Life Cycle Assessment Applied to Naphtha Catalytic Reforming

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Abstract — Life Cycle Assessment Applied to Naphtha Catalytic Reforming — Facing the increase of environmental concerns in the oil and gas industry, engineers and scientists need information to assess sustainability of chemical processes. Among the different methods available, Life Cycle Assessment (LCA) is widely used. In this study, LCA is applied to a catalytic reforming process using the Eco-Indicator 99 as life cycle impact assessment method. The main identified environmental impacts are fossil fuels consumption, climate change and respiratory effects due to inorganics compounds. The influence of different process parameters (feed composition, reaction temperature) is determined with respect to environmental impacts. Two allocation methods are analysed (mass and exergetic allocation) and two different process versions are compared in order to determine the effect of some improvements on environmental impact.
INTRODUCTION

In the current context, oil and gas industry processes have to be developed considering technical and economical issues but also sustainability. Climate change is one of the main environmental impacts because its consequences could be considerable in some decades. But other impacts such as resource depletion, eutrophication, toxicity and ozone layer depletion have also to be taken into account when different products or processes are compared. A classical method used to quantify the environmental impact of a process or a product is Life Cycle Assessment. In this method each step of the life cycle is considered and an indicator is calculated for each impact. In this work, Life Cycle Assessment is applied to a process from the oil and gas industry: the naphtha catalytic reforming process.

1 LCA METHODOLOGY

1.1 System Life Cycle

A system is the whole set of unit operations corresponding to a product, a process or an activity. The life cycle is the whole set of sequential phases comprised in a system from raw materials acquisition to disposal or recycling (from cradle to grave). Each step of life cycle (extraction and treatment of raw materials, energy conversions, transportation, distribution, waste disposal or recycling...) has an impact on environment and must be taken into account. If only a part of the chain is studied, what could appear as an environmental improvement on this part could lead to a worsening of the environmental impact on other upstream or downstream parts of the chain (Bouvart and Prieur, 2009). These pollution transfers can occur from one phase to another phase of the life cycle or from one impact to another impact.

1.2 LCA Steps

LCA is a tool used to evaluate environmental impact at each step of a system life cycle. This methodology has been developed from chemical engineering principles and is based on mass and energy balances. LCA has mainly been applied to products but it can be applied for process design, selection and optimisation (Azapagic, 1999), (Burgess and Brennan, 2001a). In 1990, the Society for Environmental Toxicology and Chemistry (SETAC) initiated activities to develop a methodology for LCA (Consoli et al., 1993). The International Organisation for Standardisation (ISO) started a similar work (Guinée et al., 2000). LCA is divided into four steps corresponding to a set of standardised ISO norms:

- Objectives and scope definition (ISO 14040, 2000),
- Life Cycle Inventory analysis (ISO 14041, 2000),
- Life Cycle Impact Assessment (ISO 14042, 2000),
- Improvement analysis (ISO 14043, 2000).

Its main benefit, over other site specific methods, is to include all burdens and impact in the life cycle of a product or a process, and not focusing on the emissions and wastes generated by the plant or manufacturing site only.

The first step of the study consists in precisely defining the goal of the work, because it determines the way to lead the analysis. For example, if processes should be compared, some life cycle phases could be eliminated because they could be identical in the processes under comparison. It is also important to set up boundaries. For that purpose, life

NOMENCLATURE

A Reactor section
\( C_p^0 \) Specific heat capacity
\( m_i \) Mass flow rate of product \( i \)
\( Q \) Quality index
\( Q_m \) Mass flow rate
\( r_i \) Production rate of chemical reaction \( i \)
\( r_{i,j} \) Production rate of component \( j \) in reaction \( i \)
\( T \) Temperature
\( z \) Reactor abscissa
\( \alpha_i \) Monetary specific value of product \( i \)
\( \Delta H_i^0 \) Standard enthalpy of reaction \( i \)
\( \upsilon_{i,j} \) Stoichiometric coefficient of component \( j \) in reaction \( i \)
\( \mu \) Partial molar Gibbs energy
\( \rho \) Catalyst density

