



Life Cycle Analysis applied to acrylic acid production process with different fuels for steam generation



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ABSTRACT

Acrylic acid, one of the most important monomers, has a wide range of uses e.g. in the paints adhesives, textile finishing, leather processing or super absorbents. The production process from propylene is well known and used at industrial scale in the USA, Europe, and Asia. The present paper focuses on the evaluation of the environmental impact of the acrylic acid production process from propylene. Steam is a major raw material in the process under study, consequently different paths to obtain steam are investigated. The process was simulated using commercial software (Aspen Plus, PROII). A productivity capacity of 50,000 tones/year of acrylic acid has been considered. The environmental assessment, evaluated using Life Cycle Analysis method, depends on the material and energy balances generated by simulations. The present work uses a cradle-to-grave approach. The functional unit, to which all the environmental results for the cases under study are reported, is one tone of acrylic acid produced. The boundaries of the system cover: i) acrylic acid production; ii) upstream processes for example catalyst and molten salt production; steam production using various fuels (e.g. natural gas, anthracite, lignite, heavy fuel oil, light fuel oil and biomass) and iii) downstream processes for example: acrylic acid and acetic acid transport to other chemical plants for further processing. The CML (An LCA method developed by the Center of Environmental Science of Leiden University) 2001 impact assessment method was used for comparison between different case studies. The best value for Global Warming Potential (GWP) e.g. 1094.5 kg CO₂-Equiv./tone is obtained when biomass is used to generate the steam required by the process. For other indicators such as Acidification Potential (AP), Photochemical Oxidation Potential (PCOP) and Eutrophication Potential (EP), the best value is obtained when steam is generated from natural gas. A sensitivity analysis of the environmental impact categories using the different combination of natural gas and biomass was also investigated. The study investigates also the association of the post-combustion amine-based carbon capture technologies with the conventional acrylic acid production process. Such association decreases the value of some environmental impact categories (e.g. GWP) while other impact categories are increasing e.g. AP, Human Toxicity Potential (HTP), Terrestrial Ecotoxicity Potential (TETP).

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1. Introduction

The products of petrochemical industry are used in all life sectors (Chen et al., 2014). For instance, acrylic acid can have many uses such as intermediates for other chemical products, coatings, floor polishes, finishing products for textile and leather industry. It is also considered an important raw material in the manufacture of various thermoplastics, resins and rubbers (BASF, 2012). There is an

increasing demand for crude acrylic acid on the market. This growth is forecast at almost 4.5%/year until 2018 and is due to continuous growth in superabsorbent polymers at 4.8%/year and acrylate esters at 4.3%/year. The growth in China and other regions of Asia is expected to be higher e.g. 13–14%/year until 2018. The growth will be much more moderate in other regions such as North America, Western Europe or Japan (HIS, 2014).

There are various methods for acrylic acid production (e.g. ethylene cyanohydrin method; propiolactone method; carbonyl reaction; catalytic carbonyl reaction; (stoichiometric) carbonyl reaction; propylene oxidation method; acrylic ester method; vinyl grignard method). Currently, most of the acrylic acid is being

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commercially produced through the oxidation of propylene or propane (Corma et al., 2007). Bio-based production of acrylic acid from renewable resources such as sugar is a new and attractive alternative to petroleum based chemicals but it is still at early stages of development (Chu et al., 2015). The attention of the present work is focused on the traditional and mature technology for acrylic acid production starting from propylene. According to Zhang and co-authors there are some concerns related to this process. The high demands for fossil fuel and the relative low reserves of oil, the prices of propylene and its downstream products which go up dramatically, the issues of groundwater pollution and air pollution caused by fossil fuel extraction represent the burdens of the acrylic acid production from propylene. All these aspects leads to increasing pressure to the production line of acrylic acid from propylene (Zhang et al., 2016).

Over the last 30 years, one of the priorities of the petrochemical industry has been represented by the improvement of its energy efficiency and the reduction of the greenhouse gas emissions (Mohammadi et al., 2013). In the context of being so widely used all over the world, the environmental impact of acrylic acid production process should be quantified. This work has been previously performed by Fermeglia and Toma (Fermeglia et al., 2009; Toma, 2008), who calculated eight sustainability indexes for the process under investigation, but the attention was focused only on the chemical process and not on the whole product life cycle, which is of paramount importance nowadays in the petrochemical industry. The main goal of the present work is to evaluate the environmental impact of the acrylic acid production process from propylene. In order to reach the proposed goal specific tools such as LCA and process modelling and simulation are used. Another aspect investigated in the present paper is the comparison, in terms of environmental indicators, between the classical acrylic acid production process and the acrylic acid production process in association with post-combustion CO₂ capture using amine. The latter approach is important for the petrochemical industry to moderate the effects of climate change and minimise its environmental impact (Petrochemicals Europe, 2015).

The paper is organised as follows: Section 2 is dedicated to the LCA methodology, detailing the LCA phases. Results and discussions are presented in Section 3. Finally, the conclusions are reported in Section 4.

2. Life Cycle Analysis (LCA)

LCA is an environmental tool used to evaluate the effects of a process or product on the environment. It quantifies the environmental benefits and impacts of production processes and reveals cross-media issues (Yilmaz et al., 2015). An LCA study takes into consideration different phases. Usually, the study starts with the extraction, processing and transport of the raw material used in the process, continues with the manufacturing process and ends with the distribution, transport and usage of the product and by-products. The study includes also the recycling or disposal of the products and by-products at the end of their life. Emissions and depletion of resources are considered in each single phase of the LCA (Strazza et al., 2011). One essential aspect of this type of analysis is that the environmental burdens are not transferred accidentally from one stage to another during process improvements (Helling, 2014).

LCA is a methodology that offers a complete view of a product life-cycle. In addition to the manufacturing process, complementary processes such as raw materials acquisition, processing, and transportation as well as downstream processes should be taken into account. A methodological framework, called ISO 14044, for performing an LCA study was established by the International

Standards Organization (ISO) and it consists of four phases: 1) the definition of the goal and scope; 2) the life Cycle Inventory (LCI) analysis; 3) the life cycle impact assessment (LCIA); and 4) the interpretation of the results (Korre et al., 2010; ISO 14040, 2006). These steps are detailed in the next section.

2.1. LCA: goal, functional unit, system boundaries, assumptions

The aim of the present study is to determine the environmental impact of the acrylic acid production using propylene as raw material. The production of one tone of acrylic acid represents the functional unit of the systems considered in the LCA assessment.

