally, the extraction of natural gas as fossil fuel associated to the "Ethylene Production" stage is the resource with the higher contribution to the *Abiotic Depletion* impact category (Table 15).

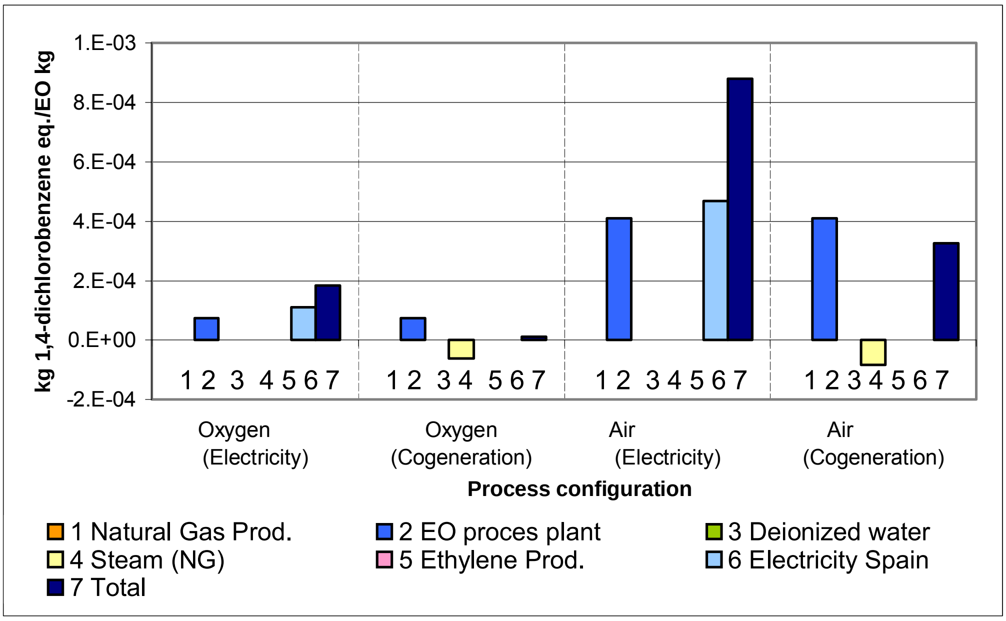


Figure 25 Contribution per stage of the EO process to Terrestrial ecotoxicity (inf.)

Table 16 Total emissions and releases associated to the Terrestrial sedimental ecotoxicity (inf.)

	Configuration			
	Oxygen		Air	
	Electricity kg 1,4-dichlorobenzene eq./EO kg	Cogeneration kg 1,4-dichlorobenzene eq./EO kg	Electricity kg 1,4-dichlorobenzene eq./EO kg	Cogeneration kg 1,4-dichlorobenzene eq./EO kg
Natural Gas Prod.	-	3.29E-14	-	1.38E-13
EO proces plant	7.35E-05	7.35E-05	4.11E-04	4.11E-04
Deionized water	-	2.30E-09	-	1.14E-08
Steam (NG)	-	-6.25E-05	-	-8.38E-05
Ethylene Prod.	1.66E-12	1.66E-12	7.71E-12	7.71E-12
Electricity Spain	1.11E-04	-6.32E-10	4.68E-04	-5.28E-10
Total	1.85E-04	1.10E-05	8.79E-04	3.27E-04

Since the CO_2 is the main emission related to the primary process, Global Warming category was evaluated. Figure 26 shows the contribution to greenhouse effect associated to the considered stages for each configuration (detailed values are reported in Table 17). The differences are directly related to the used raw material. CO_2 generated due to electricity consumption, in both processes using air as raw material are similar because the reduction of CO_2 emissions due to the use of cogeneration is balanced with the increase of electricity consumption for compressing the air to the reactor.

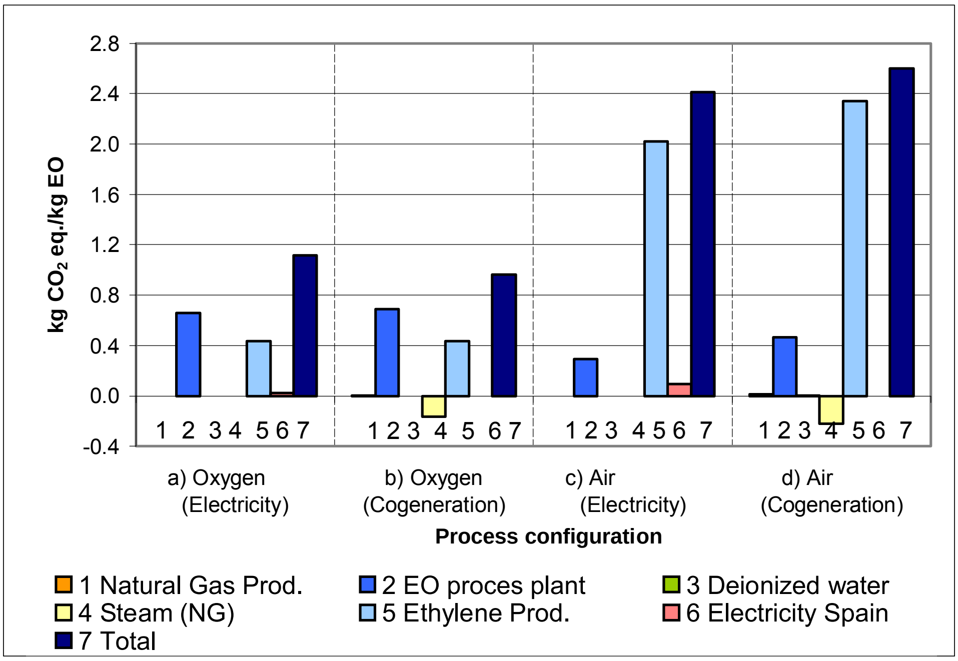


Figure 26 Contribution per stage of the EO process to Greenhouse effect (100 years)

Table 17 Total emissions associated to the GWP (100 years)

	Configuration			
	Oxygen		Air	
	Electricity	Cogeneration	Electricity	Cogeneration
	kg CO_2 eq./kg EO	kg CO_2 eq./kg EO	kg CO_2 eq./kg EO	kg CO_2 eq./kg EO
Natural Gas Prod.	-	3.54E-03	-	1.49E-02
EO proces plant	6.59E-01	6.88E-01	2.94E-01	4.67E-01
Deionized water	-	1.47E-04	-	7.29E-04
Steam (NG)	-	-1.64E-01	-	-2.20E-01
Ethylene Prod.	4.37E-01	4.37E-01	2.02E+00	2.34E+00
Electricity Spain	2.22E-02	-1.26E-07	9.33E-02	-1.05E-07
Total	1.12E+00	9.64E-01	2.41E+00	2.60E+00

A high amount of electricity is needed in the production stages ethylene oxide and ethylene, being the ethylene production the stage with higher energy requirements.

Processes using oxygen as prime material (a and b options), require less electricity than the processes using air (c and d option), due to it is not necessary a stream pre-treatment to obtain the oxygen from air. Employing oxygen, the process (b) needs less electricity due to the presence of cogeneration unit. CO_2 emissions due to the ethylene production are lower in process (a) and (b) because of the efficiency of the process related to the best yield at the reaction step.

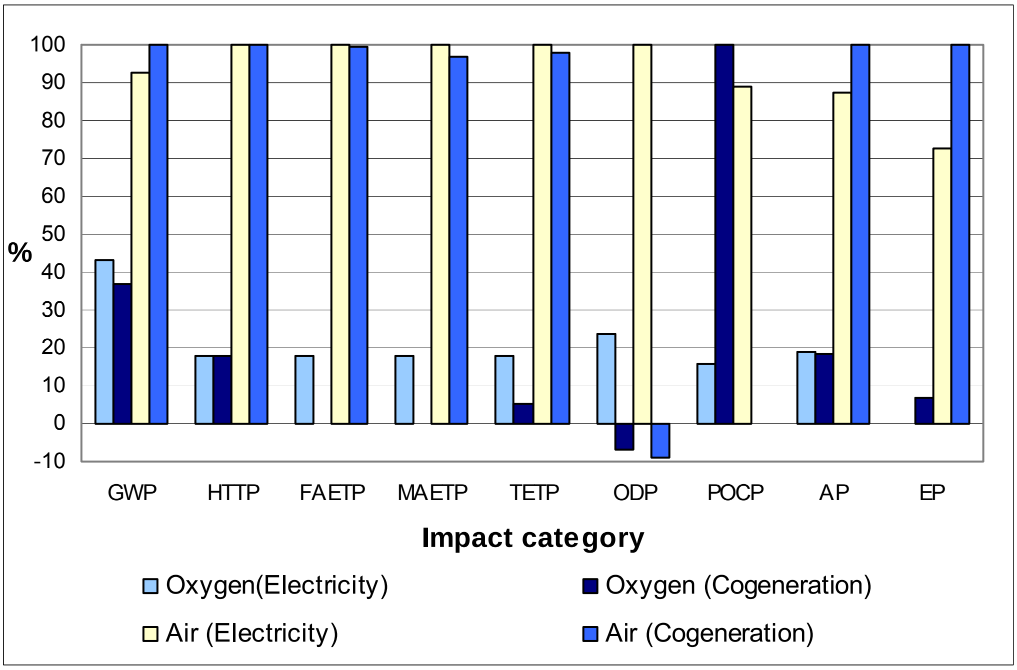


Figure 27 Impact categories diminution of the EO process associated to process configuration

As can be seen in Figure 27, the process configuration has an important role in the impact assessment profile. In order to quantifie the impact category difference between configurations, the maximum value was fixed as 100%, and then the percentage decrease was calculated to the other configurations (Table 18). In general, oxygen as raw material generates lower impact, excepting to photo-oxidant formation category (in the configuration using O_2 and cogeneration). Also, the cogeneration unit helps to reduce in the impacts; special attention has the *Freshwater aquatic ecotoxicity*, *Marine aquatic ecotoxicity*, and S*tratospheric ozone depletion* categories which have negative values when oxygen and cogeneration is used, producing a minimization in the correspondent environmental burdens. For example, in the *Global Warming* category, the configuration correspondent to oxygen and cogeneration generates a 34.9% of the impact generated in the process using air and cogeneration. Therefore, when O_2 and cogeneration is employed, the emissions are reduced in a 65%.

Table 18 Percentage decrease in the impact categories associated to the EO process.

Impact category	Process configuration			
	Oxygen		Air	
	Electricity %	Cogeneration %	Electricity %	Cogeneration %
Global warming	40.4	34.9	92.5	100.0
Human toxicity	17.9	17.9	100.0	100.0
Freshwater aquatic ecotoxicity	18.0	-0.011	100.0	99.0
Marine aquatic ecotoxicity	18.8	-0.1	100.0	85.2
Terrestrial ecotoxicity	18.4	5.6	100.0	90.9
Stratospheric ozone depletion	23.8	-6.8	100.0	-9.1
Photo-oxidant formation	16.0	100.0	89.2	0.1
Acidification	0.2	6.7	72.6	100.0
Eutrophication	17.9	0.010	100.0	100.0

In order to get information from each stage, an eco-matrix is used. The columns correspond to each stage and the rows correspond to related inputs, outputs or impacts. This method allows to evaluate "part-by-part" of the process in an independent way, and the total amount is obtained adding the columns; this arrangement facilitates the identification of the stage or stages with a bigger contribution, and it provides useful information for the optimization stage.

Table 19 shows the abbreviated eco-matrix for the process using oxygen as raw material and cogeneration. As can be seen, the secondary processes have an important role in the inventory and in the impact assessment, if just the compounds related to the primary process "EO process plant" are considered, the environmental profile will change considerably, especially in the burden minimization associated to the steam generation as by-product and the substitution in the electricity origin. The "Electricity from Spanish Network" process is included in Table 19 because the cogeneration unit generates more electricity than the necessary (less than 1% in excess), and this surplus is considered as avoided load.

Table 19 Eco-matrix of ethylene oxide based on oxygen cogeneration

Fate	Flow	Units	Stage						Total
			Methane Prod.	EO process plant	Deionized water	Steam (NG)	EthyleneProd.	Electricity Spain	
Air	(a) Acetaldehyde	kg/kg EO	-	-	6.20E-15	-2.79E-09	-	-3.77E-14	-2.79E-09
	(a) Acetic Acid	kg/kg EO	-	-	4.48E-14	-3.96E-07	-	-1.70E-13	-3.96E-07
	(a) Acetone	kg/kg EO	-	-	1.86E-14	-4.70E-10	-	-3.76E-14	-4.70E-10
	(a) Acetylene	kg/kg EO	-	-			-	-1.45E-12	-1.45E-12
	(a) Aldehyde	kg/kg EO	-	-	1.39E-12	-1.40E-09	-	-1.17E-14	-1.40E-09
	(a) Alkane	kg/kg EO	-	-	2.95E-10	-7.52E-06	-	-2.36E-12	-7.52E-06
	(a) Alkene	kg/kg EO	-	-	6.52E-13	-1.65E-08	-	-1.46E-12	-1.65E-08
	(a) Ammonia	kg/kg EO	-	-	7.77E-13	-2.84E-09	-	-1.46E-13	-2.83E-09
	(a) Arsenic	kg/kg EO	-	-	3.11E-15	-7.87E-11	-	-2.06E-14	-7.88E-11
	(a) Barium	kg/kg EO	-	-	4.00E-15	-1.01E-10	-	-1.46E-13	-1.01E-10
	(a) Benzaldehyde	kg/kg EO	-	-	1.24E-18	-3.15E-14	-	-1.56E-21	-3.15E-14
	(a) Benzene	kg/kg EO	-	-	1.62E-13	-1.06E-06	-	-1.68E-12	-1.06E-06
	(a) Benzo(a)pyrene	kg/kg EO	-	-	5.19E-16	-3.95E-11	-	-5.51E-15	-3.95E-11
	(a) Berylium	kg/kg EO	-	-	1.72E-17	-4.34E-13	-	-3.07E-15	-4.38E-13
	(a) Butane	kg/kg EO	-	-	9.23E-12	-2.15E-06	-1.18E-12	-	-2.15E-06
	(a) Butene	kg/kg EO	-	-	2.83E-14	-7.15E-10	-1.26E-14	-	-7.15E-10
	(a) Cadmium	kg/kg EO	-		4.71E-15	-1.19E-10	-1.01E-14	-	-1.19E-10
	(a) Carbon Dioxide	kg/kg EO	2.78E-03	6.88E-01	1.47E-04	-1.60E-01	4.01E-01	-1.14E-07	9.32E-01
	(a) Carbon Monoxide	kg/kg EO	2.64E-06	-	8.11E-08	-5.17E-05	1.97E-04	-9.82E-10	1.48E-04
	(a) Ethylene	kg/kg EO	-	1.83E-01	1.27E-09	-3.21E-05	-	-1.11E-11	1.83E-01
	(a) Ethylene glycol	kg/kg EO	-	1.95E-11	-	-	-	-	1.95E-11
	(a) Ethylene oxide	kg/kg EO	-	2.91E-04	-	-	-	-	2.91E-04
	(a) Hydrogen Fluoride	kg/kg EO	-	-	4.01E-13	-9.48E-09	-	-1.24E-12	-9.48E-09
	(a) Hydrogen Sulphide	kg/kg EO	-	-	4.00E-11	-1.01E-06	-	-9.38E-13	-1.01E-06
	(a) methane	kg/kg EO	3.31E-05	1.06E-08	6.43E-09	-1.67E-04	1.54E-03	-5.31E-10	1.40E-03
	(a) Nitrogen oxides (as NO2)	kg/kg EO	3.57E-05	-	7.35E-07	-8.13E-05	2.14E-03	-2.33E-10	2.10E-03
	(a) Sulphur Oxides	kg/kg EO	7.93E-06	1.40E-06	-3.82E-05	1.97E-03	-6.64E-10	-	1.94E-03
Soil	(s) Arsenic	kg/kg EO	-	-	2.15E-14	-5.45E-10	-	-2.71E-17	-5.45E-10
	(s) Cadmium	kg/kg EO	-	-	9.75E-18	-2.47E-13	-	-1.22E-20	-2.47E-13
	(s) Chromium	kg/kg EO	-	-	2.70E-13	-6.83E-09	-	-3.39E-16	-6.83E-09
	(s) Cobalt	kg/kg EO	-	-	9.89E-18	-2.50E-13	-	-1.24E-20	-2.50E-13
	(s) Copper	kg/kg EO	-	-	4.95E-17	-1.25E-12	-	-6.22E-20	-1.25E-12
	(s) Lead	kg/kg EO	-	-	2.26E-16	-5.73E-12	-	-2.84E-19	-5.73E-12
	(s) Mercury	kg/kg EO	-	-	1.80E-18	-4.55E-14	-	-2.26E-21	-4.55E-14
	(s) Nickel	kg/kg EO	-	-	7.43E-17	-1.88E-12	-	-9.33E-20	-1.88E-12
	(s) Nitrogen	kg/kg EO	-	-	8.44E-16	-2.14E-11	-	-1.06E-18	-2.14E-11
	(s) Phosphorus	kg/kg EO	-	-	2.70E-12	-6.83E-08	-	-3.39E-15	-6.83E-08
Water	(w) Ammonia	kg/kg EO	-	-	6.98E-13	-1.77E-08	1.04E-06	-8.76E-13	1.02E-06
	(w) Arsenic	kg/kg EO	-	-	5.16E-14	-1.31E-09	-	-1.49E-15	-1.31E-09
	(w) Biochemical Oxygen Demand	kg/kg EO	-	-	2.43E-09	-8.19E-08	9.03E-06	-2.62E-14	8.95E-06
	(w) Chemical Oxygen Demand	kg/kg EO	-	-	1.11E-09	-9.78E-07	4.68E-05	-4.10E-13	4.58E-05
	(w) Formaldehyde	kg/kg EO	-	-	1.65E-18	-4.18E-14	-	-2.07E-21	-4.18E-14
	(w) Methylene Chloride	kg/kg EO	-	-	3.74E-13	-9.46E-09	-	-4.69E-16	-9.46E-09
	(w) Nitrogenous compounds	kg/kg EO	-	-	8.50E-13	-2.15E-08	-	-3.81E-13	-2.15E-08
	(w) Tetrachloroethylene	kg/kg EO	-	-	3.49E-17	-8.97E-13	-	-4.38E-20	-8.97E-13

5.2.3 Economical Analysis

A global analysis is important to conclude which is the better option; for that reason the economical aspects have to be considered, combined to the environmental aspects. Table 20 shows the economical analysis results for the studied configurations. In this case study, two economical indicators were evaluated (NPV and PP, defined in section 4.4). Process using air as raw material and cogeneration has the higher Net Present Value (NPV, after 10 years of production). This is the process with the best economical yield. However, the investment is recovered earlier in the process using oxygen and cogeneration (~5 years, PP). Therefore the comparison between the four configurations shows that, from the economical point of view, the best option is obtained using cogeneration, however, the raw material selection depends on the decision-making preferences. If we want to recover the investment in less time, the oxygen has to be chosen. Otherwise, if we prefer higher benefits at the end of the project, the air is the best option.