Abbreviations

AETP Aquatic Ecotoxicity Potential
CCS CO\(_2\) Capture and Storage
CFC Chlorofluorocarbon
DALY Disability Adjusted Life Years
ELCA Exergetic Life Cycle Assessment
EDF Electricité de France
GHG Greenhouse Gas
GWP Global Warming Potential
HCFC Hydrochlorofluorocarbon
IPCC Intergovernmental Panel on Climate Change
ISO International Organisation for Standardisation
LCA Life Cycle Assessment
LCI Life Cycle Inventory
LCIA Life Cycle Impact Assessment
LPG Liquefied Petroleum Gas
MJ Mega Joule
ON Octane Number
PDF Potentially Disappeared Fraction of species
PEC Predicted Environmental Concentration
PNEC Predicted No Environmental Concentration
RDF Refuse Derived Fuel
SETAC Society for Environmental Toxicology and Chemistry
TETP Terrestrial Ecotoxicity Potential
The improvement analysis is the phase in which the results of the previous phases are analysed according to the scope of the study. The objective is to conclude and to improve the life cycle in order to give information to decision maker.

### TABLE 1

<table>
<thead>
<tr>
<th>Environmental impact</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carcinogens</td>
<td>Carcinogenic effects due to emissions of carcinogenic substances to air, water and soil</td>
</tr>
<tr>
<td>Respiratory organics</td>
<td>Respiratory effects due to emissions of organic substances to air</td>
</tr>
<tr>
<td>Respiratory inorganics</td>
<td>Respiratory effects due to dust, sulphur, and nitrogen oxides to air</td>
</tr>
<tr>
<td>Climate change</td>
<td>Global warming due to greenhouse gas emissions in atmosphere</td>
</tr>
<tr>
<td>Radiation</td>
<td>Damage resulting from radioactive radiation</td>
</tr>
<tr>
<td>Ozone layer depletion</td>
<td>Damage due to increased UV radiation as a result of emission of ozone depleting substances to air</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>Damage to ecosystem quality as a result of emission of toxic substances to air, soil and water</td>
</tr>
<tr>
<td>Acidification</td>
<td>Forest and lake destruction by acid rains due to acid air emissions</td>
</tr>
<tr>
<td>Eutrophication</td>
<td>Lack of oxygen and algae development in water streams or soil due to too high nitrogen and phosphorous concentrations</td>
</tr>
<tr>
<td>Land use</td>
<td>Damage as a result of either conversion of land or occupation of land</td>
</tr>
<tr>
<td>Minerals</td>
<td>Non renewable resource depletion due to extraction and consumption of minerals</td>
</tr>
<tr>
<td>Fossil fuels</td>
<td>Non renewable resource depletion due to extraction and consumption of fossil fuels</td>
</tr>
</tbody>
</table>

### 1.3 Allocation of Co-products

Allocation can be defined as the act of proportionally distributing the responsibility for resources consumption, emissions and waste streams between different co-products in a process. Each environmental impact should be allocated to each co-product. Different allocation methods exist. The international standard gives some guidance on how to handle allocation problems (Finnveden et al., 2009):

- subdivision or system expansion when possible;
- substitution method (avoided impact method) when possible;
- allocation reflecting physical, chemical or biological causations (for example energetic or exergetic pro rata);
- allocation based on other measures (for example mass or economical pro rata).
The allocation method depends also on the system characteristics. For processes dealing with energy conversion, energetic or exergetic pro rata seems to be the best allocation mode because it reflects products value.

2 APPLICATIONS

There are not many references in literature describing the use of LCA to processes. We will here focus on works dealing with LCA applied to chemical processes, biofuels, recycling and renewable energy. Some examples are described in Table 2.