The system boundaries included in this study are:

- i) acrylic acid production from propylene;
- ii) upstream processes for example catalyst and molten salt production; steam production using various fuels (e.g. anthracite, lignite, natural gas, heavy fuel oil, light fuel oil, biomass, or combinations of natural gas and biomass in different proportions);
- iii) downstream processes for example acrylic acid transport over a distance of 100 km to a paints adhesives plant and acetic acid (by-product) transportation over a distance of 250 km to another chemical plant.

The system boundaries for the cases under study are presented in Fig. 1.

The following case studies are discussed and compared in the LCA:

Case 1. Acrylic acid production process from propylene using steam from natural gas

Case 2. Acrylic acid production process from propylene using steam from hard coal

Case 3. Acrylic acid production process from propylene using steam from lignite

Case 4. Acrylic acid production process from propylene using steam from heavy fuel oil

Case 5. Acrylic acid production process from propylene using steam from light fuel oil

Case 6. Acrylic acid production process from propylene using steam from biomass

Case 7. Acrylic acid production process from propylene using 25% steam from natural gas and 75% steam from biomass

Case 8. Acrylic acid production process from propylene using 50% steam from natural gas and 50% steam from biomass

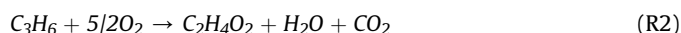
Case 9. Acrylic acid production process from propylene using 75% steam from natural gas and 25% steam from biomass

Case 10: Acrylic acid production process from propylene using steam from natural gas coupled with post-combustion amine-based CO₂ capture.

2.2. Life Cycle Inventory (LCI)

All the relative inputs and outputs are identified and quantified in the LCI phase (Flynn and Traver, 2013). The tool used to develop the LCI was process modelling and simulation. Details regarding the process model are presented in the next section of the paper.

The following reactions occur in the acrylic acid production via propylene oxidation process:



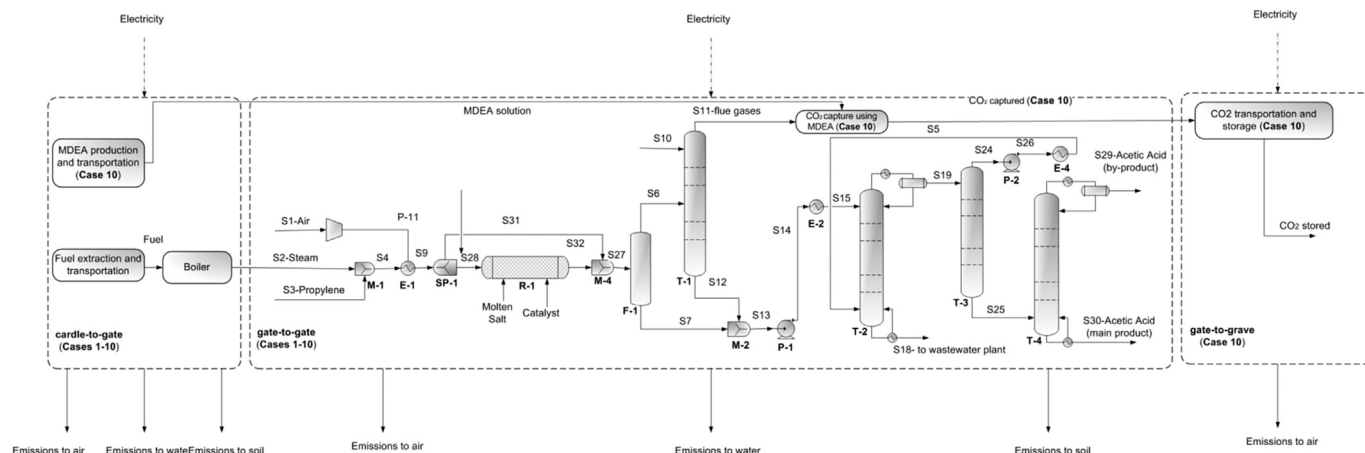


Fig. 1. Acrylic Acid Production Process from propylene. Process flow diagram and boundary conditions for LCA.



The reaction kinetics (Turton et al., 2003) is presented in Table 1. Fig. 1 illustrates the process flow diagram for the process under study as well as the boundary conditions for the LCA.

Propylene, S3, is fed from a storage tank. Air stream, S1, is compressed in the C-1 compressor and it represents the source of oxygen. Steam, S2, is used to provide thermal ballast for the exothermic heat of reaction. The use of steam also allows the reactions in homogeneous phase to be reduced, the thermal transfer to be improved and selectivity to be increased, favouring the desorption of acrolein and acrylic acid. After being mixed in M-1, the feeds enter R-1 reactor. It is assumed that the reactor is a fluidized bed reactor, and it operates isothermally at 310 °C. The vapour effluent is stripped with de-ionized water stream in T-1.

To avoid polymerization, an inhibitor is added, and the acrylic acid should be maintained in a cold liquid state. The gaseous stream containing N₂, O₂, CO₂ and propylene exit out the top together with some acrylic and acetic acid that are in the vapour phase. Deionized water is used to absorb the gasses. The solution of acrylic acid is sent to the purification section, which consists of a series of azeotropic distillation columns. The liquid stream of the flash is mixed in M-2, with the liquid stream coming from the stripper and stream S13 is formed. The non-recycled liquid is sent to the T-2 extractor, to remove the acid fraction from water. Many possible solvents can be utilized (Turton et al., 2003). In this case, diisopropyl ether (DIPE) is utilized. After usage, DIPE is recovered at the top of T-3 column and recycled to the T-2 extractor (Turton et al., 2003). The bottom stream from this column, S25, containing acrylic acid and acetic acid is sent to another column, T-4. The products of this column are: stream S30 containing 99.9% acrylic acid is obtained at the bottom of the column and stream S29 which contains acetic acid is obtained at the top. The aqueous phase is sent to a wastewater column where a small amount of DIPE is recovered and returned to the extractor. The bottom product of T-2 column, S18, containing water and trace of solvent and acid is sent to a wastewater treatment plant (Turton et al., 2003).

Table 1
Kinetic data for acrylic acid production process.

Reaction	Activation energy E _a (kcal/kmol)	Kinetic constant k _{0,i} (kmol/m ³ reactor h/(kPa) ²)
R 1	15,000	1.59 × 10 ⁵
R 2	20,000	8.83 × 10 ⁵
R 3	25,000	1.81 × 10 ⁵

There are two safety concerns about the acrylic acid process. Firstly, the reactions involve partial oxidation of a flammable and explosive gas medium (propylene), so considerable attention must be paid to the compositions of propylene and oxygen in the feed stream to the reactor (Suo et al., 2015). The second safety concern is associated with the highly exothermic polymerization of acrylic acid (Cutie et al., 1997). Acrylic acid of high concentration is dimerized at temperatures higher than 110 °C, therefore the separation sequence must be operated under vacuum to keep the bottom temperature in the distillation columns below this temperature.