Table 20 Economical Assessment results of the ethylene oxide process

	$\text{Oxygen}_{\text{Electricity}}$	$\text{Oxygen}_{\text{Cogeneration}}$	$\text{Air}_{\text{Electricity}}$	$\text{Air}_{\text{Cogeneration}}$
$\text{NPV}_{(\text{thousand €})}$	22622.81	34230.06	28830.16	36471.95
$\text{PP}_{(\text{years})}$	5.73	5.23	7.40	6.95

The economical analysis was carried out taking into account several considerations. The processes requirements establish the difference in the capital costs for the two configurations. On the other hand, the air process requires additional investment in the reactor and absorption stages. In general, the oxygen based process has a lower capital cost.

Also the operating costs have an important role in the economical assessment. The costs of the catalyst, oxygen, and ethylene are important factors. For a given catalyst type, the selectivity is higher in the oxygen process and it requires a smaller volume of catalyst. Although the cost of ethylene comprises the ~40% of the total manufacturing cost, the reaction yield have an important influence on the process economics.

The economical indicators calculated in this case study are enough to determine the viability of a process; however, in the next case, five indicators were included in the economical analysis worksheet, in order to support the final choice of the configuration process.

This case study was used to validate the developed tool, by means of the automation of the analysis (specific for this process). At the end of this evaluation, the environmental and economical assessment can be obtained. Related to the environmental evaluation, the inclusion of the secondary processes database permits the analysis from the Life Cycle methodology point of view.

This analysis demonstrates the importance of the origin of the energy, the raw material and the generated by-products. As in the previous case (LDPE production), the cogeneration reduce considerably the emissions. Both, air or oxygen as raw material has a better environmental profile when the unit cogeneration is implemented. Also, from the economic point of view, the steam production helps to increase the economical benefits; however, the investment is recovered in less time when the oxygen is employed.

Table 21 shows a score representation in order to facilitate the selection of the more favorable configuration process. On one hand, a value of 4 was assigned to the best option for each impact category and economic indicators, on the other hand, 1 represents the worst profile; for each category, an average was calculated when this category is evaluated in more than one receiving environment, perspective or time horizon.

Table 21 Environmental and economical scores summary for ethylene oxide process

	Process configuration			
Impact category	**Oxygen**		**Air**	
	Electricity	**Cogeneration**	**Electricity**	**Cogeneration**
Depletion of abiotic resources	3.0	4.0	1.0	2.0
Climate change	3.0	4.0	2.0	1.0
Stratospheric ozone depletion	2.0	3.0	1.0	4.0
Human toxicity	4.0	4.0	1.0	1.0
Ecotoxicity	2.5	3.5	1.0	3.2
Photo-oxidant formation	3.0	1.4	1.6	4.0
Acidification	3.0	4.0	2.0	1.0
Eutrophication	3.0	4.0	2.0	3.0
Average	2.9	3.5	1.5	2.4
Economical Indicator				
NPV	1	3	2	4
PP	3	4	1	2
Average	2.0	3.5	1.5	3.0

Taking into account the results obtained from the environmental and economical analysis, it can be concluded that the best process corresponds to the configuration employing oxygen and cogeneration. In this case, the same score was assigned to environment and economical analysis; however, the analysis could be only focused in the environmental or economic behavior, thus, different scores can be assigned depending on the point of view.

5.3 Case 3: Biodiesel Process

The analysis of a biodiesel plant was chosen to evaluate two different process alternatives in order to decide which is the most favorable configuration. An environmental assessment, economical evaluations and a sensitivity analysis are presented in this case study.

Recently, the awareness of energetic and environmental problems encouraged many researchers to investigate the possibility of using alternative fuels instead of crude oil and its derivatives (Carraretto et al., 2004). For this reason, biodiesel, as an alternative fuel, has many benefits. It is biodegradable and non-toxic. Compared to petroleum-based diesel, it has a more favorable combustion emission profile, such as low emissions of carbon monoxide, almost zero emissions of sulfates, particulate matter and unburned hydrocarbons (Salis, 2005).

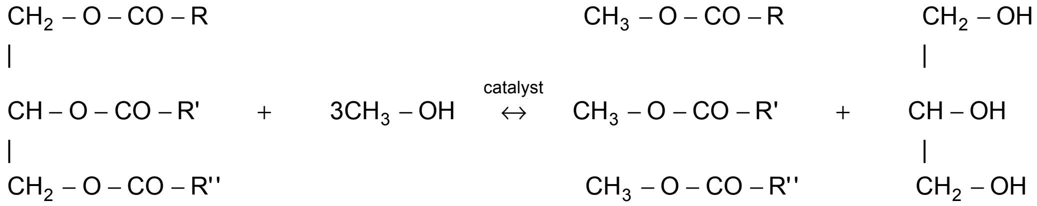
Biodiesel is a product of reaction between vegetable oil or animal fat and an alcohol (i.g. methanol). The reaction requires a catalyst, usually a strong base or acid, and produces methyl esters (biodiesel) (Van Gerpen, 2005).

5.3.1 Process Simulation

There are three basic routes to biodiesel production from oils and fats:

- Alkali catalyzed transesterification,
- Direct acid catalyzed transesterification,
- Conversion of the oil to its fatty acids and then to biodiesel.

In this work, two different configuration processes are analyzed: an alkali-catalyzed (Figure 28), and an acid-catalyzed process (Figure 29). Mass and energy balances of the processes are detailed in Annexes X and XI. The vegetable oil was simulated as triolein ($C_{57}H_{104}O_6$); the resulting biodiesel product was taken as methyl oleate ($C_{19}H_{36}O_2$). The reaction system was modeled as a standard transesterification reaction, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e. biodiesel) (Zhang et al., 2003).



$$\begin{array}{lcccccc} CH_2-O-CO-R & & & & CH_3-O-CO-R & & CH_2-OH \\ | & & & & & & | \\ CH-O-CO-R' & + & 3CH_3-OH & \overset{\text{catalyst}}{\leftrightarrow} & CH_3-O-CO-R' & + & CH-OH \\ | & & & & & & | \\ CH_2-O-CO-R'' & & & & CH_3-O-CO-R'' & & CH_2-OH \end{array}$$

Triglyceride Methanol Fatty acid methyl esther Glycerol

The information is obtained from the process simulator ASPEN Hysys® using the operation conditions and configuration process taken from the literature (Zhang et al., 2003). Some compounds were created in the simulator as hypothetical because their properties are not available in the database. The processes are divided in three stages: Pre-treatment (alkali-catalyzed process), reaction and separation step. The main process conditions are shown in Table 22.

Table 22 Description of operating conditions of biodiesel process configurations

Stage	Alkali Catalyzed	Acid Catalyzed
Pre-treatment		
Pressure (kPa)	20 – 400	-
Temperature (ºC)	28 - 70	-
Reaction		
Pressure (kPa)	400	400
Temperature (ºC)	60	80
Conversion (%)	95	97
Separation		
Pressure (kPa)	10 - 30	40 - 200
Temperature (ºC)	28 – 415	52 - 463

The alkali process requires a pre-treatment stage, consisting on an esterification reaction. The recycled and fresh methanol are mixed with the H_2SO_4 and fed to the esterification reactor, where the fatty acids are converted to methyl esters. The triolein is heated before enter to the reactor.

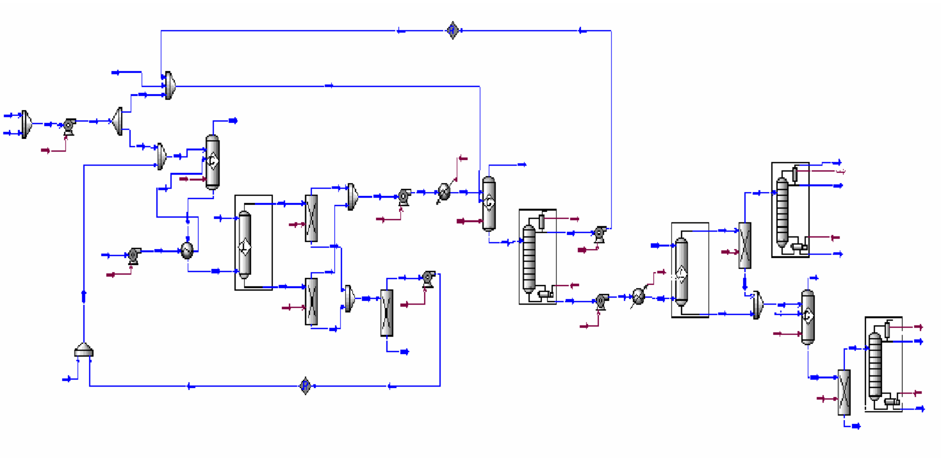


Figure 28 Alkali-catalyzed process diagram to produce biodiesel

The resulting water and acid catalyst (H_2SO_4), from the esterification reaction, is completely removed before the alkali-catalyzed transesterification employing a washing unit. The streams containing unreacted methanol is sent to a distillation column to recover it. The other stream is sent to the transesterification reactor.

The recycled and fresh methanol are mixed with the sodium hydroxide and fed to the transesterification reactor. The triolein is heated before enter to the reactor. The output stream from the reactor goes to a methanol recovery distillation column

In the separation step, a washing column is used to separate the biodiesel from the glycerol, methanol and the catalyst. The resulting stream consists of 85% biodiesel and water. This stream is sent to a distillation column in order to obtain a 99.6% biodiesel composition. This column operates under vacuum conditions in order to keep the temperatures low to prevent the degradation of the biodiesel. The biodiesel stream is obtained as a liquid distillate. Sodium hydroxide is removed by adding phosphoric acid. The resulting Na_3PO_4 is removed in a separator.

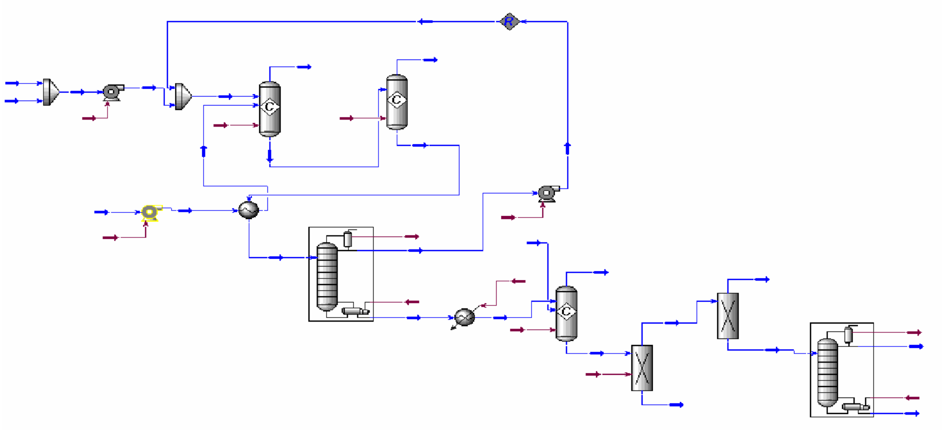


Figure 29 Acid-catalyzed process diagram to produce biodiesel

The acid-catalyzed process does not require a pre-treatment unit. The recycled and fresh methanol are mixed with the sulfuric acid and fed to the transesterification reactor. As in the alkali process, the triolein is heated before enter to the reactor. The reaction step uses two reactors operated in serial.

The second stage, the separation system, recovers the methanol in a distillation column. After that, sulfuric acid is completely removed by the reaction with calcium oxide to produce $CaSO_4$ and H_2O. A gravity separator is employed to remove the $CaSO_4$. The resulting stream consists of 79% biodiesel; the purification unit is similar to the used in the alkali process.

5.3.2 Life Cycle Inventory and Impact Assessment

Once the information is in the spreadsheet, all the values are associated to the functional unit (1 kg of biodiesel) obtaining the eco-vector (Sonneman et al., 2003). The inventory considers as "secondary processes" the electricity generation and raw material production (methanol, sulfuric acid, sodium hydroxide, calcium oxide, glycerol and deionized water). The glycerol production is considered as raw material in the alkali catalyzed process, but also as a by-product in both, the alkali as well as the acid catalyzed process, generating an avoided load in the environmental profile of the process.

Eight compounds take part in the acid-catalyzed process and ten in the alkali-catalyzed process; nevertheless, more than ~120 compounds are generated as emission in the biodiesel production, in the same way, ~40 and ~100 releases are associated to soil and water respectively. This fact is due to the Life Cycle Approach. The most important emissions related to the biodiesel production are CO_2, CH_4, NO_x, HCl, ethylene, vanadium, nickel, arsenic and HF.

Table 25 shows the environmental impact associated to emissions generated in the biodiesel proces. The main contribution to the *Marine aquatic ecotoxicity*, category comes from the emissions generated in the "methanol production" secondary process, specifically to the hydrogen fluoride and vanadium compounds. In the alkali-catalyzed, the HF is also emitted from the "Sodium hidroxide production" stage. The *Freshwater aquatic* and the *Terrestrial ecotoxicity* are produced by the vanadium generated in the "methanol production" stage.

The emissions associated to the "Methanol production stage" which mainly contributes to the S*tratospheric ozone depletion, Photo-oxidant formation, Acidification* and *Eutrophication* impact categories are the halon, ethylene, NO_x and HCl respectively.

In the *Global Warming Potential* (Figure 30), the CO_2 and the methane are the compounds which mainly contribute in this category; the detailed contributions are presented in Table 23. The carbon dioxide generated in the "calcium oxide production" stage produces a higher impact in the acid-catalyzed configuration; however, the difference with the alkali-catalyzed process is unimportant (1%). An important reduction in this category is obtained due to the avoided load, mainly in the alkali-catalyzed configuration; the CO_2 emitted in the "methanol production" stage is almost nullified with the generated as avoided load.

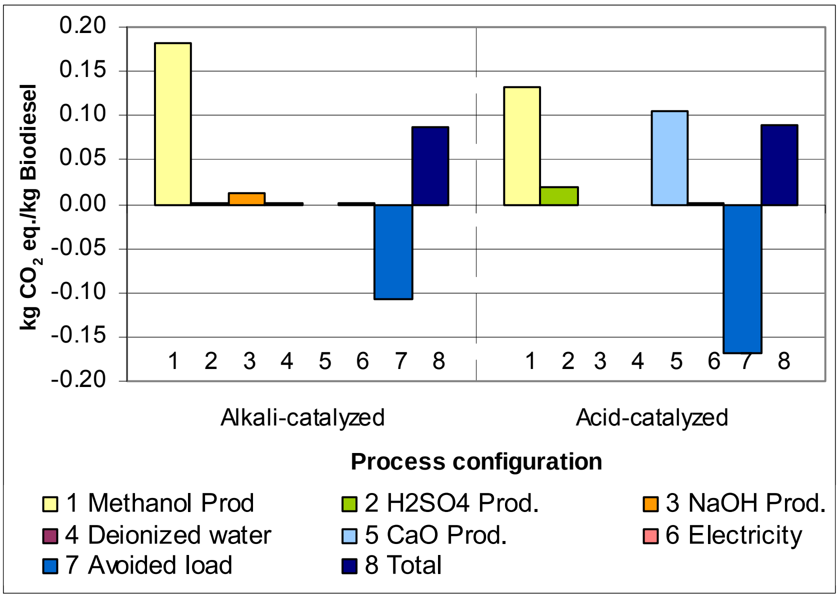


Figure 30 Contribution per stage of the biodiesel process to GWP 100

Table 23 Emissions per stage associated to GWP 100 in the biodiesel process

	Configuration	
	Alkali-catalyzed	Acid-catalyzed
	kg CO_2 eq./kg Biodiesel	kg CO_2 eq./kg Biodiesel
Methanol Prod	1.81E-01	1.32E-01
H_2SO_4 Prod.	6.60E-04	1.95E-02
NaOH Prod.	1.15E-02	-
Deionized water	3.35E-06	-
CaO Prod.	-	1.04E-01
Electricity	5.75E-04	1.28E-05
Avoided load	-1.07E-01	-1.67E-01
Total	8.75E-02	8.84E-02

The contribution from the three receiving environment to the *Human Toxicity* category is presented in Figure 31. The compounds with higher participation in this category are the HF, nickel and arsenic generated in the "methanol production stage".