<table>
<thead>
<tr>
<th>Author</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burgess and Brennan (2001b)</td>
<td>Desulphurisation of gas oil</td>
</tr>
<tr>
<td>Arena et al. (2003)</td>
<td>Waste management</td>
</tr>
<tr>
<td>Chevalier et al. (2003)</td>
<td>Municipal solid waste incinerators</td>
</tr>
<tr>
<td>Renou et al. (2008)</td>
<td>Wastewater treatment processes</td>
</tr>
<tr>
<td>Bouvart and Prieur (2009)</td>
<td>Combined hydrogen and electricity production with integrated CO₂ capture and storage</td>
</tr>
<tr>
<td>Cherubini et al. (2009)</td>
<td>Biofuel and bioenergy systems</td>
</tr>
<tr>
<td>Gebreslassie et al. (2009)</td>
<td>Absorption cooling systems</td>
</tr>
<tr>
<td>Pehnt and Henkel (2009)</td>
<td>Carbon dioxide capture and storage from lignite power plant</td>
</tr>
<tr>
<td>Stichnotte and Azapagic (2009)</td>
<td>Bioethanol routes</td>
</tr>
</tbody>
</table>

Burgess and Brennan (2001a) gave a review of LCA applied to chemical processes before 2001. Burgess and Brennan (2001b) outlined the importance of fugitive emissions in a desulphurization process of petroleum gasoil incorporating a hydrotreater unit, hydrogen plant and sulphur recovery unit.

Renou et al. (2008) studied wastewater treatment process and discuss the influence of the Life Cycle Impact Assessment method. They conclude that the impact assessment methods do not influence LCA results for most of the impacts. However, concerning local river eutrophication, LCA should be combined with microbial and chemical risk analysis. The management of Municipal Solid Wastes (MSW) was led by Arena et al. (2003): three scenarios were taken into account: landfilling, Refuse Derived Fuel (RDF) production and combustion and mass burn combustion. Different environmental impacts were quantified (material consumption, climate change, acidification, air and water emissions and solid waste production). Results showed the poor performance of landfilling option with respect to the other options. In the same field, two processes for flue gas of solid waste in municipal incinerators were studied by Chevalier et al. (2003). Several environmental impacts were calculated to compare a classical wet type process and a new transported droplets column process.

Power generation systems have been studied by Lombardi (2003). Three different configurations were compared by an Exergetic Life Cycle Assessment (ELCA) and a classical LCA to decrease greenhouse gas emissions. ELCA is an analysis method based on life cycle approach in combination with exergy analysis developed by Cornelissen (1997). Destroyed exergy is viewed as an impact indicator reflecting the depletion of natural resources. A review of different LCA and exergy coupled analysis is given in a previous publication (Portha et al., 2009) and was applied to naphtha catalytic reforming.

Cherubini et al. (2009) compared different biofuels sources and their impact on Greenhouse Gas (GHG) emissions. They conclude that bioenergy compared to their fossil reference can achieve a reduction of GHG emissions and fossil energy consumption but other environmental impacts (such as eutrophication and local air pollution) can be increased. LCA requires taking into account all environmental impact when biofuels routes are compared to classical fuel routes.

Stichnotte and Azapagic (2009) studied two bioethanol routes produced from two different feedstocks derived from household waste and show that GHG emissions decrease significantly for a given scenario but that a full life cycle approach has to be applied to take all impacts into account.

Bouvart and Prieur (2009) compared twelve scenarios concerning combined hydrogen and electricity production with and without CO₂ Capture and Storage (CCS) for different feedstocks (natural gas, bituminous coal and lignite). The study was based on two main criteria: GHG emissions and non renewable primary energy consumption. A significant reduction of the GHG emissions (between 70 and 82%) and a significant increase of the non renewable energy consumption were shown when CCS was used. Pehnt and Henkel (2009) led the same task for several lignite power plant technologies. The LCA included post combustion, pre combustion and oxyfuel capture processes transport and storage of the CO₂. The results were the same as previously. For other environmental impacts, the results depend on the chosen technology.