The design characteristics of the processes under study are shown in Table 2. The most significant input streams: air S1, steam S2, propylene S3, deionized water S10, as well as the simulation results for acrylic acid stream S30, acetic acid stream S29, wastewater stream S18, and off-gases stream S11 are summarized in Table 3.

The simulation was performed using commercial process simulation software (Aspen Plus and PROII) starting from the assumptions and data previously presented. UNIFAC thermodynamic method was used in the present simulation. As it can be noticed from streams specifications table (see Table 3), the steam S2 (e.g. 995 kmol/h) is an important raw material used in the process. Consequently, it was important to consider not only the production process but also the raw materials used in the steam generation process.

Steam can be obtained using different fuels (e.g. natural gas, anthracite, lignite, heavy fuel oil, light fuel oil, biomass, and a combination of natural gas and biomass). For Case 1, the process steam is produced in natural gas specific heat plants. Different phases such as natural gas extraction, processing, and transportation via pipelines to the boilers for the steam generation are taken into account (see Fig. 2) (PE International, 2012).

The main LCA assumptions are summarized in Table 4. For Case 2 the steam is produced from hard coal, for Case 3 steam is produced from lignite, for Case 4 it should be mentioned that the heavy fuel oil (HFO) is considered. Case 5 is similar to Case 4 the only difference consists in the fact that light fuel oil (LFO) is used instead of heavy fuel oil. For Case 6, the process steam is produced from solid biomass. The solid biomass is a mixture of wood containing softwood, hardwood, wood chips, wood residues, wood pellets and herbaceous (PE International, 2012). For Cases 7–10 different proportion of natural gas and biomass are used. The extraction, production, processing and transportation of the fuels to the boilers are considered in the study (PE International, 2012). For all cases

Table 2
Main design characteristics for acrylic acid production process from propylene.

Equipment/Unit	Cases 1–10
Reactor	Fluidized bed filled with molten salt Reactor temperature: 310 °C 10% of gas is bypassing the catalyst
Pumps	Centrifugal/electrical Pump efficiency 75%
Air compressor	Centrifugal compressor Compressor efficiency 77% Inlet pressure: 1 bar Outlet pressure: 5 bar
Steam generation	Steam temperature: 160 °C Steam pressure: 6 bar Boiler efficiency 85%
Cooling water temperature	20 °C
Heat Exchanger ΔT_{\min}	10 °C
Post-combustion carbon capture	Gas–liquid reacting system: MDEA Adsorption column: 35–55 °C Desorption column: 100–125 °C CO ₂ removal efficiency ~90%
Captured CO ₂ conditioning (compression and drying)	Multi-stage compression with intercooling at 120 bar Tri-ethylene-glycol (TEG) dehydration

the steam efficiency was assumed to be 85%. Other assumptions for the present LCA are detailed in the next section.

It is assumed that the main raw material, propylene, is obtained at the refinery from crude oil. We considered that the deionized water used in all cases is obtained from reverse osmosis. Reverse osmosis is a modern method used worldwide to convert seawater and wastewater into fresh water (Fritzmann et al., 2007). The application of reverse osmosis membrane technology is today well known for water sea desalination. According to Greenlee and co-authors, over the past 40 years this technology reach a percentage of 80% of all desalination plants worldwide (Greenlee et al., 2009). Deionized water is produced by forcing the salt-containing water (surface water) through a semipermeable membrane under pressure. Since the applied pressure is higher than the osmotic difference, the water molecules are forced through the higher concentration solution to the lower concentration. First, the surface water passes through one or more filters to remove impurities. It follows to an electromagnetic entrance valve and next to a pressure rise pump. In the membrane modules deionized water (permeate) is separated from the concentrate. Part of the concentrate can return to the process to increase the yield of the process and obtain more deionized water. The highly concentrated solution goes to wastewater treatment plant (PE International, 2012).

The synthesis of acrylic acid from propylene at industrial scale consists of two phases, the first one is represented by the propylene

oxidation to acrolein and the second one is represented by the oxidation of acrolein to acrylic acid (Oh and Woo, 2008). Different catalysts can be used in the two process phases. With time different types of catalyst have been developed, the majority being based on metallic oxides (United States Patent Office, 1970). Lintz and Müller identified three categories of catalysts. The first category is based on vanadium phosphate; the second category is represented by heteropoly acids and salts, and the third one contains multi-compound mixed metal oxides. The last group is commonly used in the propene oxidation to acrylic acid (Lintz and Müller, 2009). In the present paper the following catalysts have been used: in the first reaction a multi-component catalyst based on bismuth molybdates (e.g. $\text{Mo}_{12}\text{BiFe}_3\text{Co}_{4.5}\text{Ni}_{2.5}\text{Sn}_{0.5}\text{K}_{0.1}\text{O}_x$), while for the second reaction the catalysts are based on molybdenum and vanadium oxides (e.g., $\text{Mo}_{12}\text{V}_3\text{Cu}_{2.5}\text{Fe}_{1.25}\text{Mn}_{0.1}\text{Mg}_{0.1}\text{P}_{0.1}\text{O}_x$) (Encyclopaedia of Hydrocarbons, 2005).

Some aspects are not included in the actual format of the study e.g. the construction of plant, pipelines, railways, roads, trains and trucks and human activities.

2.3. Impact assessment method

The impact assessment was performed to determine the environmental impacts derived from the LCI. The environmental impacts are based on the energy and materials flows derived from PROII and Aspen Plus process simulators and are computed using GaBi software (PE International, 2012).

The CML (An LCA method developed by the Center of Environmental Science of Leiden University) 2001 impact assessment method, developed by Leiden University's Institute of Environmental Sciences - Centrum voor Milieukunde van Universiteit Leiden, containing various environmental impact categories, was used for comparison between different case studies. The environmental indicators considered in CML 2001 method and discussed in the next section are widely described in the scientific literature (Korre et al., 2010). As it can be noticed from Table 6, 1000 kg/h of acrylic acid (main product) and 59.1 kg/h acetic acid (co-product) result from the processes. Allocation to distribute the material and energy inputs and outputs between the two products is requested. Consequently, the portioning ratio for mass allocation is 94.42% for acrylic acid production and 5.58% for acetic acid.