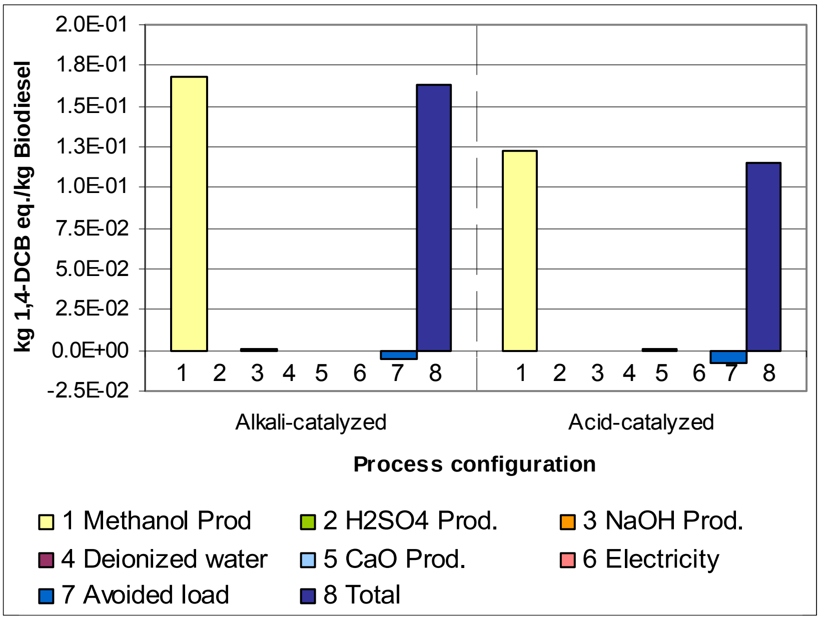


Figure 31 Contribution per stage of the biodiesel process to Human Toxicity (inf)

Table 24 Total contribution to the Human Toxicity impact category in the biodiesel process

	Configuration	
	Alkali-catalyzed	Acid-catalyzed
	kg 1,4-DCB eq./kg Biodiesel	kg 1,4-DCB eq./kg Biodiesel
Methanol Prod	1.68E-01	1.23E-01
H_2SO_4 Prod.	3.49E-08	1.03E-06
NaOH Prod.	2.71E-04	-
Deionized water	2.07E-08	-
CaO Prod.	-	7.60E-04
Electricity	1.57E-04	3.06E-06
Avoided load	-5.33E-03	-8.37E-03
Total	1.63E-01	1.15E-01

In the impact categories associated to emissions, the lower values correspond to the acid-catalyzed process; a reduction of ~25% is obtained compared to the alkaline option. Similarly, the acid-catalyzed process has a better profile when the soil as receiving environment is evaluated (Table 26).

The glycerol considered as by-product has a positive influence in the environmental profile of the biodiesel production, since avoided loads are generated. *Human toxicity*, *Freshwater aquatic ecotoxicity*, and *Marine aquatic ecotoxicity* categories generate a reduction in the environmental impact due to this fact. For the first category, the impact associated to the chromium release from the "methanol production" stage is compensated by the barium release coming from the "glycerol production" stage (avoided load). The same effect can be observed in the *Freshwater* and *Marine aquatic ecotoxicity* categories, in this case the zinc release effect are nullified by the cooper and barium releases generated as avoided load, respectively.

The difference between the acid and the alkali configurations are caused because this process obtain the glycerol as by-product, whereas the basic-catalyzed process requires more glycerol as raw material in the pre-treatment than the generated as by-product.

Table 25 Impact categories associated to the emissions to air in the biodiesel production

Method	Impact category	Characteristic	unit	Process configuration	
				Alkali-catalyzed	Acid-catalyzed
CML	Global warming	GWP100	kg CO2 eq.	8.75E-02	8.84E-02
		GWP20	kg CO2 eq.	2.14E-01	1.80E-01
		GWP500	kg CO2 eq.	3.57E-02	5.06E-02
	Human toxicity	HTP inf.	kg 1,4-dichlorobenzene eq.	1.36E-01	9.53E-02
		HTP 20	kg 1,4-dichlorobenzene eq.	8.65E-02	5.92E-02
		HTP 100	kg 1,4-dichlorobenzene eq.	8.65E-02	5.92E-02
		HTP 500	kg 1,4-dichlorobenzene eq.	8.96E-02	6.15E-02
	Freshwater aquatic ecotoxicity	FAETP inf.	kg 1,4-dichlorobenzene eq.	8.26E-03	6.03E-03
		FAETP 20	kg 1,4-dichlorobenzene eq.	5.66E-04	4.08E-04
		FAETP 100	kg 1,4-dichlorobenzene eq.	1.11E-03	8.06E-04
		FAETP 500	kg 1,4-dichlorobenzene eq.	3.08E-03	2.24E-03
	Marine aquatic ecotoxicity	MAETP inf.	kg 1,4-dichlorobenzene eq.	3.23E+02	2.34E+02
		MAETP 20	kg 1,4-dichlorobenzene eq.	3.29E-02	2.34E-02
		MAETP 100	kg 1,4-dichlorobenzene eq.	1.76E-01	1.27E-01
		MAETP 500	kg 1,4-dichlorobenzene eq.	9.22E-01	6.71E-01
	Terrestrial ecotoxicity	TETP inf.	kg 1,4-dichlorobenzene eq.	3.70E-03	2.49E-03
		TETP 20	kg 1,4-dichlorobenzene eq.	6.44E-05	4.21E-05
		TETP 100	kg 1,4-dichlorobenzene eq.	3.02E-04	1.97E-04
		TETP 500	kg 1,4-dichlorobenzene eq.	1.24E-03	8.11E-04
	Stratospheric ozone depletion	ODP5	kg CFC-11 eq.	1.04E-07	7.72E-08
		ODP10	kg CFC-11 eq.	1.05E-07	7.80E-08
		ODP15	kg CFC-11 eq.	1.06E-07	7.87E-08
		ODP20	kg CFC-11 eq.	1.06E-07	7.87E-08
		ODP25	kg CFC-11 eq.	1.07E-07	7.95E-08
		ODP30	kg CFC-11 eq.	1.08E-07	8.02E-08
		ODP40	kg CFC-11 eq.	1.09E-07	8.10E-08
	Photo-oxidant formation	POCP (high Nox)	kg ethylene eq.	1.65E-04	1.22E-04
		POCP (low Nox)	kg ethylene eq.	1.83E-04	1.37E-04
		MIR (very high Nox)	kg formed ozone	2.67E-04	2.06E-04
		MOIR (high Nox)	kg formed ozone	3.25E-04	2.49E-04
		EBIR (low Nox)	kg formed ozone	3.77E-04	2.89E-04
	Acidification	AP	kg SO2 eq.	6.15E-04	4.94E-04
	Eutrophication	EP	kg PO4--- eq.	6.78E-04	5.46E-04
ECOINDICATOR 99	Damages to human health caused by climate change		DALY	1.69E-08	1.75E-08
	Damage to Ecosystem Quality caused by the combined effect of acidification and eutrophication		PDF*m2*yr	7.04E-03	5.66E-03
IMPACT 2002+	Global Warming	GWP 500	kg CO2 eq.	3.65E-02	5.11E-02
	Human Toxicity (Carcinogenic effects)		kgeq of chloroethylene in air	6.74E-03	4.91E-03
			DALY	1.89E-08	1.38E-08
	Human Toxicity (Non-carcinogenic effects)		kgeq of chloroethylene in air	1.19E-03	8.71E-04
			DALY	3.34E-09	2.44E-09
	Total Human toxicity effects		kgeq of chloroethylene in air	7.93E-03	5.79E-03
			DALY	2.22E-08	1.62E-08
	Damage to Ecosystem Quality caused by the combined effect of acidification and eutrophication		kgeq of SO2 into air	6.76E-03	5.44E-03
			PDF*m2*yr	7.04E-03	5.66E-03

Table 26 Impact categories associated to releases to soil in the biodiesel production

Method	Impact category	Characteristic	unit	Process configuration	
				Alkali-catalyzed	Acid-catalyzed
CML	Human toxicity	HTP inf.	kg 1,4-dichlorobenzene eq.	-2.44E-05	-4.57E-05
		HTP 20	kg 1,4-dichlorobenzene eq.	-4.08E-08	-7.22E-08
		HTP 100	kg 1,4-dichlorobenzene eq.	-2.04E-07	-3.62E-07
		HTP 500	kg 1,4-dichlorobenzene eq.	-5.29E-07	-1.03E-06
	Freshwater aquatic ecotoxicity	FAETP inf.	kg 1,4-dichlorobenzene eq.	-5.39E-05	-8.73E-05
		FAETP 20	kg 1,4-dichlorobenzene eq.	-1.32E-06	-2.10E-06
		FAETP 100	kg 1,4-dichlorobenzene eq.	-7.77E-06	-1.24E-05
		FAETP 500	kg 1,4-dichlorobenzene eq.	-2.78E-05	-4.44E-05
	Marine aquatic ecotoxicity	MAETP inf.	kg 1,4-dichlorobenzene eq.	-5.23E-02	-8.27E-02
		MAETP 20	kg 1,4-dichlorobenzene eq.	-3.71E-07	-5.87E-07
		MAETP 100	kg 1,4-dichlorobenzene eq.	-1.32E-05	-2.09E-05
		MAETP 500	kg 1,4-dichlorobenzene eq.	-2.97E-04	-4.73E-04
	Terrestrial ecotoxicity	TETP inf.	kg 1,4-dichlorobenzene eq.	1.19E-04	8.76E-05
		TETP 20	kg 1,4-dichlorobenzene eq.	6.12E-08	-3.75E-08
		TETP 100	kg 1,4-dichlorobenzene eq.	3.60E-07	-9.83E-08
		TETP 500	kg 1,4-dichlorobenzene eq.	2.58E-06	8.26E-07
	Eutrophication	EP	kg PO4--- eq.	5.60E-07	4.19E-07
ECOINDICATOR 99	Carcinogenic effects on humans		DALY	4.98E-09	3.72E-09
	Damage to Ecosystem Quality caused by ecotoxic emissions		PDF*m2*yr	1.29E-04	2.78E-06
IMPACT 2002+	Aquatic ecotoxicity caused by ecotoxic emissions		kgeq of triethylene glycol in water	6.88E-02	4.46E-02
	Terrestrial ecotoxicity caused by ecotoxic emissions		kgeq of triethylene glycol in soil	3.28E-01	2.45E-01
			PDF*m2*yr	2.59E-03	1.94E-03
	Human Toxicity (Carcinogenic effects)		kgeq of chloroethylene in air	1.42E-05	1.06E-05
			DALY	3.98E-11	2.98E-11
	Human Toxicity (Non-carcinogenic effects)		kgeq of chloroethylene in air	1.42E-04	1.02E-04
			DALY	3.99E-10	2.87E-10
	Total Human toxicity effects		kgeq of chloroethylene in air	1.57E-04	1.13E-04
			DALY	4.39E-10	3.17E-10

Table 27 Impact categories associated to releases to water in the biodiesel production

Method	Impact category	Characteristic	unit	Process configuration	
				Alkali-catalyzed	Acid-catalyzed
CML	Human toxicity	HTP inf.	kg 1,4-dichlorobenzene eq.	2.73E-02	2.02E-02
		HTP 20	kg 1,4-dichlorobenzene eq.	1.92E-02	1.42E-02
		HTP 100	kg 1,4-dichlorobenzene eq.	1.95E-02	1.45E-02
		HTP 500	kg 1,4-dichlorobenzene eq.	1.96E-02	1.45E-02
	Freshwater aquatic ecotoxicity	FAETP inf.	kg 1,4-dichlorobenzene eq.	4.53E-03	3.00E-03
		FAETP 20	kg 1,4-dichlorobenzene eq.	4.50E-03	2.98E-03
		FAETP 100	kg 1,4-dichlorobenzene eq.	4.51E-03	2.98E-03
		FAETP 500	kg 1,4-dichlorobenzene eq.	4.51E-03	2.98E-03
	Marine aquatic ecotoxicity	MAETP inf.	kg 1,4-dichlorobenzene eq.	1.04E+01	7.65E+00
		MAETP 20	kg 1,4-dichlorobenzene eq.	2.10E-03	1.52E-03
		MAETP 100	kg 1,4-dichlorobenzene eq.	1.08E-02	7.74E-03
		MAETP 500	kg 1,4-dichlorobenzene eq.	5.39E-02	3.86E-02
	Terrestrial ecotoxicity	TETP inf.	kg 1,4-dichlorobenzene eq.	4.34E-06	-3.77E-07
		TETP 20	kg 1,4-dichlorobenzene eq.	3.41E-09	-3.04E-09
		TETP 100	kg 1,4-dichlorobenzene eq.	4.47E-08	-6.58E-09
		TETP 500	kg 1,4-dichlorobenzene eq.	3.75E-07	-3.51E-08
	Eutrophication	EP	kg PO4--- eq.	2.69E-06	1.54E-06
ECOINDICATOF	Carcinogenic effects on humans		DALY	2.85E-10	-1.23E-09
	Human health effects caused by ionising radiation		DALY	6.70E-16	4.95E-16
	Damage to Ecosystem Quality caused by ecotoxic emissions		PDF*m2*yr	7.47E-06	-1.19E-06
IMPACT 2002+	Aquatic ecotoxicity caused by ecotoxic emissions		kgeq of triethylene glycol in water	1.11E+00	7.37E-01
			PDF*m2*yr	5.59E-05	3.70E-05
	Terrestrial ecotoxicity caused by ecotoxic emissions		kgeq of triethylene glycol in soil	9.31E-08	6.49E-08
			PDF*m2*yr	7.36E-10	5.13E-10
	Human Toxicity (Carcinogenic effects)		kgeq of chloroethylene in air	1.04E-05	5.77E-06
			DALY	2.92E-11	1.62E-11
	Human Toxicity (Non-carcinogenic effects)		kgeq of chloroethylene in air	6.49E-04	4.61E-04
			DALY	1.82E-09	1.29E-09
	Total Human toxicity effects		kgeq of chloroethylene in air	6.59E-04	4.66E-04
			DALY	1.85E-09	1.31E-09

When the releases to water are estimated (Table 27), the compounds associated to the "methanol production" stage significantly contribute to the *Human Toxicity*, *Freshwater aquatic ecotoxicity*, *Marine aquatic ecotoxicity*, *Terrestrial ecotoxicity* and *Eutrophication* categories. The aquatic ecotoxicity is produced by the barium release generated in this stage, while the polycyclic aromatic hydrocarbons have the same effect in the *Human toxicity* category.

The extraction of natural gas as fossil fuel associated to the "Methanol Production" stage is the resource with the higher contribution to the *Abiotic Depletion* impact category. This process has the same effect in the *Land use* impact category (Table 28). The Eco-Indicator 99 and IMPACT 2002+ methods were employed to calculate the associated endpoint impact categories.

Table 28 Impact categories associated to natural resources extraction and landuse in the production of 1 kg of biodiesel

Method	**Impact category**	**unit**	**Process configuration**	
			Alkali-catalyzed	**Acid-catalyzed**
CML	Abiotic depletion	kg antimony eq.	-6.33E-04	1.28E-03
	Landuse increase of land competition	m2*yr	3.65E-05	1.41E-03
	Damage to Ecosystem Quality caused by land occupation	PDF*m2*yr	1.15E-05	4.43E-04
ECOINDICATOR 99	Damage to Resources caused by extraction of minerals	MJ surplus energy	-1.27E-05	5.24E-05
	Damage to Resources caused by extraction of fossil fuels	MJ surplus energy	-1.86E-01	3.75E-01
IMPACT 2002+	Land occupation	PDF*m2*yr	1.15E-05	4.43E-04
	Damage to Ecosystem Quality caused by land occupation	m2eq of organic arable land	1.05E-05	4.06E-04
	Mineral extraction	kgeq of iron (in ore)	-2.50E-04	1.03E-03
	Damage to Resources caused by extraction of minerals	MJ surplus energy	-1.27E-05	5.24E-05

As in the previous case, the percentage change in the impact categories was calculated in function of the process configuration. As can be seen in Figure 32, when the acid catalyst is employed, an important reduction is generated in the impact categories. Therefore, based on the obtained results of the three analyzed receiving environments, the acid-catalyzed process to obtain biodiesel is the best option from the environmental perspective.

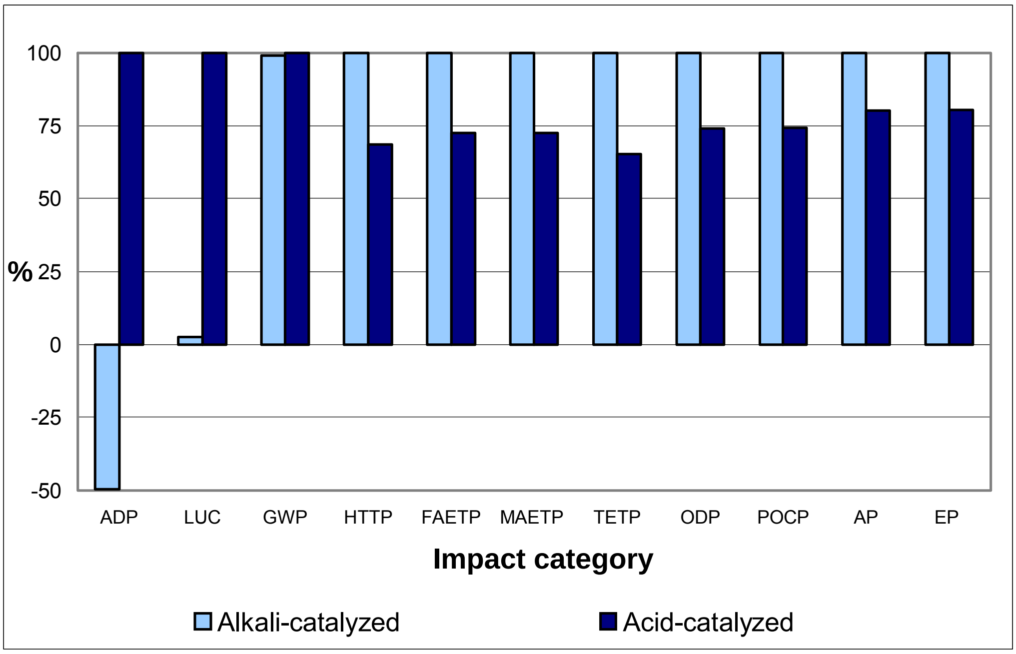


Figure 32 Impact categories diminution of the biodiesel process associated to process configuration

Table 29 Percentage decrease in the impact categories associated to the biodiesel process.