The design of a sustainable absorption cooling system was provided by Gebreslassie et al. (2009). The total annualized cost and the environmental impact of the cycle were minimized by a multiobjective optimisation method. Authors outlined that a compromise has to be found between the economic performance and fossil fuel consumption (main impact of LCA in this case).
3 CATALYTIC REFORMING PROCESS

Catalytic reforming is a chemical process used to convert naphtha (of low octane number) produced during petroleum refining, into high-octane number liquid products (Meyers, 1996) which are called reformates. Basically, the process redesigns the hydrocarbon molecules of the naphtha feed and performs aromatization. Alongside these reactions, cracking (breakage of large molecules into smaller ones) takes place. The process produces very significant amounts of hydrogen gas and some light co-products (fuel gas and liquefied petroleum gas). The process studied here is a typical continuous catalytic regeneration reforming process. Because of coke formation, this type of process (depicted in Fig. 1) is characterized by a continuous in situ regeneration of the catalyst in a special regenerator. The regeneration of catalyst by coke combustion is also a source of direct greenhouse gas emissions in the process.

The reactions taking place are globally endothermic. The reaction section is split into four catalytic reactors. To maintain an appropriate temperature, between each reactor, a furnace heats the feed back up to the desired temperature. Each reactor inlet temperature is around 500°C and pressure is around 5 bar. Reactors are moving bed catalytic reactors with a Pt-Sn/Al₂O₃ catalyst. Flash distillations and an atmospheric distillation column enable to separate products in the separation section. Catalyst regeneration is not represented in Figure 1 because the figure would be unreadable.

Two processes having the same function are considered in this study in order to be compared:

- the basic process (Process 1) described in Figure 1;
- the modified process (Process 2) corresponding to the basic process with two changes: for feed/effluent heat exchanger E1, a high performance heat exchanger is used instead of a classical one and a recycle loop is added to recycle Fuel Gas in order to have more LPG (a product having a higher price).

The vapor/liquid equilibria are calculated according to the Grayson-Streed thermodynamic model. The kinetic model used to represent chemical reactions taking place in reactors is based on the work by Marin and Froment (1981) and by Van Trimpont et al. (1988). The mechanism involves the following reactions: isomerisation, paraffins ring closure, naphthenes dehydrogenation and hydrocracking. The petroleum cuts C6, C7, C8, C9 and C10 (number of carbon atoms of the component) contained in the feed are taken into account for chemical reactions. For petroleum cut C7, the chemical reactions are described in Table 3.

Figure 1
The process is simulated with the process simulator ProII 8.0 (Simsci, Lake Forest, Illinois) coupled with a Fortran subroutine for reactor calculation. Plug flow is assumed in the reactors. Under these conditions, a mass balance has been applied for each component \( j \) of the mixture involved in chemical reaction \( i \) and is given by Equation (1):

$$
\frac{dF_j}{dz} = \sum_{i} \nu_{ij} r_{ij} \rho A
$$

with \( F_j \): molar flow rate of component \( j \) (mol.s\(^{-1}\)), \( z \): reactor abscissa (m), \( \nu_{ij} \): stoichiometric coefficient of component \( j \) in reaction \( i \), \( r_{ij} \): production rate of component \( j \) in reaction \( i \) (mol.kg\(^{-1}\).s\(^{-1}\)), \( \rho \): catalyst density (kg.m\(^{-3}\)) and \( A \): reactor section (m\(^2\)).

A global heat balance has also been applied and is given by Equation (2):

$$
\frac{dT}{dz} = - \frac{\rho A}{Q_m} \left( \sum_{i} r_i \Delta_r H_i^\circ (T) \right)
$$

with \( T \): temperature (K), \( Q_m \): mass flow rate (kg.s\(^{-1}\)), \( C_p^0 \): specific heat capacity (J.kg\(^{-1}\).K\(^{-1}\)), \( r_i \): production rate of chemical reaction \( i \) (mol.kg\(^{-1}\).s\(^{-1}\)) and \( \Delta_r H_i^\circ \): standard enthalpy of reaction \( i \) (J.kg\(^{-1}\)).

The differential equations system is solved for each reactor by a Runge-Kutta method. Results have been validated by comparison with full scale industrial data. Numerical information obtained from simulations of the studied processes is given in Table 4.
For the LCIA step, the Eco-Indicator 99 method is used. It applies a damage oriented approach meaning that the damage to human or ecosystem caused by environmental effects is modelled. At the characterisation step, eleven impacts are considered: acidification, eutrophication, ozone layer depletion, greenhouse effect, resource depletion... The damage assessment step reduces these impacts into three damage categories: human health, ecosystem quality, and resources. Impacts and damage categories are presented in Table 6. Human health presents one major drawback as it contains impacts such as climate change that do not concern directly human toxicity.