3. Results and discussions

Table 7 contains the values of the eleven environmental impact categories for Cases 1–10. There are significant differences, in terms of GWP, between the six cases which use 100% pure fuel for steam generation (Cases 1–6). The higher impact is for Case 3 (production of steam from lignite) 5528.65 kg CO₂-Equiv./tone, followed by Case

Table 3
Input and output streams specifications for acrylic acid production process from propylene.

Stream name		S1	S2	S3	S10	S30	S29	S18	S11
Stream description		Air	Steam	Propene	Water				
Temperature	C	25	159	25	25	89.9	48.8	40	50
Pressure	bar	1	6	11.5	5	0.16	0.07	2.4	1
Enthalpy	M × kcal/h	0.71	11.76	0.51	0.06	0.27	0.04	0.83	2.6
Rate	kmol/h	1362.9	992.3	127	141	88.6	6.1	1154.7	1334.9
Component rate	kmol/h								
Propene		0	0	127	0	0	0	0	12.79
Water		25.3	992.3	0	141	0	0	1153.56	155.54
Oxygen		280.9	0	0	0	0	0	0.032	48.6
Nitrogen		1056.7	0	0	0	0	0	0.43	1055.9
Acetic acid		0	0	0	0	0.09	6.05	0.09	0.49
Acrylic acid		0	0	0	0	88.5	0.06	0.08	1.05
CO ₂		0	0	0	0	0	0	0.22	60.49
DIPE		0	0	0	0	10 ^{−6}	0.007	0.32	0

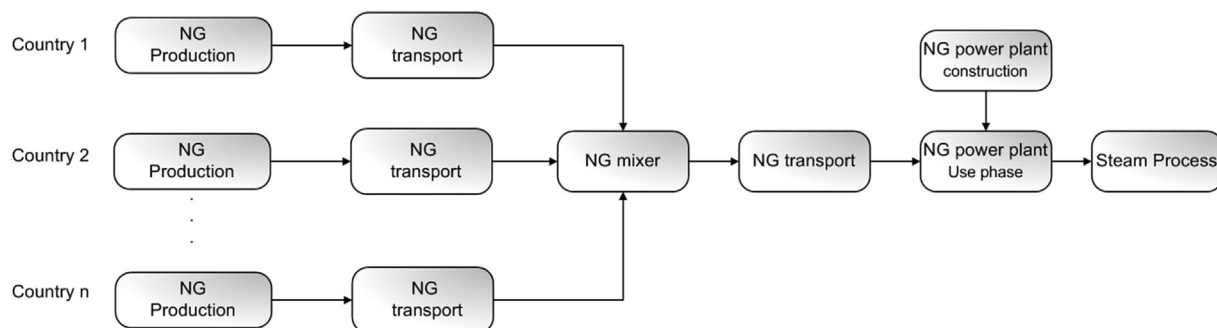


Fig. 2. Steam production from natural gas (Case 1 and Case 10).

2 (production of steam from hard coal) which has a GWP of 5525 kg CO₂-Equiv./tone. Obviously, when steam is generated by burning biomass (Case 6), the GWP has the lowest impact e.g. 1094.5 kg CO₂-Equiv./tone.

Taking into discussions the six cases which use 100% pure fuel for steam generation (Cases 1–6), the lowest value for AP impact category (e.g. 5.66 kg SO₂-Equiv./tone) is achieved when steam is produced from natural gas (Case 1) while the highest value (e.g. 148.53 kg SO₂-Equiv./tone) is obtained when steam is generated from lignite (Case 3).

The best value for EP impact category is also obtained in Case 1 when natural gas is used for steam generation. The highest value for this environmental impact category (e.g. 1.73 kg Phosphate-Equiv./tone) corresponds to Case 3, when steam is generated from lignite. It is also interesting to notice that the EP of Case 6 is very close to the higher value (e.g. 1.72 kg Phosphate-Equiv./tone).

ODP has low values in all cases. ADP_{elements} is almost the same in Case 1, 4, 5 (e.g. 5.98 kg Sb-Equiv./tone) and very close to the other cases (e.g. 5.88 kg Sb-Equiv./tone) which means that this impact category is not influenced by the steam source very much. ADP_{fossil} has the lowest impact in Case 6 (e.g. 4.59×10^{-4} MJ/tone) when biomass is used for steam generation. This value is more than double when non-renewable energy sources are used (see Table 7).

Taking into discussions the six cases which use 100% pure fuel for steam generation (Cases 1–6), the values of PCOP impact indicator are similar for Cases 1, 2, 4, 5, 6 (202 kg Ethene-Equiv./tone). The value is slightly higher, 208 kg Ethene-Equiv./tone when lignite is used for steam generation (Case 3). The values lead to the conclusion that this impact category is not influenced very much by the steam source. The best values of the four impact indicators linked to the lethal concentration LC₅₀: FAETP, HTP, TEP, MAETP are also obtained in Case 1.

Looking deeper into the results of Cases 1 and 6, which seem to be the most environmentally friendly designs, other scenarios (Cases 7, 8, 9) are created. In these cases, different proportions of natural gas and biomass are used for steam generation (e.g. 25% natural gas and 75% biomass are used for steam generation in Case 7; 50% natural gas and 50% biomass are used for steam generation in Case 8 and 75% natural gas and 25% biomass are used for steam generation in Case 9). The environmental impact categories results are reported in Table 7. The combination of natural gas and biomass for steam generation doesn't improve the environmental impact categories (see Table 7) if Case 1 is set as reference case. The best scenario for steam generation is Case 1 an exception being represented by the GWP impact indicator, ADP_{elements} and ADP_{fossil}. The discussions will be focused only on the GWP impact indicator, the values for ADP_{elements} and ADP_{fossil} being very low. If the combination of natural gas and biomass for the steam generation is compared to Case 6 which uses pure biomass for the same purpose,

it can be noticed that the GWP, ADP_{elements} and ADP_{fossil} indicators give worst values (see Table 7). All the other environmental impact categories (e.g. AP, EP, ODP, FAETP, HTP, TEP, MAETP) give better results when steam is used from natural gas and biomass compared to pure biomass.

As was concluded before, the best scenario for steam generation is Case 1 an exception being represented by the GWP impact indicator. In order to improve the GWP a new case study Case 10: Acrylic acid production process from propylene using steam from natural gas coupled with carbon capture and storage (CCS) is developed in order to see the influence of the CCS technologies on the overall environmental impact categories. The attention was focused on the post-combustion CO₂ capture using amine (i.e. MDEA has been utilized in the present study). Methyl-diethanol-amine (MDEA) is an important solvent used in the removal of CO₂. Some of its advantages are: low energy requirements, high absorption capacity and good stability (Bandyopadhyay, 2011).