Impact category	**Process configuration** **Alkali-catalyzed** %	 **Acid-catalyzed** %
Abiotic depletion	-49.51	100.00
Landuse increase of land competi	2.59	100.00
Global warming	99.00	100.00
Human toxicity	100.00	68.49
Freshwater aquatic ecotoxicity	100.00	72.55
Marine aquatic ecotoxicity	100.00	72.50
Terrestrial ecotoxicity	100.00	65.19
Stratospheric ozone depletion	100.00	74.06
Photo-oxidant formation	100.00	74.27
Acidification	100.00	80.26
Eutrophication	100.00	80.46

Table 30 corresponds to the abbreviated inventory of the biodiesel process. Due to the glycerol is considered as by-product, all its emissions and releases are represented as avoided loads (negative values). This fact derives in a diminution in the associated impact categories. The same effect has this stage in the alkali-catalyzed process, but not in the same magnitude since, as it was mentioned above, this process configuration requires the glycerol as raw material, and the generated avoided load correspond to the difference between the associated burdens.

Table 30 Inventory of the acid-catalyzed biodiesel process

Fate	**Flow**			**Stage**				
		Biodiesel	**Methanol Prod.**	**CaO Prod.**	**Electricity**	**H_2SO_4 Prod.**	**Avoided load**	**Total**
		kg/kg biodiesel	kg/kg biodiesel	kg/kg biodiesel	kg/kg biodiesel	kg/kg biodiesel	kg/kg biodiesel	kg/kg biodiesel
Air	(a) Acetaldehyde	-	1.63E-07	4.97E-07	3.84E-12	-	-	6.60E-07
	(a) Acetic Acid	-	9.96E-07	7.05E-08	1.73E-11	-	-4.41E-05	-4.30E-05
	(a) Ammonia	-	5.12E-07	5.14E-10	1.48E-11	-	-6.91E-07	-1.78E-07
	(a) Arsenic	-	6.56E-08	7.00E-25	5.60E-22	-	-4.61E-12	6.56E-08
	(a) Berylium	-	5.15E-09	9.32E-12	5.61E-13	-	-1.15E-12	5.16E-09
	(a) Butane	-	7.72E-06	7.75E-14	3.13E-13	-	-	7.72E-06
	(a) Carbon Dioxide	-	7.81E-02	3.13E-09	1.16E-05	1.95E-02	-	9.75E-02
	(a) Carbon Monoxide	-	4.09E-04	1.03E-01	9.99E-08	2.73E-06	-7.94E-05	1.03E-01
	(a) Cobalt	-	4.53E-08	-	2.44E-12	-	-2.94E-12	4.53E-08
	(a) Cyanide	-	7.05E-09	1.38E-10	1.77E-13	-	-	7.19E-09
	(a) Dioxins (unspecified)	-	5.27E-14	1.48E-11	1.34E-18	-	-4.20E-12	1.07E-11
	(a) Formaldehyde	-	1.13E-06	9.64E-14	2.02E-11	-	-4.47E-09	1.13E-06
	(a) Hexane	-	1.08E-06	9.19E-27	2.56E-11	-	-	1.08E-06
	(a) Hydrogen	-	5.90E-12	6.26E-09	1.51E-16	-	-2.61E-06	-2.60E-06
	(a) Hydrogen Fluoride	-	4.66E-06	1.27E-08	1.26E-10	3.60E-10	-1.25E-08	4.66E-06
	(a) Hydrogen Sulphide	-	5.53E-06	1.77E-09	9.55E-11		-4.66E-09	5.53E-06
	(a) Mercury	-	8.82E-09	2.62E-09	2.36E-13	-	-6.68E-10	1.08E-08
	(a) methane	-	2.36E-03	6.00E-14	5.41E-08	-	-4.42E-05	2.31E-03
	(a) Methanol	-	5.47E-07	4.54E-05	1.30E-11	-	-2.22E-05	2.38E-05
	(a) Molybdenum	-	2.83E-08	5.99E-11	1.37E-12	-	-2.36E-14	2.84E-08
	(a) Nitrogen oxides (as NO2)	-	8.77E-04	8.29E-10	2.37E-08	1.13E-04	-3.24E-05	9.57E-04
	(a) Phosphorus	-	2.32E-07	4.30E-14	8.65E-12	-	-5.26E-13	2.32E-07
	(a) Phosphorus Pentoxide	-	1.57E-10	1.93E-11	4.03E-15	-	-	1.76E-10
	(a) Propylene	-	1.62E-06	4.72E-09	1.54E-10	-	-	1.62E-06
	(a) Toluene	-	1.27E-06	1.21E-11	4.33E-11	-	-1.60E-08	1.26E-06
	(a) Zinc	-	2.19E-07	3.97E-09	9.76E-12	-	-1.69E-08	2.06E-07
Soil	(s) Aluminium	-	2.82E-06	1.26E-16	6.90E-12	-	-3.28E-07	2.49E-06
	(s) Arsenic	-	1.13E-09	2.43E-04	2.76E-15	-	-1.31E-10	2.43E-04
	(s) Barium	-	-	9.71E-11	-	-	-1.64E-07	-1.64E-07
	(s) Cadmium	-	-	-	1.25E-18	-	-	1.25E-18
	(s) Calcium	-	1.13E-05	4.39E-14	2.76E-11	-	-1.31E-06	9.96E-06
	(s) Calcium Oxide	-	-	9.71E-07	-	-	-	9.71E-07
	(s) Calcium Sulphate	1.97E-01	-	-	-	-	-	1.97E-01
	(s) Chloride	-	-	7.29E-07	-	-	-1.15E-06	-4.19E-07
	(s) Chromium	-	1.41E-08	-	3.45E-14	-	-1.64E-09	1.25E-08
	(s) Copper	-	2.59E-12	4.45E-14	6.33E-18	-	-1.19E-07	-1.19E-07
	(s) Iron	-	5.64E-06	2.23E-13	1.38E-11	-	-6.56E-07	4.98E-06
	(s) Phosphorus	-	1.41E-07	1.44E-09	3.45E-13	-	-1.64E-08	1.26E-07
	(s) Silicon	-	-	-	-	-	-3.28E-08	-3.28E-08
	(s) Sodium	-	-	-	-	-	-6.56E-07	-6.56E-07
	(s) Sulphur	-	1.69E-06	-	4.13E-12	-	-1.97E-07	1.49E-06
Water	(w) Acids	-	4.53E-08	3.65E-09	1.49E-12	1.01E-03	-	1.01E-03
	(w) Aluminium	-	1.71E-06	8.08E-10	9.80E-11	-	-2.39E-10	1.71E-06
	(w) Ammonia	-	3.03E-06	1.18E-07	8.92E-11	-	-	3.15E-06
	(w) Benzene	-	4.86E-07	3.44E-06	9.18E-12	-	-	3.93E-06
	(w) Biochemical Oxygen Demand	-	7.44E-06	8.80E-09	2.66E-12	2.90E-05	-9.09E-06	2.74E-05
	(w) Cadmium	-	1.59E-09	1.10E-09	4.63E-14	-	-4.08E-09	-1.38E-09
	(w) Chemical Oxygen Demand	-	4.18E-06	1.58E-10	-	2.08E-09	-1.45E-05	-1.03E-05
	(w) Cyanides	-	2.07E-07	6.26E-10	5.19E-12	-	-3.95E-08	1.68E-07
	(w) Dissolved Organic Carbon	-	2.25E-06	4.46E-08	5.50E-12	1.75E-06	-6.50E-06	-2.46E-06
	(w) Methanol	-	-	1.95E-11	-	-	-5.21E-07	-5.21E-07
	(w) Phosphates	-	1.64E-08	8.18E-09	1.31E-13	-	-	2.46E-08
	(w) Sulphates	-	9.57E-05	2.94E-07	1.71E-08	-	-6.28E-10	9.60E-05
	(w) Triethylene glycol	-	2.25E-06	1.57E-13	5.50E-12	-	-	2.25E-06
	(w) VOC	-	1.22E-06	1.95E-11	2.45E-11	-	-	1.22E-06
	(w) Zinc	-	7.55E-08	4.61E-08	1.10E-12	-	-9.32E-08	2.84E-08

5.3.3 Importance of the allocation in LCA

In the previous analysis, the glycerol was considered as by-product, and, therefore, its environmental loads are assigned as "avoided load". According to this consideration the production of glycerol in biodiesel process is avoiding the production of this chemical by a typical petrochemical route from a fossil resource. The environmental balance is consequently done by assigning to the glycerol stream the ecovector corresponding to this product in the Eco-invent database and its environmental load is subtracting the global environmental load due to the whole process. This way we can consider that the glycerol is "cleaning" the biodiesel.

To show the importance of allocation (see section 3.2.1.2), in LCA and the capability of the developed methodology, an additional application has been considered. The biodiesel process has been evaluated from other environmental perspective: the glycerol as product (multiple-output system).

In this case, the environmental loads are distributed, both in the biodiesel as well as in the glycerol, following the allocation on the basis of mass. This new profile illustrates the importance of the environmental load distribution and the consideration of the process configuration as multi-product manufacturer.

The Global Warming Potential (Figure 33) is the category selected to compare the variation associated to the environmental burden allocation. A decrease in the CO_2 eq. is obtained in some secondary processes, due to the increase in the product mass flow (biodiesel and glycerol). However, due to the absence of the avoided load, the total impact is higher than in the "by-product perspective" (see Table 23).

As it can be seen in Table 31, in each process, alkali and acid, the overall environmental load is assigned to the biodiesel and to the glycerol stream proportionally to its mass flow. The amount of CO_2 equivalent per unit of mass is the same for both products.

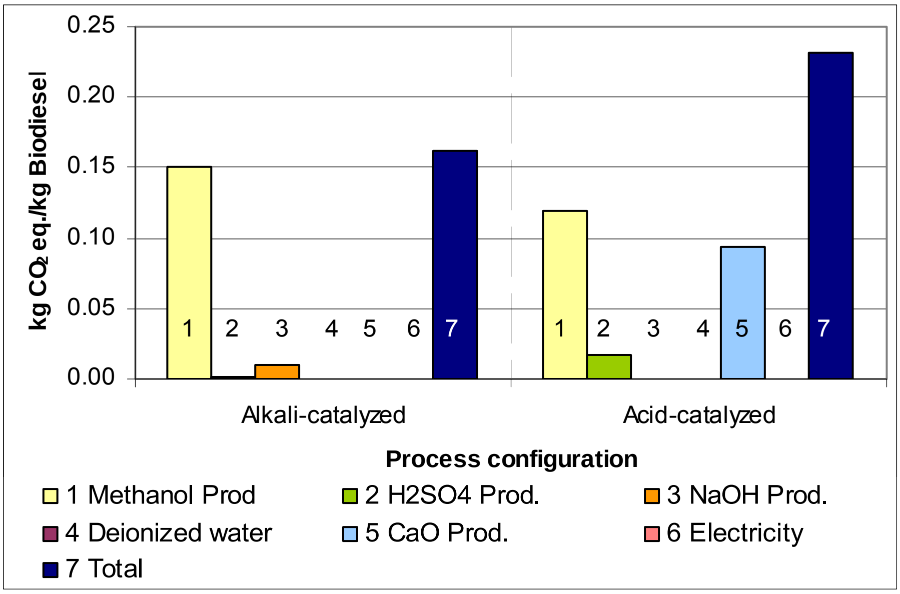


Figure 33 Contribution per stage of the biodiesel process to GWP 100, considering the glycerol as product

Table 31 Total emissions associated to the GWP (100 years), considering the glycerol as product.

	Configuration	
	Alkali-catalyzed kg CO_2 eq./kg Biodiesel	Acid-catalyzed kg CO_2 eq./kg Biodiesel
Methanol Prod	1.50E-01	1.20E-01
H_2SO_4 Prod.	1.13E-03	1.76E-02
NaOH Prod.	9.85E-03	-
Deionized water	6.75E-06	-
CaO Prod.	-	9.42E-02
Electricity	4.89E-04	1.16E-05
Total	1.61E-01	2.32E-01

The tool is able to evaluate a single-product process and the related by-product(s) by the assignation of its environmental loads as avoided load; this will generate a benefit effect in the environmental profile. On the other hand, the functional unit could be established as the sum of the total production (products and by-products), generating a different behavior in the evaluated impact categories. In this way, it is possible to assess the same process from different perspectives.

5.3.4 Economical Analysis

The economical evaluation developed in this process consists in the evaluation of the five economical indicators described in Section 4.4. As in the previous case, the criterion established in Table 3 was followed.

The inclusion of these additional indicators helps to obtain a better economical profile for the studied process. The NPV and the PP give an idea about the economic viability of the process; however, a complete analysis considers the five indicators proposed in this work to guarantee the feasibility of the studied process. The obtained results are presented in Table 32.

The economical indicators of the acid-catalyzed process are better than the alkali-catalyzed: almost six years are necessary to recover the original investment (Payback period), however more than six years are required in the alkali process. In a similar way, the highest Net Present Value is obtained in the acid process. For acid-catalyzed process, the internal rate of return (IRR), the modified internal rate of return (MIRR), and the discounted payback period (DPP) also are higher than the alkali process.

Table 32 Economical Assessment results of biodiesel process

	Alkali catalyzed	Acid catalyzed
$NPV_{(thousand\ €)}$	14430.69	18175.74
$IRR_{(\%)}$	11.94	12.62
$MIRR_{(\%)}$	9.51	10.73
$PP_{(years)}$	6.36	5.67
$DPP_{(years)}$	8.33	7.21

The difference in the economical analysis is principally produced by the pre-treatment unit employed in the alkali process. Even though the costs associated to transesterification and separation units are higher in the acid configuration, additional equipment is required in the alkali configuration. Also, more compounds are related in the alkali process, increasing the manufacturing costs.

As in the previous case study, a score was assigned to each impact category and economical indicators, these scores are attributed giving the same importance to environmental and economic. Also, there is not difference between the categories in the impact assessment; all of them have the same importance. However, if the analysis has to be focused in the economical analysis, the scores can be readjusted. In similar way, if the analysis is centered in the impact assessment, depending on the user necessities, a higher weight could be assigned to a specific impact category. Table 33 shows the score results obtained for the biodiesel production. In this case, a value of 2 or 1 was assigned to the best or worst option, respectively. As in the previous case, the calculated average is presented when the category is evaluated in more than one receiving environment, perspective or time horizon.

Table 33 Environmental and economical scores summary for biodiesel process

Impact category	**Process configuration** **Alkaly catalyzed**	 **Acid catalyzed**
Depletion of abiotic resources	1.0	2.0
Land use	1.0	2.0
Climate change	1.3	1.7
Stratospheric ozone depletion	1.0	2.0
Human toxicity	1.0	2.0
Ecotoxicity	1.0	2.0
Photo-oxidant formation	1.0	2.0
Acidification	2.0	1.0
Eutrophication	1.0	2.0
Average	1.1	1.9

Economical Indicator		
NPV	1	2
IRR	1	2
MIRR	1	2
PP	1	2
DPP	1	2
Average	1.0	2.0

The acid catalyzed process has better scores than the alkali process, both in the environmental profile as well as in the economic analysis.

5.3.5 Sensitivity Analysis

Finally, the sensitivity analysis associated to the environmental impact of the biodiesel process is estimated using the Crystal Ball software. The evaluation is focused in the acid-catalyzed process configuration since this is considered as the best option. This analysis helps to identify the process stage which could be modified in order to obtain a better environmental profile.

The generated results worksheets, “Air_Results”, “Soil_Results”, and “Water_Results”, are employed to accomplish this analysis. These worksheets report the emission or release, and its related stage (primary or secondary process), thus, it will be possible to identify the process stage which mainly contribute to the evaluated impact. All the impact categories are established as the *objective function*, and its associated emissions or releases are fixed as *variables*.

As was mentioned in section 4.5, the probability distributions assigned are the normal and log-normal models. For the avoided loads, the lognormal distribution can not be used because these are represented in the impact assessment as negative values. Once the probability distribution is established, the variation coefficient is the required information for each one of these variables. The variation coefficient of 10% has been adopted, because the analyzed case study has some possibilities for errors generated in the process simulation.

Figure 34 shows the obtained result of the sensitivity analysis. The compounds associated to the *glycerol production* stage have an important influence in the impact assessment; this fact is due to the environmental load associated to this stage. As can be seen in Table 34, the highest values correspond to the carbon dioxide emission generated in the “glycerol production” and “calcium oxide production”. However, the effect of the “glycerol production” is most significant.