The characterisation factors are described in Table 7.

For instance, the characterisation factors for different greenhouse gases are given in Table 8. The considered factor is the global warming potential calculated over 100 years and defined by the IPCC (2007).
To show in what extent an impact category has a significant contribution, the normalisation step is used. Results from impacts characterisation are divided by an inhabitant equivalent (environmental effects that an average European causes in a year). In the weighting step, some impacts are considered to be more important by the decision makers. Weighting factors are also allocated to environmental impacts. Results presented in the next part take into account this last step.

5 RESULTS

In this paragraph, all results given in Figures 3-6 are also reported in Appendix in the form of tables.

5.1. Influence of Temperature

The inlet temperature range of a furnace is comprised between 497°C (770 K) and 537°C (810 K). The inlet temperature of a furnace is identical for each furnace for a given simulation. The temperature level has a direct impact on the quality of reformate and on the quantity of energy used in a furnace. Increasing the temperature means that the quantity of aromatic products and the octane number are higher. But it means also that utility consumption increases and that the corresponding environmental impacts are greater. This result is described in Figure 3. The value of an environmental impact is given in milli-Eco-Indicator points. Numbers on the abscissa axis correspond to the different impacts described in Table 5. An increase of the inlet temperature involves an increase of all environmental impacts. In this figure, the main impact is fossil fuels consumption (88.3% of the total). Fossil fuels are used especially to produce heat in natural gas furnaces. The others significant impacts are climate change (4.5%), respiratory effects due to inorganics (3.4%) and land use (2.2%).

The temperature increase implies an increase of reformate octane number and an increase of the quality factor (including all co products). The scenarios comparison presents difficulties because the functional unit (quality of reformate) is changed when temperature is modified. The comparison is possible when normalisation is performed by dividing the total environmental impact by the reformate octane number. This shows that the process working at \( T = 770 \) K presents the lower environmental impact for a given octane number.

The naphtha production life cycle is here not taken into account because the aim of the work is to compare different process conditions. This is a good assumption when the same
quantity of reformate is produced for a given quantity of naphtha feed. The quantity of feed is always identical. But, as presented in Table 9, the quantity of reformate decreases when the temperature increases. So, strictly speaking, the naphtha production life cycle should be taken into account in the analysis.

### Table 9
Temperature influence on products quality for 1 kg of reformate (Process 1, naphtha 1)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Octane number (ON)</th>
<th>Quality factor (€.h⁻¹)</th>
<th>Reformate quantity (kg.h⁻¹)</th>
<th>Total environmental impact (mPt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>770</td>
<td>88.3</td>
<td>21 889</td>
<td>57 858</td>
<td>10.37</td>
</tr>
<tr>
<td>790</td>
<td>92.7</td>
<td>23 229</td>
<td>56 940</td>
<td>11.07</td>
</tr>
<tr>
<td>810</td>
<td>96.4</td>
<td>24 602</td>
<td>55 650</td>
<td>11.51</td>
</tr>
</tbody>
</table>

#### 5.2 Distribution of the Environmental Impact between the Life Cycle Steps

The life cycle phases that contribute to the three main environmental impacts in our case study (fossil fuels consumption, climate change and respiratory effects due to inorganics) are presented in Figure 4. For each impact, the main contribution is due to the heat produced in natural gas industrial furnaces. Electricity represents less than 25% because it corresponds to the French electricity mix with a large part of nuclear energy (Tab. 5), which does not affect fossil fuels consumption and climate change.

The direct emissions (greenhouse gas emissions of CO₂) taking place in the process itself are induced by the catalyst regeneration unit (by coke combustion) but it represents only 0.8% of the total impact of climate change. Concerning this impact, the contribution of heat furnaces and electricity represents respectively 91.9% and 7.3%.