A cradle-to-grave approach was assumed in this case. The following sub-systems have been considered: i) acrylic acid production process; ii) steam production from natural gas; iii) MDEA production process; iv) post-combustion CO₂ capture from the steam production process using MDEA; v) post-combustion CO₂ capture from the acrylic acid production plant using MDEA; vi) CO₂ transport and storage (see also Fig. 1 for the boundary conditions). It is assumed that MDEA solution for CO₂ capture was obtained from MEA, ethylene oxide and water. The carbon capture rate was set to 90% that is a reasonable value for the amine capture technologies (Fluor, 2000). In the supply chain, the CO₂ compression and transportation through pipelines (over a distance of 500 km) to the storage site (e.g. ocean storage, depth storage 2000 m) is considered (Petrescu et al., 2014). The LCI for MDEA production and transportation as well as the LCI for CO₂ transportation and storage are presented in Table 5 (input data) and Table 6 (output data).

The eleven environmental impact indicators obtained in Case 10 are presented in Table 7. Compared to Case 1, the introduction of CCS technologies leads to a decrease in the GWP indicator by 2.3, as it can be noticed from Table 7 (1673.45 kg CO₂-Equiv./tone in the case with CCS vs. 3877 kg CO₂-Equiv./tone in the case without CCS). The introduction of CCS technology has a significant impact on other impact categories such as AP, HTP, TEP. EP and TEP indicators double their values when considering CCS. The amount of HTP increases 1.37 times when taking into account the post-combustion CCS using MDEA. There can be also noticed a slight rise in some impact categories such as ADP_{elements}, ADP_{fossil}, FAETP, PCOP.

The contributions of various process steps to the most relevant impact categories (GWP, AP, EP, MAETP) for all cases are also presented (see Figs. 3–6).

It can be noticed from Fig. 3 that the greatest contribution to the total GWP is given by the steam generation process (Cases 1–10), an

Table 4LCA assumptions for acrylic acid production process from propylene (**Cases 1–10**).

Parameter	Units	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7		Case 8		Case 9		Case 10
Fuel type	–	NG	Hard coal	Lignite	HFO	LFO	Bio	NG	Bio	NG	Bio	NG	Bio	NG
Fuel composition	(%)	100	100	100	100	100	100	25	75	50	50	75	25	100
Upstream processes														
Fuel extraction/collection		drilling	under ground	under ground	petroleum distillation	petroleum distillation	cutting	drilling	cutting	drilling	cutting	drilling	cutting	drilling
Fuel pre-processing		H ₂ O	crushing	crushing	V	S	drying	H ₂ O	drying	H ₂ O	drying	H ₂ O	drying	H ₂ O
		Hg	screening	screening	S	removal	loading	Hg	loading	Hg	loading	Hg	loading	Hg
		H ₂ S	cleaning	cleaning	Na		chipping	H ₂ S CO ₂	chipping	H ₂ S	chipping	H ₂ S CO ₂	chipping	H ₂ S
		CO ₂	blending	blending	removal		unloading	removal	unloading	CO ₂	unloading	removal	unloading	CO ₂
Fuel transportation		removal	dedusting	dedusting						removal				removal
		pipe line	rail	rail	truck	truck	rail	pipe line	rail	pipe line	rail	pipe line	rail	pipe line
Fuel conversion efficiency	(%)	85	85	85	85	85	85	85		85		85		85
Propylene production		crude oil	crude oil	crude oil	crude oil	crude oil	crude oil	crude oil		crude oil		crude oil		crude oil
Deionized water production		reverse osmosis	reverse osmosis	reverse osmosis	reverse osmosis	reverse osmosis	reverse osmosis	reverse osmosis		reverse osmosis		reverse osmosis		reverse osmosis
MDEA transportation														
Transportation distance	km	–	–	–	–	–	–	–		–		–		100
Transportation type	–	–	–	–	–	–	–	–		–		–		rail
Electricity for transportation	MJ	–	–	–	–	–	–	–		–		–		137
Downstream processes														
Acrylic Acid transportation distance	km	100	100	100	100	100	100	100		100		100		100
Acetic Acid transportation distance	km	150	150	150	150	150	150	150		150		150		150
Acrylic Acid & Acetic Acid transportation type	–	truck	truck	truck	truck	truck	truck	truck		truck		truck		truck
Fuel for Acrylic Acid & Acetic Acid transportation	–	diesel	diesel	diesel	diesel	diesel	diesel	diesel		diesel		diesel		diesel
CO₂ transportation and storage														
Injection pressure	bar	–	–	–	–	–	–	–		–		–		120
Pressure drop	bar	–	–	–	–	–	–	–		–		–		48
Pipeline distance	km	–	–	–	–	–	–	–		–		–		500
No. of compressor stations	–	–	–	–	–	–	–	–		–		–		5
Storage depth	km	–	–	–	–	–	–	–		–		–		2
Distance between compression stations	km	–	–	–	–	–	–	–		–		–		100

NG-natural gas; HFO-heavy fuel oil; LFO-light fuel oil; Bio-biomass.

Table 5
LCI inputs for acrylic acid production process from propylene (**Cases 1–10**).

Parameter	Units	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7		Case 8		Case 9		Case 10
Fuel type	—	NG	Hard coal	Lignite	HFO	LFO	Bio	NG	Bio	NG	Bio	NG	Bio	NG
Fuel composition	(%)	100	100	100	100	100	100	25	75	50	50	75	25	100
Steam Production Process														
Fuel energy	MJ	37,696	37,696	37,696	37,696	37,696	37,696	9424	28,272	18,848	18,848	28,272	9424	37,696
Acrylic Acid Production Process														
Propylene	kg/h	853	853	853	853	853	853	853		853		853		853
Air	m³/h	899	899	899	899	899	899	899		899		899		899
Deionized water	kg/h	406	406	406	406	406	406	406		406		406		406
River water	kg/h	828	828	828	828	828	828	828		828		828		828
Molten salt	kg/h	172	172	172	172	172	172	172		172		172		172
Catalyst 1	kg/h	0.2	0.2	0.2	0.2	0.2	0.2	0.2		0.2		0.2		0.2
Catalyst 2	kg/h	0.2	0.2	0.2	0.2	0.2	0.2	0.2		0.2		0.2		0.2
Cooling water	kg/h	659	659	659	659	659	659	659		659		659		659
Electricity used in pumps & compressors	MJ	1416	1416	1416	1416	1416	1416	1416		1416		1416		1416
MDEA production														
Ethylene oxide	kg/h	-	-	-	-	—	-	—		—		—		4969.13
Water	kg/h	-	-	-	-	—	-	—		—		—		6728.82
Methyl amine	kg/h	-	-	-	-	—	-	—		—		—		1753.87
Total CO₂ transportation														
CO₂ from plant	kg/h	-	-	-	-	—	-	—		—		—		4920.14
Electricity for compressors	MJ	-	-	-	-	—	-	—		—		—		1906.04
Electricity for injection	MJ	-	-	-	-	—	-	—		—		—		120.05