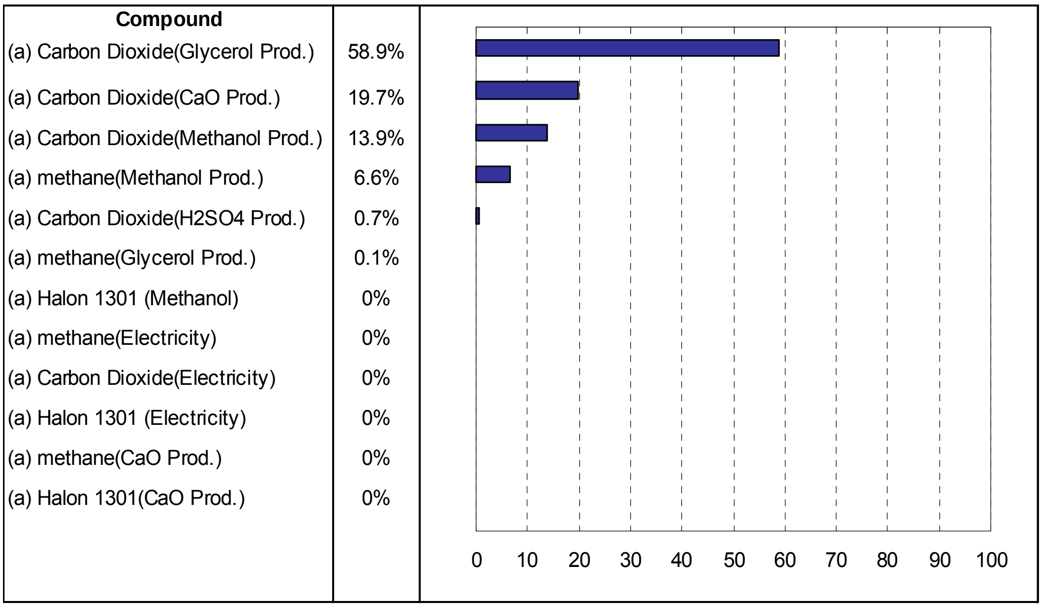


Figure 34 Sensitivity chart of the biodiesel process associated to GWP (time horizon 100)

Table 34 Contribution of each compound and the correspondent stage to Global Warming

	Global Warming **GWP 100** **kg CO_2 eq./ kg Biodiesel**
(a) Carbon Dioxide(Methanol)	7.81E-02
(a) Carbon Dioxide(Glycerol)	-1.66E-01
(a) Carbon Dioxide(H2SO4)	1.95E-02
(a) Carbon Dioxide(CaO)	1.03E-01
(a) Carbon Dioxide(Electricity)	1.16E-05
(a) Halon 1301 (Methanol)	5.10E-05
(a) Halon 1301(CaO)	7.58E-07
(a) Halon 1301 (Electricity)	1.00E-09
(a) methane(Methanol)	5.43E-02
(a) methane(Glycerol)	-1.02E-03
(a) methane(CaO)	1.05E-03
(a) methane(Electricity)	1.24E-06
Total	8.84E-02

Also, the Human Toxicity category (Figure 35) was analyzed, considering air, water and soil receiving environments. In this case, the nickel, arsenic, vanadium and polycyclic aromatic hydrocarbons generated in the “methanol production” stage mainly influence in this category.

Compound	
(a) Nickel (Methanol Prod.)	33.8%
(a) Arsenic (Methanol Prod.)	23.1%
(a) Vanadium (Methanol Prod.)	14.2%
(w) Polycyclic Aromatic Hydrocarbons (Methanol Prod.)	8.2%
(a) Hydrogen Fluoride (Methanol Prod.)	7.3%
(a) Dioxins (unspecified)(Glycerol Prod.)	2.6%
(a) Benzene (Methanol Prod.)	1.7%
(a) Cadmium (Methanol Prod.)	1.5%
(w) Barium(Methanol Prod.)	1.0%
(a) Selenium(Methanol Prod.)	0.4%
(w) Copper (Methanol Prod.)	0.2%
(a) Berylium(Methanol Prod.)	0.2%
(a) antimony(Electricity)	0.2%
(s) Cobalt(Electricity)	0.2%
(w) Toluene (CaO Prod.)	0.2%
(a) Phenol (Methanol Prod.)	0.2%
(a) Lead (Electricity)	0.2%
(a) Cobalt (Electricity)	0.1%

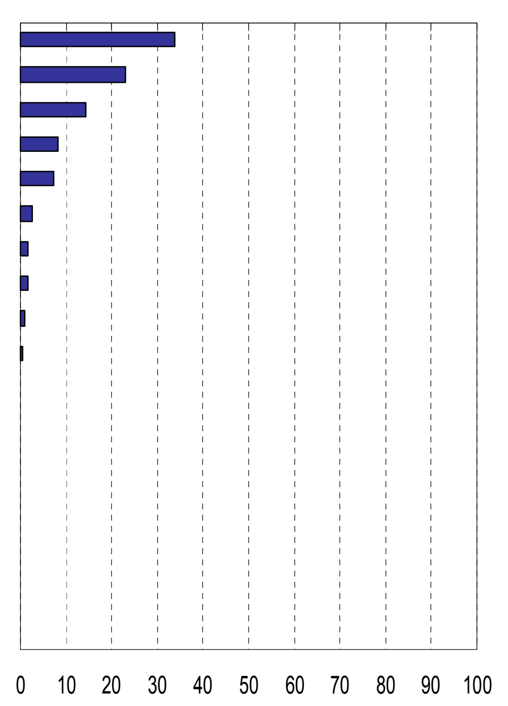


Figure 35 Sensitivity chart associated to the Human Toxicity category (inf.)

After this analysis, it can be concluded that, in the biodiesel process, the “methanol production” and “glycerol production” stages have the main influence in the impact categories. However, the “methanol production” affect the environmental behavior because generates a negative impact, whereas the “glycerol production” produce the opposite effect. Therefore, an improvement of the process could be focus in the methanol as raw material, especially in the reduction of the main emissions and releases with the higher sensitivity contribution.

6. Conclusions and Future work

The objective of this research work was the development of a methodology and the correspondent tool for the automation of the process assessment. This assessment includes a Life Cycle Inventory, Life Cycle Impact assessment, economical evaluation, and a sensitivity analysis.

The methodology helps to decision-making by showing several options using different raw material, topologies, operational conditions, etc. It consists of five levels, which satisfy the objectives established in section 2.2:

- Process Simulation
- Inventory
- Impact Assessment
- Economical Analysis
- Sensitivity Analysis.

The tool allows to analyze the process in a cyclic way, since the information can be modified at anytime, evaluating an unlimited number of possible configurations, helping in this way to the stage corresponding to the decision-making of the process. The user is able to decide, depending on his necessities, the best option.

The analyzed case studies help to know the usefulness of the proposed methodology and tool, due to the possibility to evaluate several configurations and considerations for the same process. The LDPE and EO processes show the importance of an appropriate choice of the energy origin. In both cases, a better environmental profile is obtained when cogeneration is used to produce electricity. Also, in the EO processes, two different raw materials were evaluated (air and oxygen). At the end of the analysis, it can be concluded that the oxygen as raw material has environmental and economic benefits.

The simulation of EO and Biodiesel production processes showed the importance of the information about the process in the assessment. Using a simulator, an unlimited number of processes can be modeled, in order to obtain their environmental profile.

However, the limitations of the tool we propose are mainly referred to the simulator, since ASPEN Hysys® has restrictions associated to the modeling of mechanical activities. However, it is possible to obtain the environmental and economic profile of these activities by introducing their information in the Excel® worksheet “Hysys”, and continuing with the other steps of the assessment without any additional change.

The constructed database for the Inventory and Impact assessment levels can be modified at any moment; this is an important point because the environmental information changes continually, and therefore, it can be updated when it is necessary (e.g. characterization factors modification or addition in an impact category, new secondary processes). Also, the user can personalize this information in order to accomplish the requirements for the process under study. The characterization factors database consider several mid and end point categories, time horizon, and methods (CML, Impact 2002+, Eco-indicator 99), and therefore the results can be used to compare or verify the values between categories (for same category, but different methods). Furthermore, it is possible to determine the effect of the time horizon in a specific category.

The scenarios analysis and the sensitivity analysis provide valuable information. The first shows the behavior of the same process under different configurations. Simulating various scenarios, the user can make a better decision on the optimal configuration of the process under analysis. This decision could be focused on both, environmental and economic perspective, or only on one of them. The environmental and economic profiles were obtained for the EO and Biodiesel production processes; a decision about the adequate configuration could be taken based on the results obtained for each of the configurations. The first one has a better profile employing oxygen and cogeneration as raw material. The best configuration process for the biodiesel production corresponds to the acid-catalyzed option.

The sensitivity analysis allows knowing the effect of a change in a variable on the environmental profile. The biodiesel production process was employed to validate this part of the methodology. At the end of the analysis, it is possible to identify which is the process stage that could be modified to obtain a better configuration.

By means of the developed tool, the following information can be obtained:

- A detailed description of all the input and output streams through the PFD obtained from ASPEN Hysys®,
- An estimation of the environmental impact of each process stage by a section analysis,
- Possible improvements of the process environmental behavior that can be obtained by changing streams or process,
- The environmental profile of the process by the estimation of environmental impact categories,
- The viability of the process through an evaluation of five economic indicators, and finally
- The best process configuration, by considering all the information given above.

Nevertheless, the results are directly related to the initial information. The methodology and the tool efficiency depend on the quality and quantity of available data to perform the analysis. However, final results can be compared with information reported in literature.

In general way, the aspects that could be future research lines are: the integration of the sensitivity analysis in the tool, without an external software intervention, and the incorporation of the necessary algorithms to perform a better optimization by the automatic comparison between all the studied configurations.

7. References

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Annexes

ANNEX I: Programming code (ASPEN Hysys®-Excel)

```
Option Explicit

Private Sub CommandButton1_Click()

Dim excBook As Workbook
Dim hyApp As Object
Dim hyCase As Object
Dim hyFlowsheet As Object
Dim hyOperation As Object
Dim hyMatStream As Object
Dim hyStreams As Object
Dim hyEnergy As Object
Dim hyEnergyStr As Object
Dim hyComponents As Variant
Dim hyVal As Double
Dim hyTemp As Double
Dim hyPress As Double
Dim hyIndex As Variant
Dim hyCompMassFrac As Variant
Dim J As Integer
Dim hyValue As Variant



'Setting the variables and objects
Set hyApp = GetObject("", "HYSYS.Application")
Set hyCase = hyApp.ActiveDocument
Set hyMatStream = hyCase.Flowsheet.MaterialStreams
Set hyStreams = hyMatStream.Item(0)
Set hyEnergyStr = hyCase.Flowsheet.EnergyStreams
```

```
Set excBook = ThisWorkbook

‘Send the mass stream flow from Hysys to Excel
Set hyStreams = hyMatStream.Item("Mass_stream_name")
hyVal = hyStreams.MassFlow.Getvalue("kg/h")
excBook.ActiveSheet.Range("Cell number in excel_1") = hyVal
hyTemp = hyStreams.Temperature.Getvalue("C")
excBook.ActiveSheet.Range("Cell number in excel_2") = hyTemp
hyPress = hyStreams.Pressure.Getvalue("kPa")
excBook.ActiveSheet.Range("Cell number in excel_3") = hyPress
Set hyComponents =
hyCase.BasisManager.FluidPackages.Item(0).Components
J = 0
While J <= (Number of compounds –1)
hyIndex = hyComponents.Index(J)
hyCompMassFrac = hyStreams.ComponentMassFlowValue
hyValue = hyCompMassFrac(hyIndex) * 3600
'The hyValue must be multiplied by 3600 because the default unit is kg/s
excBook.ActiveSheet.Range("Excel_column_name" & J +
Excel_row_number) = hyValue
‘Note 1: The programme will write the component mass flow starting in
the cell B9 in excel, if the cell changes, the “B” must be replaced by the
corresponded column and the 9  for the corresponded row
J = J + 1
Wend

‘Send the energy stream flow from Hysys to Excel
Set hyEnergy = hyEnergyStr.Item("Energy_stream_name ")
hyVal = hyEnergy.HeatFlow.Getvalue("MJ/h")
excBook.ActiveSheet.Range("Cell number in excel_4") = hyVal
```

```
End Sub

Private Sub CommandButton2_Click()

Dim excBook As Object
Dim hyApp As Object
Dim hyCase As Object
Dim hyFlowsheet As Object
Dim hyOperation As Object
Dim hyMatStream As Object
Dim hyStreams As Object
Dim xlRange As Excel.Range
Dim hyStream As Object
Dim xlSheet As Excel.Worksheet
Dim hyVal As Double
Dim hyCompMassFrac As Variant
Dim hyComponents As Object
Dim hyIndex As Variant
Dim hyCompMassFlow As Variant


Set hyApp = GetObject("", "HYSYS.Application")
Set hyCase = hyApp.ActiveDocument
Set hyStreams = hyCase.Flowsheet.MaterialStreams
Set hyMatStream = hyCase.Flowsheet.MaterialStreams
Set excBook = ThisWorkbook
Set xlSheet = ThisWorkbook.Sheets("Hysys")
Set xlRange = xlSheet.Range("B25")

'Put the Solver in Hold mode
```

```
hyCase.Solver.CanSolve = False

‘Send the mass stream flow from Excel to Hysys
Set hyStreams = hyMatStream.Item("Mass_stream_name ")
Set xlRange = xlSheet.Range("Cell number in excel_1")
xlRange = excBook.ActiveSheet.Range("Cell number in excel_1").Value
hyStreams.MassFlow.SetValue CDbl(xlRange.Value), "kg/h"
Set xlRange = xlSheet.Range("Cell number in excel_2")
xlRange = excBook.ActiveSheet.Range("Cell number in excel_2").Value
hyStreams.Temperature.SetValue CDbl(xlRange.Value), "C"
Set xlRange = xlSheet.Range("Cell number in excel_3")
xlRange = excBook.ActiveSheet.Range("Cell number in excel_3").Value
hyStreams.Pressure.SetValue CDbl(xlRange.Value), "kPa"


‘Compound # 1
Set xlRange = xlSheet.Range("Excel_column_name_Excel_row_number ")
‘B9 can be changed, as was explained above (Note 1)
Set hyComponents = hyCase.BasisManager.FluidPackages.Item(0).Components
hyIndex = hyComponents.Index(0) / 3600
hyCompMassFrac = hyStreams.ComponentMassFlowValue
xlRange = excBook.ActiveSheet.Range("Excel_column_name_Excel_row_number").Value
hyCompMassFrac(hyIndex) = CDbl(xlRange.Value)
hyStreams.ComponentMassFractionValue = hyCompMassFrac

‘Send the energy stream flow from Excel to Hysys
'Put the Solver in Solve mode
```

```
hyCase.Solver.CanSolve = True

End Sub

Private Sub Worksheet_SelectionChange(ByVal Target As Excel.Range)

End Sub
```

ANNEX II: Secondary Processes database

Butane production

Gasoline production

Propane production

Benzene production

Butadiene production

Cement production

Chlorine production

Electricity generation in refineries,

Electricity generation in European Union,

High Density polyethylene production

Hydrogen production

Hydrogen peroxide production

Limestone production

Low density polyethylene production

Methane production

Polyethylene production

Polyurethane production

Polyvinyl chloride (PVC) production

Potassium Chloride production

Sodium Chloride production

Steam production in refineries

Rail transport

Road transport

Sea transport

Fluvial transport

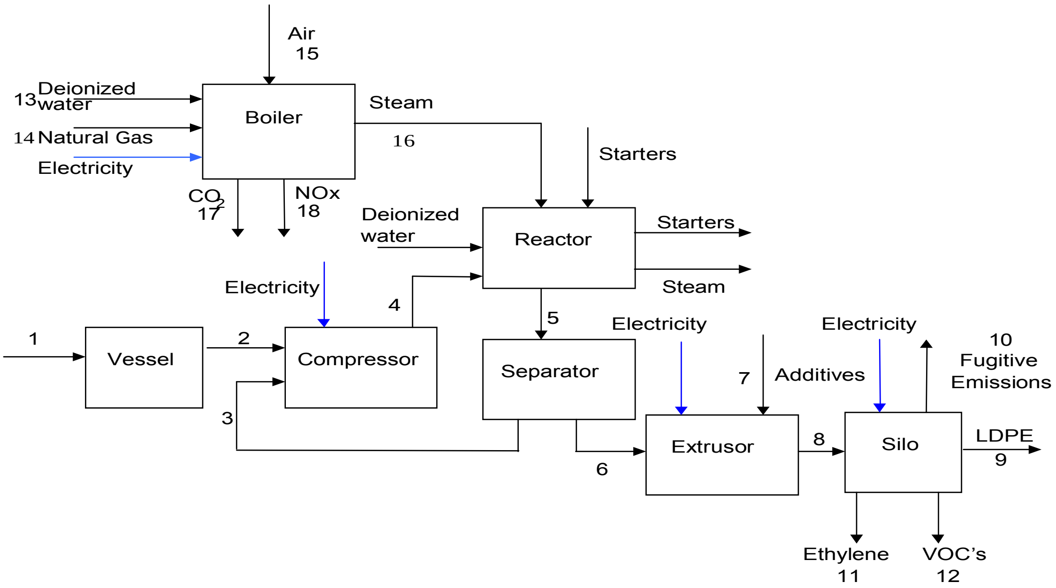
Air transport

ANNEX III: Impact Categories

Impact category	**Initial emission or extraction**	**Characteristics**	**Method**	**Units**
Depletion of abiotic resources	natural resources		CML	kg antimony eq.
Land use	Landscape		CML	m2*yr
Global warming	Air	Time horizon: 20, 100, net 100 min, net 100 max, 500	CML, IMPACT 2002+	kg CO2 eq.
Ozone layer depletion	Air	Steady state, Time horizon: 5, 10, 15, 20, 25, 30, 40	CML	kg CFC-11 eq.
Human toxicity	Air, water, soil	inf., Time horizon: 20, 100, 500	CML	kg 1,4-dichlorobenzene eq.
Freshwater aquatic ecotoxicity	Air, water, soil	inf., Time horizon: 20, 100, 500	CML 2004	kg 1,4-dichlorobenzene eq.
Marine aquatic ecotoxicity	Air, water, soil	inf., Time horizon: 20, 100, 500	CML 2004	kg 1,4-dichlorobenzene eq.
Freshwater sedimental ecotoxicity	Air, water, soil	inf., Time horizon: 20, 100, 500	CML 2004	kg 1,4-dichlorobenzene eq.
Marine sedimental ecotoxicity	Air, water, soil	inf., Time horizon: 20, 100, 500	CML 2004	kg 1,4-dichlorobenzene eq.
Terrestrial ecotoxicity	Air, water, soil	inf., Time horizon: 20, 100, 500	CML 2004	kg 1,4-dichlorobenzene eq.
Photochemical oxidation	Air	High NOx, very high NOx, low NOx	CML 2004	kg ethylene eq., kg formed ozone
Acidification	Air, water, soil	average Europe total	CML 2004	kg SO2 eq.
Eutrophication	Air, water, soil	average Europe total	CML 2004	kg PO4--- eq., kg NOx eq.
Radiation	Air, water		CML 2004	DALY
Odour	Air		CML 2004	m^3
Carcinogenic effects on humans	Air, water, soil	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	DALY
Respiratory effects on humans caused by organic substances	Air	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99, IMPACT 2002+	kgeq of ethylene into air, DALY
Respiratory effects on humans caused by inorganic substances	Air	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99, IMPACT 2002+	kgeq of PM2.5 into air, DALY
Damages to human health caused by climate change	Air	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	DALY
Human health effects caused by ionising radiation	Air, water	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	DALY
Human health effects caused by ozone layer depletion	Air	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99, IMPACT 2002+	kgeq of CFC-11 into air, DALY
Damage to Ecosystem Quality caused by ecotoxic emissions	Air, water, soil	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	PDF*m2*yr
Damage to Ecosystem Quality caused by the combined effect of acidification and eutrophication	Air	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	kgeq of SO2 into air, PDF*m2*yr
Aquatic ecotoxicity caused by ecotoxic emissions	Air, water, soil		IMPACT 2002+	kgeq of triethylene glycol in water, PDF*m2*yr
Terrestrial ecotoxicity caused by ecotoxic emissions	Air, water, soil		IMPACT 2002+	kgeq of triethylene glycol in soil, PDF*m2*yr
Total Human toxicity effects	Air, water, soil		IMPACT 2002+	kgeq of chloroethylene in air, DALY
Human Toxicity (Carcinogenic effects)	Air, water, soil		IMPACT 2002+	kgeq of chloroethylene in air, DALY
Human Toxicity (Non-carcinogenic effects)	Air, water, soil		IMPACT 2002+	kgeq of chloroethylene in air, DALY
Damage to Ecosystem Quality caused by land occupation	Landscape	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99, IMPACT 2002+	PDF*m2*yr
Damage to Ecosystem Quality caused by land conversion	Landscape	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	PDF*m2*yr
Damage to Resources caused by extraction of minerals	natural resources	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	MJ surplus energy
Damage to Resources caused by extraction of fossil fuels	natural resources	Perspective: hierarchist, egalitarian and individualist	ECOINDICATOR 99	MJ surplus energy