#### 5.3 Process Comparison

The two compared processes have been described previously (Sect. 3). The environmental impacts associated with both processes are given in Figure 5. Fossil fuels consumption...
represents the main environmental impact. The global environ-
mental impact (sum of all impacts) presents a decrease of
1.77% for process 2 with respect to process 1. This result was
expected because the high performance heat exchanger
enables a saving of fossil fuels.

The comparison is here possible because the octane number
is the same in both processes as shown in Table 10. The
global quality index of co products is higher for process 2
because the recycle loop involves a higher production of
LPG (a product having a better monetary value).

<table>
<thead>
<tr>
<th>TABLE 10</th>
<th>Process influence on products quality for 1 kg of reformate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>1</td>
</tr>
<tr>
<td>Octane number</td>
<td>96.4</td>
</tr>
<tr>
<td>Quality factor (€.h⁻¹)</td>
<td>24 602</td>
</tr>
</tbody>
</table>

### 5.4 Influence of Feed

Processes are simulated by using six different feeds. The feed
composition is given in Table 11. The feed is a heavy
gasoline cut from the atmospheric distillation unit. It contains
hydrocarbon chains with six, seven, eight, nine or ten carbon
atoms. It is mainly composed of paraffins and naphthenes
and has also a low octane number. The feed composition
depends on crude oil geographic origin.

<table>
<thead>
<tr>
<th>TABLE 11</th>
<th>Feeds molar composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>1 2 3 4 5 6</td>
</tr>
<tr>
<td>n-paraffin</td>
<td>19.0 24.7 27.2 28.6 18.5 16.7</td>
</tr>
<tr>
<td>iso-paraffin</td>
<td>23.7 31.6 39.4 36.4 23.5 21.3</td>
</tr>
<tr>
<td>naphthenes</td>
<td>41.6 30.5 19.8 20.0 34.0 52.0</td>
</tr>
<tr>
<td>aromatic</td>
<td>15.7 13.2 13.7 15.0 24.0 10.0</td>
</tr>
</tbody>
</table>

The results, presented in Figure 6, show that, for each feed,
the process 2 has a lower impact than process 1. Here the
naphtha life cycle should be included in the analysis. But as
the impact of the feed composition on chemical reactions was
investigated in this study the naphtha pathway was not
considered. Moreover, even if the flow rate of naphtha 3 is
very high with respect to the others, the simulations can be
compared because the reformate/naphtha ratio is almost
constant (Tab. 12). The results show that an increase of iso
paraffins involves a decrease of the global environmental
impact. This could be explained by the fact that iso paraffins
are favourably converted by exothermic cracking reactions.
This implies that heat supplied by furnaces should be lower.
But a high proportion of iso paraffins means also a low
reformate octane number (Tab. 12). The other significant
parameter is the proportion of naphthenes. An increase of
naphthenes involves an increase of the global environmental
impact associated with an increase of the octane number (for
instance for Naphtha 1 and 6). Naphthenes are converted by
endothermic dehydrogenation reaction into aromatics. This
implies that heat supplied by furnaces should be higher when
the naphthenes proportion is high. The octane number is also
high. It is the case for instance for Naphtha 6.

Finally, production of reformate with low octane number
leads to a low total environmental impact. The required
specification to produce gasoline with a high octane number
is also not reached, so the environmental impact is just

<table>
<thead>
<tr>
<th>TABLE 12</th>
<th>Feed influence on products quality for 1 kg of reformate (Process 1, T = 810 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>1 2 3 4 5 6</td>
</tr>
<tr>
<td>Naphtha (kg,h⁻¹)</td>
<td>60 605 59 612 91 122 60 897 59 528 59 525</td>
</tr>
<tr>
<td>Reformate flow rate (kg,h⁻¹)</td>
<td>55 650 54 202 82 947 55 158 54 828 54 704</td>
</tr>
<tr>
<td>Reformate/Naphtha ratio (%)</td>
<td>91.8 90.9 91.0 90.6 92.1 91.9</td>
</tr>
<tr>
<td>Octane Number (ON)</td>
<td>96.4 93.2 87.1 91.5 98.3 95.9</td>
</tr>
<tr>
<td>Quality factor/ reformate flow rate (€.kg⁻¹)</td>
<td>0.4421 0.4396 0.4162 0.4373 0.4483 0.4387</td>
</tr>
<tr>
<td>Total environmental impact (mPt)</td>
<td>11.5 10.9 9.6 10.4 10.6 12.4</td>
</tr>
</tbody>
</table>
exported. Indeed, when specification is not met at the outlet of this specific process, actions should be undertaken, for example refining in another unit to reach the specification needed for use of gasoline.