NG-natural gas; HFO-heavy fuel oil; LFO-light fuel oil; Bio-biomass; Total CO₂- CO₂ from steam production and from acrylic acid production processes.

exception being represented by **Case 6** where the GWP of the acrylic acid production process and propylene production process is higher than the GWP resulted from the steam generation process. The GWP impacts of the propylene production process and acrylic acid production process are the same for all cases under study (433 kg CO₂ Equiv./tone for the propylene production process and respectively 425 kg CO₂ Equiv./tone acrylic acid production). For **Case 3**, which seems to be the worst scenario considering the GWP, a quantity of 4663 kg CO₂-Equiv./tone from the total 5521 CO₂-Equiv./tone (representing 84.46%) comes from steam production using lignite while the production of the other raw material-propylene represents only 7.84% (433 kg CO₂-Equiv./tone from the total 5521 CO₂-Equiv./tone). A percentage of 7.70% (calculated from 425 kg CO₂-Equiv./tone from the total 5521 CO₂-Equiv./tone) of the total GWP comes from the acrylic acid production. For **Case 6**,

which seems to be the most environmentally friendly considering the GWP, a quantity of 225 kg CO₂-Equiv./tone from the total 1083 CO₂-Equiv./tone (representing 20.77%) comes from steam production using biomass, while the production of the other raw material-propylene represents almost double 39.98% (433 kg CO₂-Equiv./tone from the total 1083 CO₂-Equiv./tone). A percentage of 39.24% (calculated from 425 kg CO₂-Equiv./tone from the total 1083 CO₂-Equiv./tone) of the total GWP comes from the acrylic acid production, more exactly from the off-gases released into the atmosphere.

The contribution of various steps to the AP impact category for all cases is summarized in Fig. 4.

It can be noticed from Fig. 4 that the greatest contribution to the total AP impact category is given by the steam generation process (**Cases 2–6**), an exception being represented by **Case 1** where the AP of the propylene production process is a little bit higher than the

Table 6
LCI outputs for acrylic acid production process from propylene (**Cases 1–10**).

Parameter	Units	Case1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7		Case 8		Case 9		Case 10
Fuel type	-	NG	Hard coal	Lignite	HFO	LFO	Bio	NG	Bio	NG	Bio	NG	Bio	NG
Fuel composition	(%)	100	100	100	100	100	100	25	75	50	50	75	25	100
Steam Production Process														
Steam	kg/h	12,160	12,160	12,160	12,160	12,160	12,160	3040	9120	6080	6080	9120	3040	12,160
Acrylic Acid Production Process														
Acrylic acid	kg/h	1000	1000	1000	1000	1000	1000	1000		1000		1000		1000
Acetic Acid	kg/h	59.1	59.1	59.1	59.1	59.1	59.1	59.1		59.1		59.1		59.1
Off gas														
Propene	kg/h	86	86	86	86	86	86	86		86		86		86
Water	kg/h	447.3	447.3	447.3	447.3	447.3	447.3	447.3		447.3		447.3		447.3
Oxygen	kg/h	248.3	248.3	248.3	248.3	248.3	248.3	248.3		248.3		248.3		248.3
Nitrogen	kg/h	4722.8	4722.8	4722.8	4722.8	4722.8	4722.8	4722.8		4722.8		4722.8		4722.8
Acetic acid	kg/h	4.7	4.7	4.7	4.7	4.7	4.7	4.7		4.7		4.7		4.7
Acrylic acid	kg/h	12.03	12.03	12.03	12.03	12.03	12.03	12.03		12.03		12.03		12.03
CO ₂	kg/h	425	425	425	425	425	425	425		425		425		425
Water to wastewater treatment	kg/h	3329	3329	3329	3329	3329	3329	3329		3329		3329		3329
MDEA production and transportation														
MDEA produced	kg/h	—	—	—	—	—	—	—		—		—		13,458
Total CO ₂ transportation and storage														
CO ₂ stored	kg/h	—	—	—	—	—	—	—		—		—		4759.18
CO ₂ losses pipeline	kg/h	—	—	—	—	—	—	—		—		—		155
CO ₂ losses compressors	kg/h	—	—	—	—	—	—	—		—		—		1.64
CO ₂ losses injection	kg/h	—	—	—	—	—	—	—		—		—		4.76

NG-natural gas; HFO-heavy fuel oil; LFO-light fuel oil; Bio-biomass; Total CO₂- CO₂ from steam production and from acrylic acid production processes.

Table 7LCA results according to CML 2001 (**Cases 1–10**).

KPI	Units	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8	Case 9	Case 10
Steam feedstock	Fuel type	NG	Coal	Lignite	HFO	LFO	Bio	NG	Bio	NG	Bio
	Fuel composition (%)	100	100	100	100	100	100	25	75	50	50
CO ₂ capture rate	(%)	—	—	—	—	—	—	—	—	—	—
GWP	kg CO ₂ -Equiv./tone	3877.00	5525.0	5528.65	4756.04	4648.08	1094.5	1790.43	2486.05	3181.67	1673.45
AP	kg SO ₂ -Equiv./tone	5.66	22	148.53	28.8	11.06	11.32	9.90	8.49	7.07	11
EP	kg Phosphate-Equiv./tone	0.49	1.5	1.73	1.13	1.11	1.72	1.42	1.01	0.8	0.6
ODP × 10 ⁸	kg R11-Equiv./tone	6.27	1.32	1.12	2.42	2.43	7.34	7.07	6.81	6.54	16.4
ADP _{elements} × 10 ³	kg Sb-Equiv./tone	5.98	5.88	5.87	5.97	5.98	5.9	5.92	5.94	5.96	6.01
ADP _{fossil} × 10 ⁴	MJ/tone	9.25	9	8.99	9.26	9.64	4.59	5.76	6.92	8.09	9.6
FAETP	kg DCB-Equiv./tone	18.74	20.3	20.8	57.16	38.5	21.75	21	20.25	19.5	19.46
HTP	kg DCB-Equiv./tone	80.89	307.16	718	408.63	133.02	375.76	302.05	228.33	155	110.78
PCOP	kg Ethene-Equiv./tone	201.97	202.6	208	203	202.66	202.66	202.48	201.32	202.15	202.21
TEP	kg DCB-Equiv./tone	0.93	4.04	12.3	9.46	1.17	14.32	10.97	7.62	4.28	1.93
MAETP × 10 ^{−4}	kg DCB-Equiv./tone	5.31	33.9	582	23.48	8.95	388.9	293	197.11	101.21	6.97

NG-natural gas; HFO-heavy fuel oil; LFO-light fuel oil; Bio-biomass.