ANNEX IV: Process Flow Diagram of the LDPE process

Mass balances



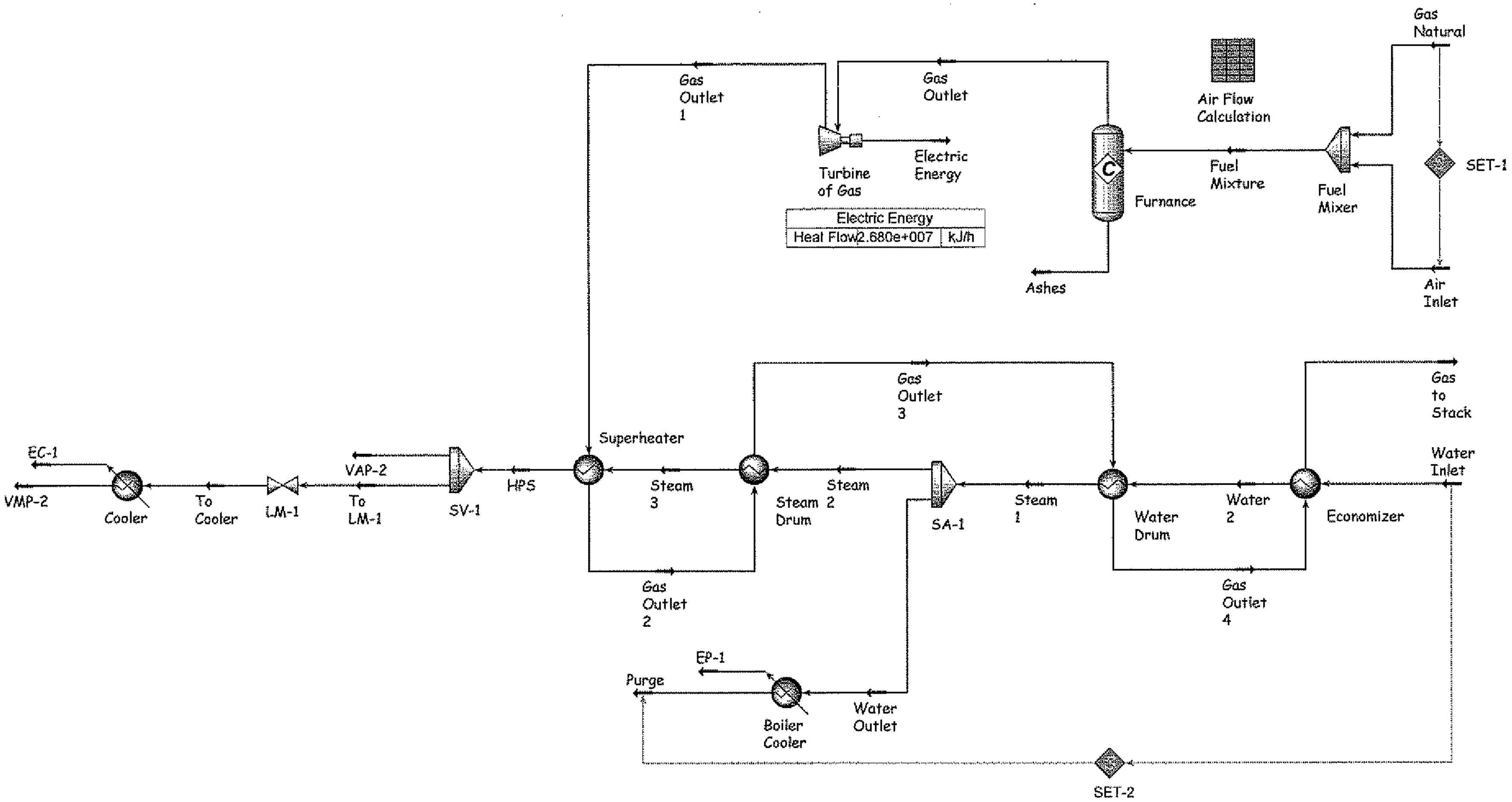
	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9
	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)
Ethylene	91920	91920	2256	94176	2436	180	0	180	0
LDPE	0	0	0	0	91702	91702	0	93330	93330
Fugitive Emissions	0	0	0	0	8	8	0	8	0
Dissolvents/VOC	0	0	0	0	30	30	0	30	0
Starters	0	0	0	0	0	0	0	0	0
Additives	0	0	0	0	0	0	1628	0	0
Water	0	0	0	0	0	0	0	0	0
Natural gas	0	0	0	0	0	0	0	0	0
Air	0	0	0	0	0	0	0	0	0
Steam	0	0	0	0	0	0	0	0	0
Carbon Dioxide	0	0	0	0	0	0	0	0	0
Nitrogen oxides	0	0	0	0	0	0	0	0	0
	91920	91920	2256	94176	94176	91920	1628	93548	93330

* LDPE + Additives

	Stream 10	Stream 11	Stream 12	Stream 13	Stream 14	Stream 15	Stream 16	Stream 17	Stream 18
	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)	(Ton/year)
Ethylene	0	180	0	0	0	0	0	0	0
LDPE	0	0	0	0	0	0	0	0	0
Fugitive Emissions	8	0	0	0	0	0	0	0	0
Dissolvents/VOC	0	0	30	0	0	0	0	0	0
Starters	0	0	0	0	0	0	0	0	0
Additives	0	0	0	0	0	0	0	0	0
Water	0	0	0	179830	0	0	0	0	0
Natural gas	0	0	0	0	9218	0	0	0	0
Air	0	0	0	0	0	25860	0	0	0
Steam	0	0	0	0	0	0	179830	0	0
Carbon Dioxide	0	0	0	0	0	0	0	25830	0
Nitrogen oxides	0	0	0	0	0	0	0	0	30
	8	180	30	179830	9218	25860	179830	25830	30

ANNEX V: Process Flow Diagram of the Cogeneration unit employed in the LDPE process

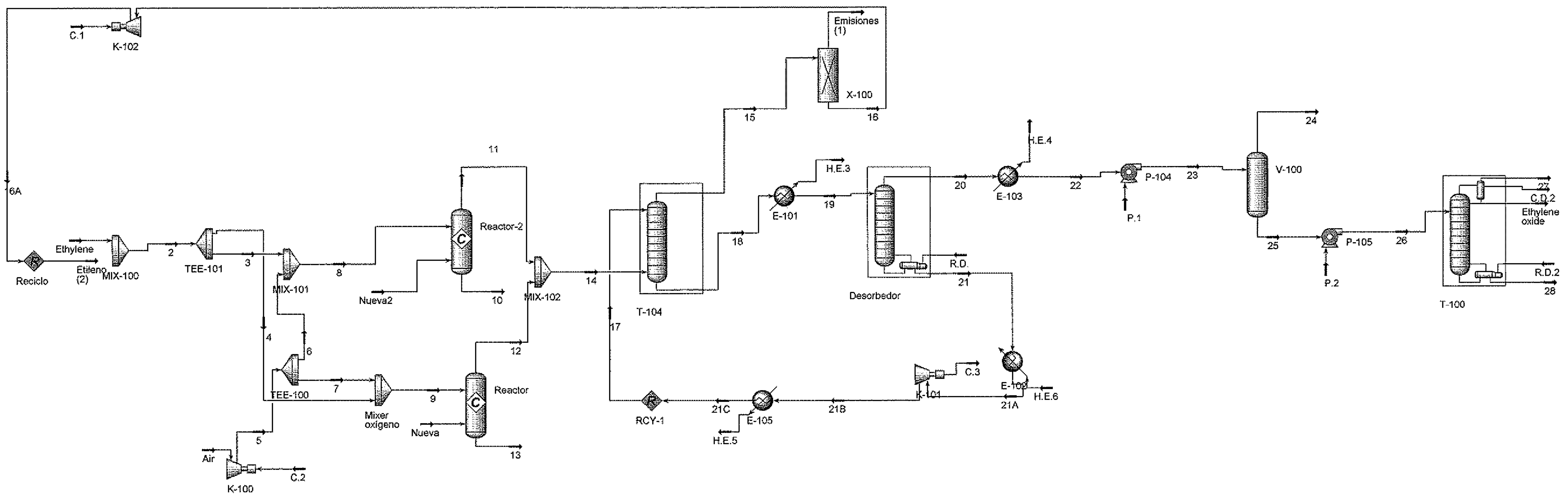
Mass and energy balances generated in ASPEN Hysys®



		Streams								
		Gas Natural	Air Inlet	Fuel Mixture	Gas Outlet	Gas Outlet 1	Steam 3	Steam 1	Water 2	Water Inlet
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000
Temperature	C	50.00	25.00	27.88	2013	1658	275.7	275.7	160.0	135.0
Pressure	kPa	199.1	199.1	199.1	199.1	55.89	5884	5884	5884	6374
Molar Flow	kgmole/h	152.6	1500	1652	1657	1657	53.36	54.48	54.48	54.48
Mass Flow	kg/h	2610	4.349e+004	4.610e+004	4.610e+004	4.610e+004	961.2	981.4	981.4	981.4
Liquid Volume Flow	m3/h	8.406	49.65	58.05	54.99	54.99	0.9632	0.9834	0.9834	0.9834
Heat Flow	kJ/h	-1.122e+007	-2.429e+004	-1.125e+007	-1.125e+007	-3.805e+007	-1.254e+007	-1.438e+007	-1.496e+007	-1.507e+007
Molar Enthalpy	kJ/kgmole	-7.353e+004	-16.20	-6807	-6788	-2.296e+004	-2.351e+005	-2.640e+005	-2.746e+005	-2.767e+005
		Gas Outlet 2	Gas Outlet 3	Gas Outlet 4	Gas to Stack	HPS	Ashes	Steam 2	Water Outlet	Purge
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000
Temperature	C	1652	1630	1622	1620	450.0	2013	275.7	275.7	40.00
Pressure	kPa	55.89	55.89	55.89	55.89	5001	199.1	5884	5884	7.294
Molar Flow	kgmole/h	1657	1657	1657	1657	53.36	0.0000	53.36	1.119	1.119
Mass Flow	kg/h	4.610e+004	4.610e+004	4.610e+004	4.610e+004	961.2	0.0000	961.2	20.17	20.17
Liquid Volume Flow	m3/h	54.99	54.99	54.99	54.99	0.9632	0.0000	0.9632	2.021e-002	2.021e-002
Heat Flow	kJ/h	-3.847e+007	-4.001e+007	-4.059e+007	-4.070e+007	-1.212e+007	0.0000	-1.408e+007	-2.955e+005	-3.182e+005
Molar Enthalpy	kJ/kgmole	-2.321e+004	-2.415e+004	-2.450e+004	-2.456e+004	-2.272e+005	-6788	-2.640e+005	-2.640e+005	-2.842e+005
		VAP-2	To LM-1	To Cooler	VMP-2	Electric Energy	EP-1	EC-1		
Vapour Fraction		1.0000	1.0000	1.0000	1.0000					
Temperature	C	450.0	450.0	427.2	157.0					
Pressure	kPa	5001	5001	1600	559.0					
Molar Flow	kgmole/h	0.0000	53.36	53.36	53.36					
Mass Flow	kg/h	0.0000	961.2	961.2	961.2					
Liquid Volume Flow	m3/h	0.0000	0.9632	0.9632	0.9632					
Heat Flow	kJ/h	0.0000	-1.212e+007	-1.212e+007	-1.264e+007	2.680e+007	2.269e+004	5.150e+005		
Molar Enthalpy	kJ/kgmole	-2.272e+005	-2.272e+005	-2.272e+005	-2.368e+005					

ANNEX VI: Process Flow Diagram of the Ethylene Oxide production (Air-based oxidation)