5.5 Influence of the Allocation Method

Two allocation methods are applied to the studied system: mass pro rata and exergetic pro rata (physical and chemical exergy are taken into account). The expressions of exergy are given in previous works (Portha et al., 2008, 2009). The mass and exergetic percentages are given in Table 13. The reformate represents almost 92% in mass of the total mass of co products but only 86% when exergy is used to allocate co products. This is due to the high exergetic value per mass of hydrogen. This result is also true for energy.

<table>
<thead>
<tr>
<th>Table 13</th>
<th>Mass and exergetic pro rata for co products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass allocation (%)</td>
</tr>
<tr>
<td>Reformate</td>
<td>91.8</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>7.0</td>
</tr>
<tr>
<td>LPG</td>
<td>1.0</td>
</tr>
<tr>
<td>Fuel Gas</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The results presented in Figure 7 show that the exergetic allocation implies a decrease of the impacts relative to reformate. This was expected because the proportion of reformate is lower for exergetic allocation than for mass allocation. The reformate has also a different impact depending on whether exergetic or mass allocation is considered.

The substitution method was applied for one impact: climate change. This method consists in allocating all GHG emissions to the main product. After a calculation of the GHG emissions of the co-products produced by alternative processes, these emissions are summed. The difference between these two quantities gives the GHG emissions of the main product. The considered alternative pathway for hydrogen production was methane reforming. The contributions of other co-products were neglected. The results with this allocation method are presented in Table 14. Results show that reformate produced by catalytic reforming implies a saving of GHG emissions. This result is explained by the fact that catalytic reforming is the best process, from a sustainability point of view, to produce hydrogen.

<table>
<thead>
<tr>
<th>Table 14</th>
<th>Allocation method influence on climate change for 1 kg reformate (Process 1, T = 810 K, naphtha 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allocation method</td>
<td>GHG emissions relative to 1 kg reformate (g eq CO2)</td>
</tr>
<tr>
<td>Mass</td>
<td>123.1</td>
</tr>
<tr>
<td>Exergetic</td>
<td>115.1</td>
</tr>
<tr>
<td>Substitution</td>
<td>-745.5</td>
</tr>
</tbody>
</table>

CONCLUSION

Life Cycle Assessment is an interesting tool for chemical engineering. It provides information about process sustainability which is a relevant criterion for process selection and design. This tool is widely used in literature in different fields. A naphtha catalytic reforming process has been selected and evaluated by LCA using the Eco-Indicator 99 method. This methodology shows that the main environmental impacts are fossil fuels consumption, climate change and respiratory effects due to inorganics. The main contribution in terms of unit operation is due to the heat furnaces. The comparison performed to analyze two versions of the process displays that an addition of a high performance heat exchanger and a recycle loop to improve products quality are beneficial to decrease environmental impacts. Temperature and feed composition influence on environmental impacts were investigated: an increase of reactor temperature implies an increase of the impacts due to the endothermic chemical reactions; an increase of the iso-paraffins/n-paraffins ratio involves a decrease of environmental impacts because iso-paraffins are easily converted by exothermic cracking reaction; an increase of the naphthenes/aromatics ratio leads to a increase of the impacts because naphthenes are converted by endothermic dehydrogenation reactions. The quality of the obtained products is a relevant parameter because the
functional unit is defined with respect to a reformate having a
given quality. In chemical processes, this is a complicated
task because the compositions of crude oil and process para-
meters (temperature, pressure...) have an impact on com-
position and quality of the products.