AP resulted from the steam generation process (2.97 vs. 2.63 kg SO₂ Equiv./tone). The AP impact of the propylene production process has the same value for all cases under study (3 kg SO₂ Equiv./tone). For **Case 3**, which seems to be the worst scenario considering the AP impact category, a quantity of 146 kg SO₂-Equiv./tone from the total 149 SO₂-Equiv./tone (representing 97.8%) comes from the steam production using lignite while the production of the other raw material - propylene represents only 2% (3 kg SO₂-Equiv./tone from the total 148 SO₂-Equiv./tone). A percentage of 0.2% is represented by truck transportation and by waste to landfill disposal. For **Cases 1** and **10** which seem to be the most environmentally friendly considering the AP, a quantity of 3 kg SO₂-Equiv./tone from the total 6 SO₂-Equiv./tone comes from the steam production using natural gas; the production of propylene contributing to the other half of the total AP.

The contributions of various process steps to the total EP indicator for the six cases under study is also reported (see Fig. 5).

The greatest contribution to the total EP impact category is also given by the steam generation process. The same quantity of 0.14 kg Phosphate Equiv./tone comes from the propylene production process while 0.02 kg Phosphate Equiv./tone comes from the wastewater treatment for all the cases under study. The total contribution to the EP impact category for the worst scenario (**Case 3**) is divided as follows: 1.56 kg Phosphate-Equiv./tone from the total 1.72 kg Phosphate-Equiv./tone representing a percentage of 90.1% from the total EP value comes from the process steam generation using lignite as fuel, 0.14 kg Phosphate-Equiv./tone representing 8.1% comes from the propylene production process and a small amount 0.02 kg Phosphate-Equiv./tone from the total 1.72 kg Phosphate-Equiv./tone (1.16%) comes from the wastewater treatment plant.

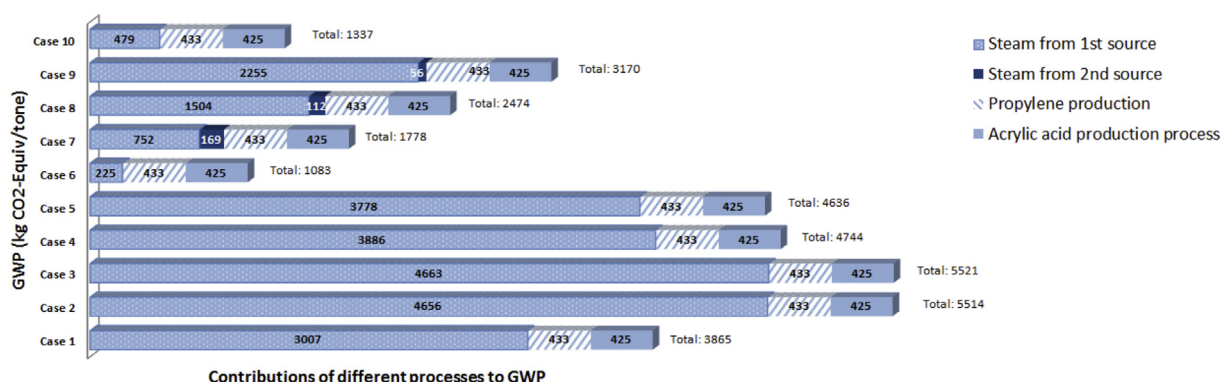
The total contribution to the EP impact category for the best scenario (**Case 1**) is divided as follows: 0.31 kg Phosphate-Equiv./tone from the total 0.47 kg Phosphate-Equiv./tone representing a percentage of 65.96% from the total EP value comes from the process steam generation using natural gas as fuel, 0.14 kg Phosphate-Equiv./tone from the total 0.47 kg Phosphate-Equiv./tone, representing 29.78% comes from the propylene production process and a small amount 0.02 kg Phosphate-Equiv./tone (4.25%) comes from the wastewater treatment plant.

MAETP indicator for the cases under study is presented in Fig. 6.

Steam from different sources has the biggest contribution to this impact category. The acrylic acid production process has the same contribution (e.g. 40,735 kg DCB-Equiv./tone) for all cases. In the best scenario (**Case 1**), from the total 52,305 kg DCB-Equiv./tone the steam production process represents 21.79%, the propylene production process represents 76.71%, and the rest is coming from deionised water and wastewater treatment processes. In the worst scenario (**Case 3**), the steam production process represents 99.25% from the total 5,817,322 kg DCB-Equiv./tone, the propylene production process represents 0.7%, and the rest is coming from deionised water and wastewater treatment processes.

4. Conclusions

The present paper investigates the acrylic acid production process from propylene. The process has been simulated using commercial process simulation software and furthermore, investigated from the environmental point of view using the material and energy balances derived from simulation. Evaluated plant concept produces 50,000 tones/year of acrylic acid. The flow rate of low-

**Fig. 3.** Contributions of various processes to the total GWP for acrylic acid production using various fuels for steam generation.

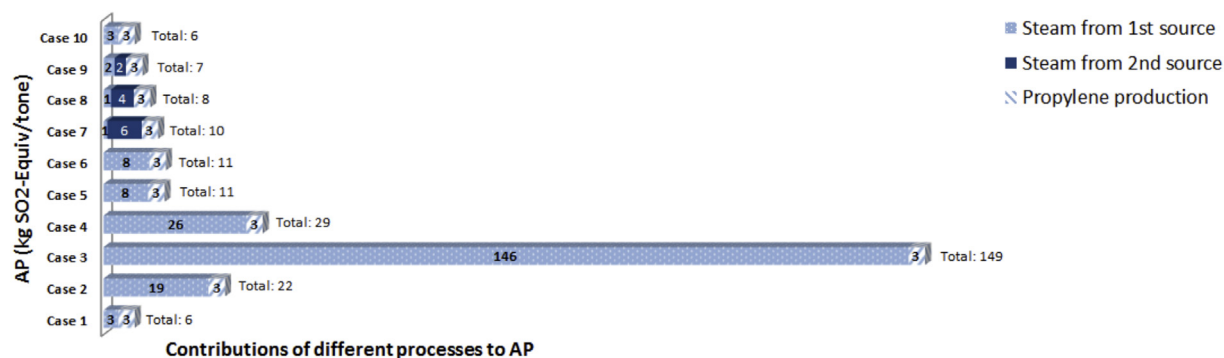


Fig. 4. Contributions of various processes to the total AP for acrylic acid production using various fuels for steam generation.