Mass and energy balances generated in ASPEN Hysys®

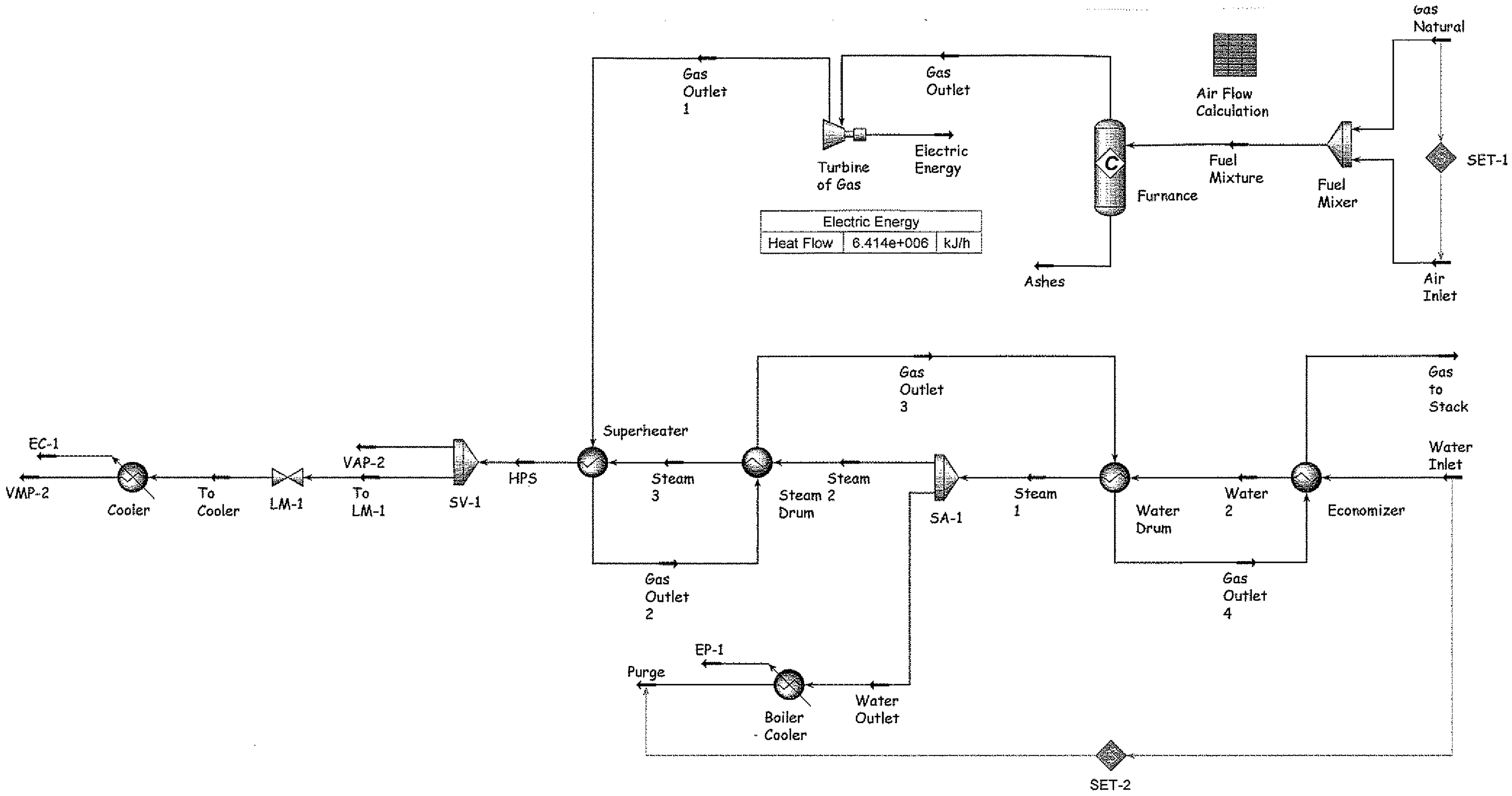


		Material Streams										
		Ethylene	2	Etileno (2)	9	13	15	18	19	21	20	22
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
Temperature	C	25.00	25.00	106.9	105.6	300.0	8.871	8.824	90.00	180.9	128.7	-224.6
Pressure	kPa	2865	2865	2865	2865	1965	1044	1237	1023	1023	810.6	506.6
Molar Flow	kgmole/h	625.0	625.0	329.8	793.2	0.0000	330.8	1.260e+008	1.260e+008	1.260e+008	1558	1558
Mass Flow	kg/h	1.753e+004	1.753e+004	9352	2.277e+004	0.0000	9391	2.270e+009	2.270e+009	2.270e+009	4.364e+004	4.364e+004
Liquid Volume Flow	m3/h	45.75	45.75	23.73	38.77	0.0000	23.76	2.275e+006	2.275e+006	2.275e+006	50.60	50.60
Heat Flow	kJ/h	3.175e+007	3.175e+007	1.764e+007	1.837e+007	0.0000	1.628e+007	-3.603e+013	-3.528e+013	-3.441e+013	-1.601e+008	-2.208e+008
		23	24	25	26	Ethylene oxide	28	27	17	Emisiones (1)	16	12
Vapour Fraction		0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	1.0000	1.0000	1.0000
Temperature	C	-224.6	-224.6	-224.6	-224.6	-49.53	127.7	-49.53	9.000	-160.1	6.363	300.0
Pressure	kPa	516.8	516.8	516.8	516.9	101.3	253.3	101.3	500.0	810.6	810.6	1965
Molar Flow	kgmole/h	1558	0.0000	1558	1558	222.0	520.0	816.3	1.260e+008	0.9741	329.8	718.1
Mass Flow	kg/h	4.364e+004	0.0000	4.364e+004	4.364e+004	9777	9367	2.450e+004	2.270e+009	38.92	9352	2.277e+004
Liquid Volume Flow	m3/h	50.60	0.0000	50.60	50.60	11.09	9.386	30.12	2.275e+006	2.840e-002	23.73	33.38
Heat Flow	kJ/h	-2.208e+008	0.0000	-2.208e+008	-2.208e+008	-1.948e+007	-1.442e+008	-2.951e+007	-3.603e+013	-4090	1.629e+007	-1.244e+007
		10	11	7	6	21B	21A	21C	4	3	8	14
Vapour Fraction		0.0000	1.0000	1.0000	1.0000	0.9716	1.0000	0.0000	1.0000	1.0000	1.0000	1.0000
Temperature	C	300.0	300.0	204.6	204.6	151.8	180.9	9.000	25.00	25.00	105.6	300.0
Pressure	kPa	1965	1965	2865	2865	500.0	1023	500.0	2865	2865	2865	1965
Molar Flow	kgmole/h	0.0000	718.1	480.7	480.7	1.260e+008	1.260e+008	1.260e+008	312.5	312.5	793.2	1436
Mass Flow	kg/h	0.0000	2.277e+004	1.400e+004	1.400e+004	2.270e+009	2.270e+009	2.270e+009	8767	8767	2.277e+004	4.553e+004
Liquid Volume Flow	m3/h	0.0000	33.38	15.89	15.89	2.275e+006	2.275e+006	2.275e+006	22.88	22.88	38.77	66.76
Heat Flow	kJ/h	0.0000	-1.244e+007	2.489e+006	2.489e+006	-3.000e+013	-2.977e+013	-3.603e+013	1.588e+007	1.588e+007	1.837e+007	-2.488e+007

		Energy Streams										
		R.D.	H.E.4	P.1	P.2	C.D.2	R.D.2	H.E.3	C.3	H.E.6	H.E.5	C.2
Heat Flow	kJ/h	8.761e+011	6.074e+007	553.9	5.057	1.813e+009	1.840e+009	-7.458e+011	2.316e+011	4.642e+012	6.032e+012	5.061e+006

ANNEX VII: Process Flow Diagram of the Cogeneration unit employed in the Ethylene Oxide production (Air-based oxidation)

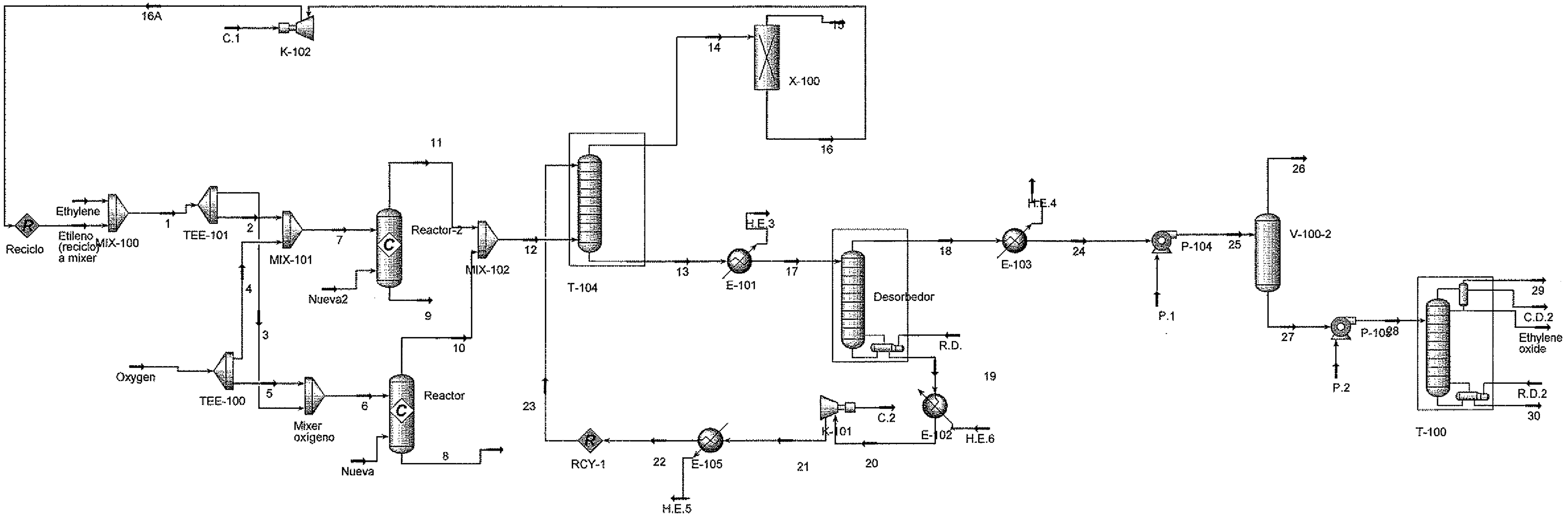
Mass and energy balances generated in ASPEN Hysys®



		Streams										
		Gas Natural	Air Inlet	Fuel Mixture	Gas Outlet	Gas Outlet 1	Steam 3	Steam 1	Water 2	Water Inlet	Gas Outlet 2	Gas Outlet 3
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Temperature	C	50.00	25.00	27.88	2013	1658	275.7	275.7	160.0	135.0	1442	574.7
Pressure	kPa	199.1	199.1	199.1	199.1	55.89	5884	5884	5884	6374	55.89	55.89
Molar Flow	kgmole/h	36.53	358.9	395.5	396.6	396.6	452.1	461.5	461.5	461.5	396.6	396.6
Mass Flow	kg/h	624.7	1.041e+004	1.103e+004	1.103e+004	1.103e+004	8144	8315	8315	8315	1.103e+004	1.103e+004
Liquid Volume Flow	m3/h	2.012	11.88	13.89	13.16	13.16	8.160	8.331	8.331	8.331	13.16	13.16
Heat Flow	kJ/h	-2.686e+006	-5813	-2.692e+006	-2.692e+006	-9.106e+006	-1.063e+008	-1.218e+008	-1.267e+008	-1.277e+008	-1.267e+007	-2.574e+007
Molar Enthalpy	kJ/kgmole	-7.353e+004	-16.20	-6807	-6788	-2.296e+004	-2.351e+005	-2.640e+005	-2.746e+005	-2.767e+005	-3.195e+004	-6.489e+004
		Gas Outlet 4	Gas to Stack	HPS	Ashes	Steam 2	Water Outlet	Purge	VAP-2	To LM-1	To Cooler	VMP-2
Vapour Fraction		1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	1.0000
Temperature	C	208.9	135.0	450.0	2013	275.7	275.7	40.00	450.0	450.0	427.2	300.0
Pressure	kPa	55.89	55.89	5001	199.1	5884	5884	7.294	5001	5001	1600	1600
Molar Flow	kgmole/h	396.6	396.6	452.1	0.0000	452.1	9.484	9.484	0.0000	452.1	452.1	452.1
Mass Flow	kg/h	1.103e+004	1.103e+004	8144	0.0000	8144	170.8	170.8	0.0000	8144	8144	8144
Liquid Volume Flow	m3/h	13.16	13.16	8.160	0.0000	8.160	0.1712	0.1712	0.0000	8.160	8.160	8.160
Heat Flow	kJ/h	-3.065e+007	-3.159e+007	-1.027e+008	0.0000	-1.193e+008	-2.503e+006	-2.696e+006	0.0000	-1.027e+008	-1.027e+008	-1.049e+008
Molar Enthalpy	kJ/kgmole	-7.729e+004	-7.966e+004	-2.272e+005	-6788	-2.640e+005	-2.640e+005	-2.842e+005	-2.272e+005	-2.272e+005	-2.272e+005	-2.321e+005

ANNEX VIII: Process Flow Diagram of the Ethylene Oxide production (Oxygen-based oxidation)

Mass and energy balances generated in ASPEN Hysys®

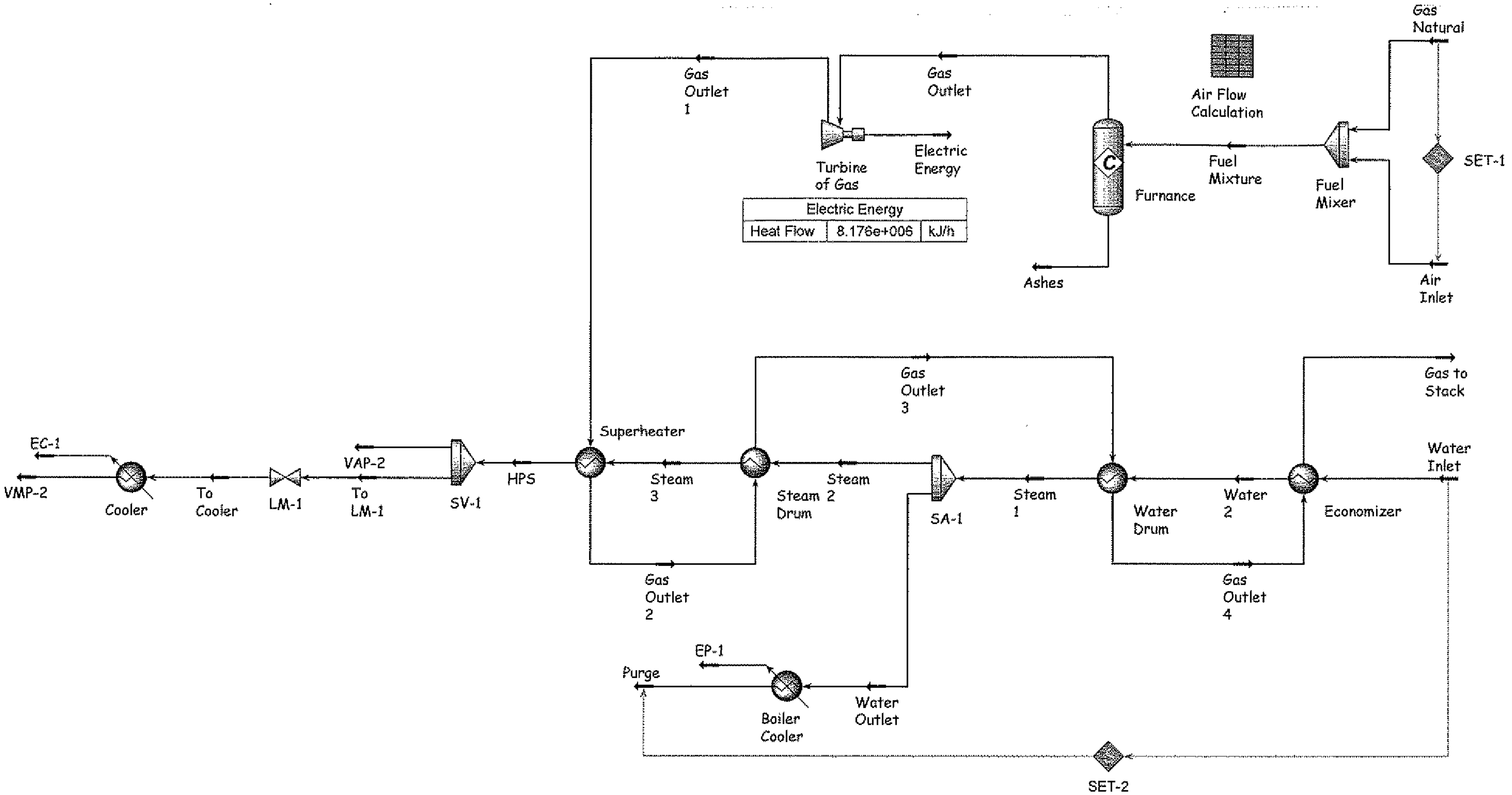


Material Streams												
		Ethylene	1	Etileno (reciclo) a mixer	6	8	14	13	17	19	18	24
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
Temperature	C	25.00	123.5	123.5	123.5	300.0	24.87	28.00	15.00	180.9	141.9	40.98
Pressure	kPa	2865	2865	2865	2865	1965	1044	1237	1023	1023	810.6	506.6
Molar Flow	kgmole/h	625.0	1.871e+006	1.871e+006	9.361e+005	0.0000	1.870e+006	1.260e+008	1.260e+008	1.260e+008	2380	2380
Mass Flow	kg/h	1.753e+004	5.246e+007	5.244e+007	2.624e+007	0.0000	5.242e+007	2.270e+009	2.270e+009	2.270e+009	7.484e+004	7.484e+004
Liquid Volume Flow	m3/h	45.75	1.366e+005	1.366e+005	6.833e+004	0.0000	1.365e+005	2.275e+006	2.275e+006	2.275e+006	82.27	82.27
Heat Flow	kJ/h	3.175e+007	1.030e+011	1.030e+011	5.150e+010	0.0000	9.472e+010	-3.585e+013	-3.597e+013	-3.441e+013	-3.436e+008	-4.312e+008
		25	26	27	28	Ethylene oxide	30	29	23	15	16	10
Vapour Fraction		0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	1.0000	1.0000	1.0000
Temperature	C	41.07	41.13	41.13	41.14	-0.9953	127.7	-0.9953	25.00	-46.10	22.36	300.0
Pressure	kPa	808.3	508.3	508.3	526.9	101.3	253.3	101.3	500.0	810.6	810.6	1965
Molar Flow	kgmole/h	2380	3.747e-002	2380	2380	1220	1101	58.55	1.260e+008	784.6	1.869e+006	9.358e+005
Mass Flow	kg/h	7.484e+004	1.614	7.484e+004	7.484e+004	5.243e+004	1.984e+004	2561	2.270e+009	3.439e+004	5.239e+007	2.624e+007
Liquid Volume Flow	m3/h	82.27	1.916e-003	82.27	82.27	59.38	19.88	3.008	2.275e+006	41.30	1.365e+005	6.831e+004
Heat Flow	kJ/h	-4.312e+008	-7406	-4.312e+008	-4.312e+008	-1.125e+008	-3.054e+008	-1.097e+007	-3.588e+013	-3.024e+008	9.502e+010	6.176e+010
		9	11	5	4	21	20	22	3	2	7	12
Vapour Fraction		0.0000	1.0000	1.0000	1.0000	0.9715	1.0000	0.0000	1.0000	1.0000	1.0000	1.0000
Temperature	C	300.0	300.0	204.6	204.6	151.8	180.9	25.00	123.5	123.5	123.5	300.0
Pressure	kPa	1965	1965	2865	2865	500.0	1023	500.0	2865	2865	2865	1965
Molar Flow	kgmole/h	0.0000	9.358e+005	437.2	437.2	1.260e+008	1.260e+008	1.260e+008	9.357e+005	9.357e+005	9.361e+005	1.872e+006
Mass Flow	kg/h	0.0000	2.624e+007	1.400e+004	1.400e+004	2.270e+009	2.270e+009	2.270e+009	2.623e+007	2.623e+007	2.624e+007	5.249e+007
Liquid Volume Flow	m3/h	0.0000	6.831e+004	12.31	12.31	2.275e+006	2.275e+006	2.275e+006	6.831e+004	6.831e+004	6.833e+004	1.366e+005
Heat Flow	kJ/h	0.0000	6.176e+010	2.310e+006	2.310e+006	-3.000e+013	-2.977e+013	-3.588e+013	5.150e+010	5.150e+010	5.150e+010	1.235e+011

Energy Streams											
		R.D.	H.E.4	P.1	P.2	C.D.2	R.D.2	H.E.3	C.2	H.E.6	H.E.5
Heat Flow	kJ/h	1.566e+012	8.762e+007	3.403e+004	2101	1.231e+008	1.255e+008	1.198e+011	2.316e+011	4.642e+012	5.885e+012

ANNEX IX: Process Flow Diagram of the Cogeneration unit employed in the Ethylene Oxide production (Oxygen-based oxidation)