REFERENCES


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Published online in October 2010
## APPENDIX

Table related to Figure 3: Temperature influence on environmental impacts for 1 kg reformate  
(Process 1, naphtha 1, mass allocation)

<table>
<thead>
<tr>
<th>Impact</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 770 K</td>
<td>1.99E-2</td>
<td>1.09E-3</td>
<td>3.55E-1</td>
<td>4.66E-1</td>
<td>4.38E-2</td>
<td>4.40E-4</td>
<td>2.11E-2</td>
<td>6.5E-2</td>
<td>2.3E-1</td>
<td>1.89E-2</td>
<td>9.15</td>
</tr>
<tr>
<td>T = 790 K</td>
<td>2.1E-2</td>
<td>1.16E-3</td>
<td>3.78E-1</td>
<td>4.97E-1</td>
<td>4.61E-2</td>
<td>4.64E-4</td>
<td>2.24E-2</td>
<td>6.93E-2</td>
<td>2.42E-1</td>
<td>2.01E-2</td>
<td>9.78</td>
</tr>
<tr>
<td>T = 810 K</td>
<td>2.18E-2</td>
<td>1.2E-3</td>
<td>3.92E-1</td>
<td>5.17E-1</td>
<td>4.76E-2</td>
<td>4.81E-4</td>
<td>2.32E-2</td>
<td>7.2E-2</td>
<td>2.5E-1</td>
<td>2.08E-2</td>
<td>10.16</td>
</tr>
</tbody>
</table>

Table related to Figure 4: Assignment of the three main environmental impacts  
(Process 1, T = 810 K, naphtha 1, mass allocation)

<table>
<thead>
<tr>
<th>Impact</th>
<th>Resp. inorganics</th>
<th>Climate change</th>
<th>Fossil fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat furnace</td>
<td>77.7</td>
<td>91.9</td>
<td>98.6</td>
</tr>
<tr>
<td>Electricity</td>
<td>22.3</td>
<td>7.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Catalyst regeneration unit</td>
<td>0</td>
<td>0.8</td>
<td>0</td>
</tr>
</tbody>
</table>

Table related to Figure 5: Process influence on environmental impacts for 1 kg of reformate  
(T = 810 K, naphtha 1, mass allocation)

<table>
<thead>
<tr>
<th>Impact</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process 1</td>
<td>2.18E-2</td>
<td>1.2E-3</td>
<td>3.92E-1</td>
<td>5.17E-1</td>
<td>4.76E-2</td>
<td>4.81E-4</td>
<td>2.32E-2</td>
<td>7.2E-2</td>
<td>2.5E-1</td>
<td>2.08E-2</td>
<td>10.16</td>
</tr>
<tr>
<td>Process 2</td>
<td>2.16E-2</td>
<td>1.18E-3</td>
<td>3.87E-1</td>
<td>5.08E-1</td>
<td>4.76E-2</td>
<td>4.81E-4</td>
<td>2.32E-2</td>
<td>7.2E-2</td>
<td>2.49E-1</td>
<td>2.06E-2</td>
<td>9.98</td>
</tr>
</tbody>
</table>

Table related to Figure 7: Allocation method influence on environmental impacts for 1 kg of reformate  
(Process 1, T = 810 K, naphtha 1)

<table>
<thead>
<tr>
<th>Impact</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass allocation</td>
<td>2.18E-2</td>
<td>1.2E-3</td>
<td>3.92E-1</td>
<td>5.17E-1</td>
<td>4.76E-2</td>
<td>4.81E-4</td>
<td>2.32E-2</td>
<td>7.2E-2</td>
<td>2.5E-1</td>
<td>2.08E-2</td>
<td>10.16</td>
</tr>
<tr>
<td>Exergetic allocation</td>
<td>2.04E-2</td>
<td>1.13E-3</td>
<td>3.68E-1</td>
<td>4.84E-1</td>
<td>4.46E-2</td>
<td>4.5E-4</td>
<td>2.18E-2</td>
<td>6.74E-2</td>
<td>2.34E-1</td>
<td>1.95E-2</td>
<td>9.52</td>
</tr>
</tbody>
</table>