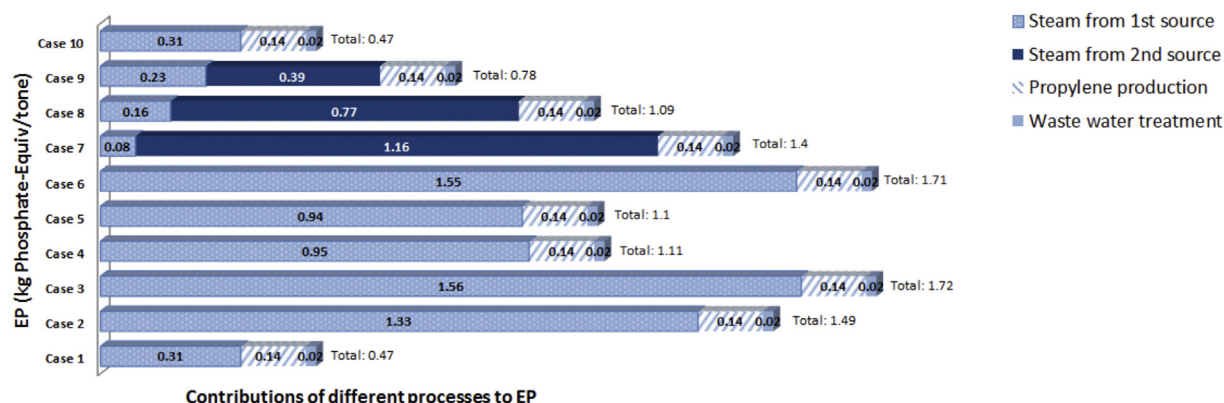


Fig. 5. Contributions of various processes to the total EP for acrylic acid production using various fuels for steam generation.

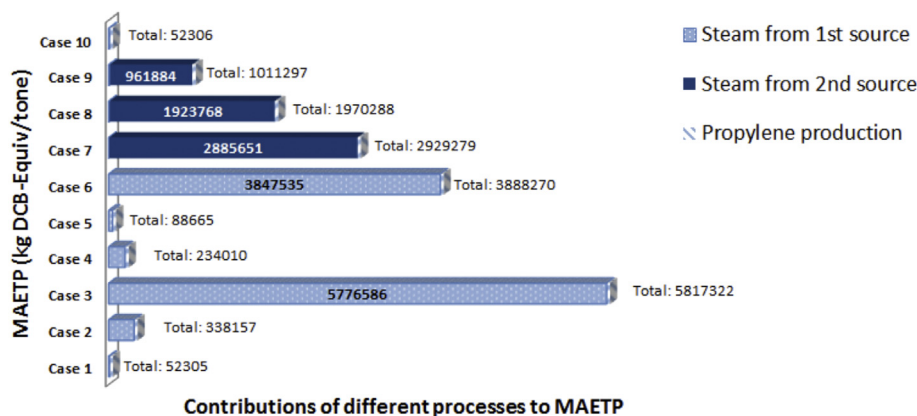


Fig. 6. Contributions of various processes to the total MAETP for acrylic acid production using various fuels for steam generation.

pressure steam (6 bar, 160 °C) used in the plant is 992 kmol/h. The focus of the present work lies in the environmental evaluation of the acrylic acid production process using different fuels for steam generation (e.g. natural gas, lignite, hard coal, heavy fuel oil, light fuel oil and biomass) through Life Cycle Analysis (LCA) method. The boundaries of the system included in the LCA study are drawn around: i) acrylic acid production; ii) upstream processes for example: catalyst and molten salt production; steam production using various fuels (e.g. lignite, hard coal, natural gas, biomass, fuel oil); iii) downstream processes for example: acrylic acid transport over a distance of 100 km to a paints-adhesives plant and acetic acid (by-product) transportation over a distance of 250 km to another chemical plant.

The installation, commissioning and decommissioning of the chemical plant is not included in the present format of this paper. The LCA was performed using the GaBi6 software. The four steps of LCA are presented in detail. Eleven environmental impact categories, comprised in the method, were calculated and compared.

Based on the results previously presented, the following conclusions can be drawn: i) the worst case from environmental point of view is represented by **Case 3**, when lignite is used for steam generation; ii) the best cases from environmental point of view are **Case 1** and **Case 6**, when steam is generated by burning natural gas or biomass; the usage of natural gas leads to lower values in the following environmental impact indicators: AP, EP, FAETP, HTP, TEP, MAETP, while the biomass usage gives lower values for GWP,

ADP_{elements} and ADP_{fossil} impact indicators; iii) different combinations between natural gas and biomass, for steam generation, improve the GWP but the other environmental impact categories are increasing (taking into account **Case 1** as benchmark); iv) the introduction of amine-based post-combustion CCS technologies improve the GWP indicator, double other indicators such as: AP, HTP, EP and TEP, or has a minor effect on other environmental impact categories: ADP_{elements}, ADP_{fossils}, FAETP, PCOP.

Nomenclature

ADP	Abiotic Depletion Potential
AP	Acidification Potential
CCS	Carbon Capture and Storage
DIPE	Diisopropyl Ether
EP	Eutrophication Potential
FAETP	Freshwater Aquatic Ecotoxicity Potential
GWP	Global Warming Potential
HFP	Heavy Fuel Oil
HTP	Human Toxicity Potential
ISO	International Standards Organization
LCA	Life Cycle Analysis
LCI	Life Cycle Inventory
LCIA	Life Cycle Inventory Assessment
LFO	Light Fuel Oil
MAETP	Marine Aquatic Ecotoxicity Potential
MDEA	Methyl diethanolamine
ODP	Ozone Layer Depletion Potential
PCOP	Photochemical Ozone Creation Potential
PM	Particulate Matter
UNIFAC	Uniquac Functional-group Activity Coefficient
TEG	Tri-ethylene-glycol
TETP	Terrestrial Ecotoxicity Potential

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