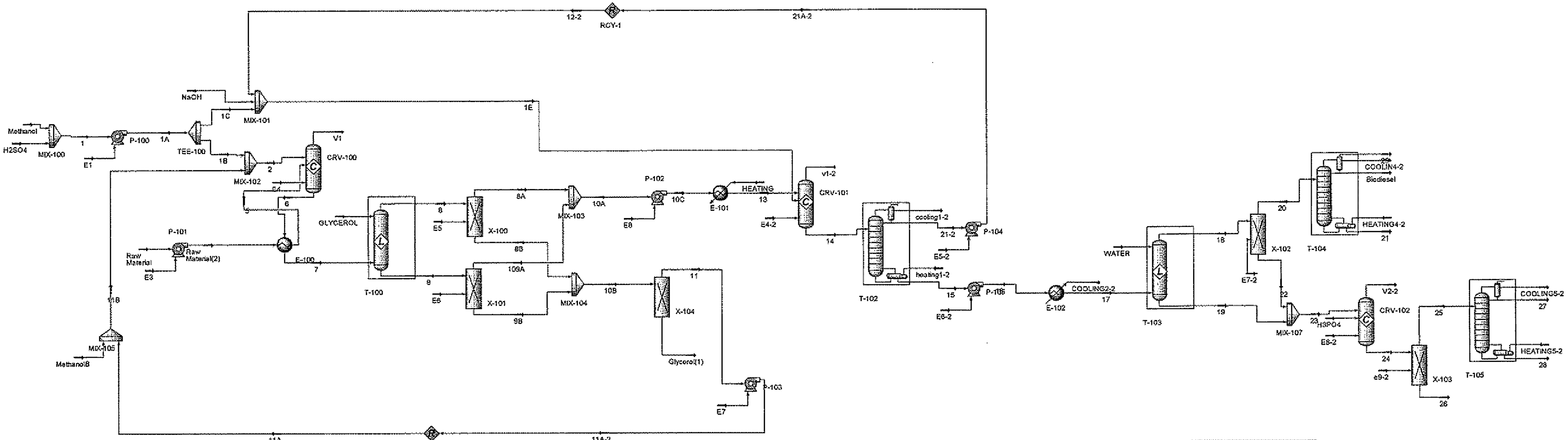
Mass and energy balances generated in ASPEN Hysys®



		Streams										
		Gas Natural	Air Inlet	Fuel Mixture	Gas Outlet	Gas Outlet 1	Steam 3	Steam 1	Water 2	Water Inlet	Gas Outlet 2	Gas Outlet 3
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Temperature	C	50.00	25.00	27.88	2013	1658	275.7	275.7	160.0	135.0	1442	574.8
Pressure	kPa	199.1	199.1	199.1	199.1	55.89	5884	5884	5884	6374	55.89	55.89
Molar Flow	kgmole/h	46.56	457.5	504.1	505.5	505.5	576.1	588.2	588.2	588.2	505.5	505.5
Mass Flow	kg/h	796.3	1.327e+004	1.406e+004	1.406e+004	1.406e+004	1.038e+004	1.060e+004	1.060e+004	1.060e+004	1.406e+004	1.406e+004
Liquid Volume Flow	m3/h	2.564	15.15	17.71	16.78	16.78	10.40	10.62	10.62	10.62	16.78	16.78
Heat Flow	kJ/h	-3.424e+006	-7410	-3.431e+006	-3.431e+006	-1.161e+007	-1.354e+008	-1.553e+008	-1.615e+008	-1.627e+008	-1.615e+007	-3.280e+007
Molar Enthalpy	kJ/kgmole	-7.353e+004	-16.20	-6807	-6788	-2.296e+004	-2.351e+005	-2.640e+005	-2.746e+005	-2.767e+005	-3.195e+004	-6.489e+004
		Gas Outlet 4	Gas to Stack	HPS	Ashes	Steam 2	Water Outlet	Purge	VAP-2	To LM-1	To Cooler	VMP-2
Vapour Fraction		1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	1.0000
Temperature	C	209.1	135.2	450.0	2013	275.7	275.7	40.00	450.0	450.0	427.2	300.0
Pressure	kPa	55.89	55.89	5001	199.1	5884	5884	7.294	5001	5001	1600	1600
Molar Flow	kgmole/h	505.5	505.5	576.1	0.0000	576.1	12.09	12.09	0.0000	576.1	576.1	576.1
Mass Flow	kg/h	1.406e+004	1.406e+004	1.038e+004	0.0000	1.038e+004	217.7	217.7	0.0000	1.038e+004	1.038e+004	1.038e+004
Liquid Volume Flow	m3/h	16.78	16.78	10.40	0.0000	10.40	0.2182	0.2182	0.0000	10.40	10.40	10.40
Heat Flow	kJ/h	-3.907e+007	-4.027e+007	-1.309e+008	0.0000	-1.521e+008	-3.191e+006	-3.436e+006	0.0000	-1.309e+008	-1.309e+008	-1.337e+008
Molar Enthalpy	kJ/kgmole	-7.728e+004	-7.965e+004	-2.272e+005	-6788	-2.640e+005	-2.640e+005	-2.842e+005	-2.272e+005	-2.272e+005	-2.272e+005	-2.321e+005

ANNEX X: Process Flow Diagram of the Biodiesel production (Alkali-catalyzed)

Mass and energy balances generated in ASPEN Hysys®



Material Streams

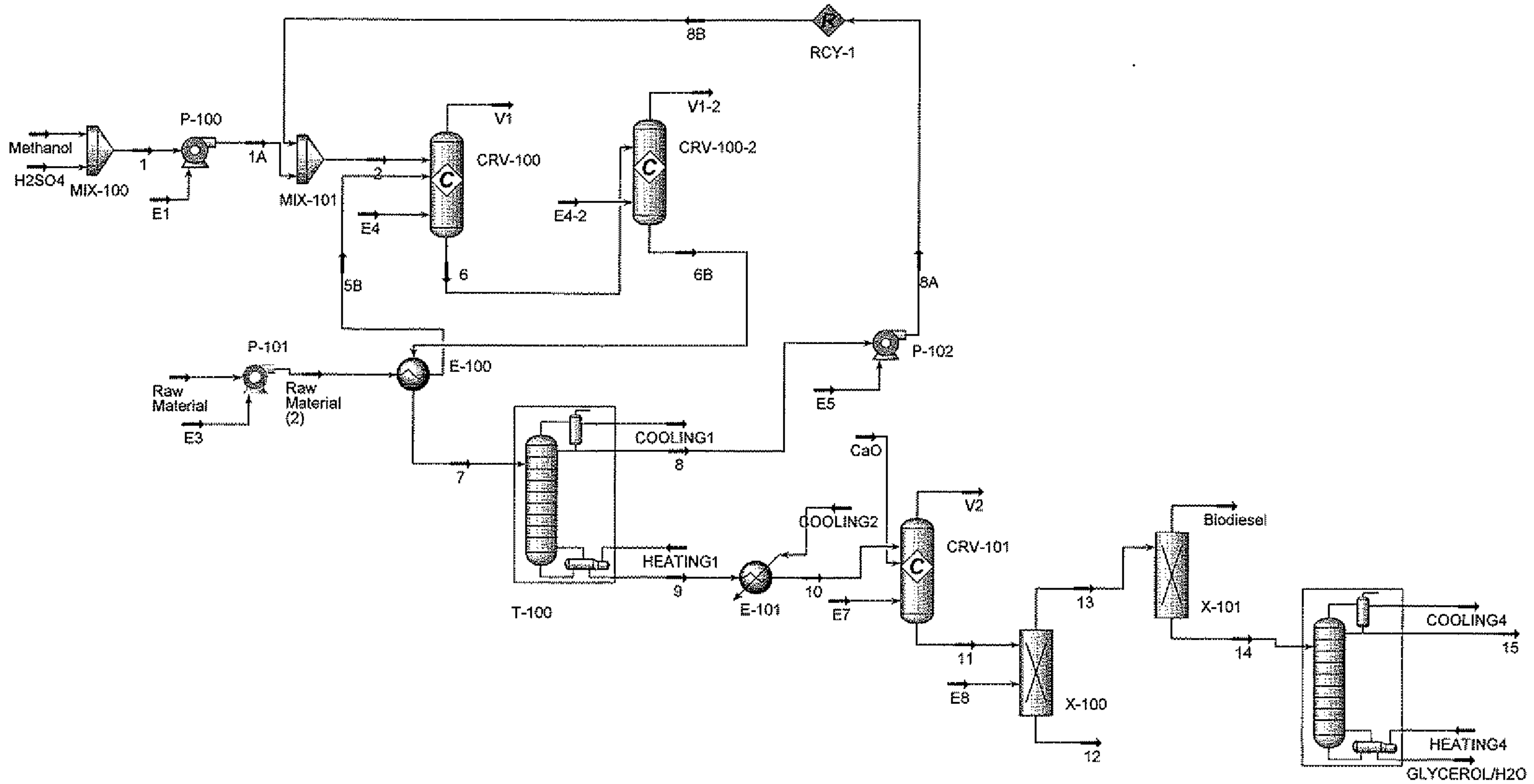
		Methanol	H2SO4	1	1A	1C	1B	1E	2	5	V1	6	Raw Material(2)
Vapour Fraction		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000
Temperature	C	25.00	25.00	24.93	24.96	24.96	24.96	-128.8	24.98	60.00	70.00	70.00	34.07
Pressure	kPa	100.0	100.0	100.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0
Molar Flow	kgmole/h	3.998	0.1020	4.100	4.100	2.050	2.050	193.9	7.917	1.236	0.0000	9.154	1.236
Mass Flow	kg/h	128.1	10.00	138.1	138.1	69.05	69.05	6218	257.1	1050	0.0000	1307	1050
Liquid Volume Flow	m3/h	0.1610	5.403e-003	0.1664	0.1664	8.319e-002	8.319e-002	7.803	0.3195	1.153	0.0000	1.467	1.153
Heat Flow	kJ/h	-9.892e+005	-9.628e+004	-1.085e+006	-1.085e+006	-5.427e+005	-5.427e+005	-5.277e+007	-1.994e+006	-2.369e+006	0.0000	-4.420e+006	-2.409e+006
		7	Raw Material	GLYCEROL	11B	8	9	8A	8B	109A	9B	10A	10C
Vapour Fraction		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Temperature	C	59.00	34.29	25.00	25.00	57.33	59.18	28.00	83.84	28.00	88.00	28.00	28.03
Pressure	kPa	190.0	100.0	200.0	400.0	200.0	200.0	190.0	190.0	190.0	190.0	190.0	400.0
Molar Flow	kgmole/h	9.154	1.236	1.194	5.867	5.292	5.056	3.417	1.875	1.459e-011	5.056	3.417	3.417
Mass Flow	kg/h	1307	1050	110.0	188.0	1112	304.7	1034	78.80	4.326e-009	304.7	1034	1034
Liquid Volume Flow	m3/h	1.467	1.153	8.725e-002	0.2383	1.273	0.2803	1.177	9.606e-002	4.933e-012	0.2803	1.177	1.177
Heat Flow	kJ/h	-4.459e+006	-2.409e+006	-8.617e+005	-1.452e+006	-2.985e+006	-2.336e+006	-2.571e+006	-4.831e+005	-1.079e-005	-2.300e+006	-2.571e+006	-2.571e+006
		13	10B	11	v1-2	14	21-2	15	21A-2	12-2	16	17	WATER
Vapour Fraction		0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Temperature	C	60.00	86.17	25.00	60.00	60.00	-131.0	286.1	-131.0	-131.0	288.2	60.00	25.00
Pressure	kPa	400.0	190.0	20.00	400.0	400.0	20.00	30.00	400.0	400.0	200.0	200.0	110.0
Molar Flow	kgmole/h	3.417	6.931	4.484	0.0000	197.3	193.5	3.820	193.5	191.6	3.820	3.820	0.6106
Mass Flow	kg/h	1034	383.5	143.7	0.0000	7251	6199	1052	6199	6139	1052	1052	11.00
Liquid Volume Flow	m3/h	1.177	0.3763	0.1806	0.0000	8.980	7.791	1.190	7.791	7.714	1.190	1.190	1.102e-002
Heat Flow	kJ/h	-2.501e+006	-2.783e+006	-1.110e+006	0.0000	-4.934e+007	-5.270e+007	-1.986e+006	-5.270e+007	-5.218e+007	-1.986e+006	-2.621e+006	-1.739e+005
		18	19	20	22	23	H3PO4	V2-2	24	29	Biodiesel	21	25
Vapour Fraction		0.0000	0.0000	0.0000	0.0000	0.4944	0.0000	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000
Temperature	C	58.07	58.96	60.00	387.6	145.6	25.00	60.00	60.00	64.05	64.05	279.7	60.00
Pressure	kPa	110.0	120.0	110.0	110.0	110.0	101.3	101.3	101.3	10.00	10.00	20.00	110.0
Molar Flow	kgmole/h	3.920	0.5107	3.670	0.2502	0.7609	8.334e-002	0.0000	0.8443	0.1097	3.500	6.000e-002	0.7609
Mass Flow	kg/h	1047	15.79	1037	10.01	25.80	8.167	0.0000	33.95	1.977	1017	18.41	20.30
Liquid Volume Flow	m3/h	1.188	1.287e-002	1.182	5.619e-003	1.848e-002	4.388e-003	0.0000	2.582e-002	1.982e-003	1.159	2.095e-002	1.739e-002
Heat Flow	kJ/h	-2.602e+006	-1.920e+005	-2.556e+006	-1.483e+004	-2.068e+005	-1.876e+004	0.0000	-2.927e+005	-2.629e+004	-2.474e+006	-3.423e+004	-2.625e+005
		26	27	28	NaOH	Glycerol(1)	11A-2	11A	MethanolB				
Vapour Fraction		0.0000	0.0000	0.0000	0.0000	0.0304	0.0000	0.0000	0.0000				
Temperature	C	60.00	-191.3	88.27	25.00	144.4	25.05	25.05	24.85				
Pressure	kPa	110.0	40.00	50.00	400.0	30.00	400.0	400.0	400.0				
Molar Flow	kgmole/h	8.334e-002	0.3255	0.4354	0.2500	2.447	4.484	4.484	1.383				
Mass Flow	kg/h	13.66	5.871	14.43	10.00	239.8	143.7	143.7	44.32				
Liquid Volume Flow	m3/h	8.434e-003	5.887e-003	1.150e-002	5.611e-003	0.1957	0.1806	0.1806	5.569e-002				
Heat Flow	kJ/h	-3.037e+004	-9.841e+004	-1.692e+005	-4.552e+004	-1.674e+006	-1.109e+006	-1.109e+006	-3.422e+005				

Energy Streams

		E1	E4	E3	E5	E6	E8	HEATING	E4-2	cooling1-2	heating1-2	E5-2
Heat Flow	kJ/h	67.35	-5.604e+004	457.0	-6.857e+004	3.554e+004	332.0	6.930e+004	5.936e+006	4.152e+007	3.617e+007	3367
		E6-2	COOLING2-2	E7-2	E8-2	COOLIN4-2	HEATING4-2	e9-2	COOLINGS-2	HEATINGS-2	E7	
Heat Flow	kJ/h	348.1	6.350e+005	3.150e+004	-6.713e+004	2.350e+006	2.371e+006	-218.3	6.713e+004	7.245e+004	92.62	

ANNEX XI: Process Flow Diagram of the Biodiesel production (Acid-catalyzed)

Mass and energy balances generated in ASPEN Hysys®



Material Streams

		Methanol	H2SO4	1	1A	Raw Material (2)	7	Raw Material	V1	6
Vapour Fraction		0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	1.0000	1.0000	0.0000
Temperature	C	25.00	25.00	25.00	25.15	-171.6	58.14	-176.1	80.00	80.00
Pressure	kPa	100.0	100.0	100.0	400.0	400.0	400.0	100.0	400.0	400.0
Molar Flow	kgmole/h	3.998	1.529	5.527	5.527	1.163	7.382	1.163	0.0000	7.382
Mass Flow	kg/h	128.1	150.0	278.1	278.1	1030	1330	1030	0.0000	1330
Liquid Volume Flow	m3/h	0.1610	8.105e-002	0.2420	0.2420	1.130	1.394	1.130	0.0000	1.395
Heat Flow	kJ/h	-9.572e+005	-1.222e+006	-2.179e+006	-2.179e+006	-2.269e+006	-4.752e+006	-2.270e+006	0.0000	-4.685e+006
		2	5B	V1-2	6B	8	9	10	V2	11
Vapour Fraction		0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0524	1.0000	0.0000
Temperature	C	31.37	60.00	80.00	80.00	81.36	181.4	232.9	60.00	60.00
Pressure	kPa	400.0	400.0	400.0	400.0	190.0	200.0	200.0	200.0	200.0
Molar Flow	kgmole/h	6.219	1.163	0.0000	7.382	0.6917	6.691	6.691	0.0000	8.220
Mass Flow	kg/h	300.3	1030	0.0000	1330	22.16	1308	1308	0.0000	1394
Liquid Volume Flow	m3/h	0.2699	1.130	0.0000	1.394	2.785e-002	1.367	1.367	0.0000	1.384
Heat Flow	kJ/h	-2.340e+006	-2.208e+006	0.0000	-4.691e+006	-1.610e+005	-4.228e+006	-4.050e+006	0.0000	-3.775e+006
		CaO	13	12	14	8A	8B	Biodiesel	15	GLYCEROL/H2O
Vapour Fraction		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000
Temperature	C	25.00	60.00	60.00	76.56	81.46	81.46	56.40	56.04	256.8
Pressure	kPa	200.0	130.0	130.0	120.0	400.0	400.0	110.0	40.00	50.00
Molar Flow	kgmole/h	1.529	6.660	1.560	3.173	0.6917	0.6917	3.488	2.006	1.167
Mass Flow	kg/h	85.77	1185	208.8	150.4	22.16	22.16	1035	43.31	107.1
Liquid Volume Flow	m3/h	2.599e-002	1.313	7.108e-002	0.1325	2.785e-002	2.785e-002	1.180	4.757e-002	8.498e-002
Heat Flow	kJ/h	2.226e-011	-3.793e+006	1.778e+004	-1.314e+006	-1.610e+005	-1.610e+005	-2.479e+006	-5.429e+005	-7.184e+005

Energy Streams

		E1	E3	E4	E4-2	COOLING1	HEATING1	COOLING2	E7	E8	E5	COOLING4	HEATING4
Heat Flow	kJ/h	96.99	982.0	-1.369e+005	-6111	7.770e+004	4.407e+005	1.783e+005	2.753e+005	-1.589	8.576	5.679e+006	5.733e+006