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Comparison of Different Chemical Processes from a Life Cycle Perspective

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Life Cycle Assessment methodology was applied to the industrial sector, with the aim to evaluate the environmental sustainability of different chemical processes. In particular, the ammoxidation reaction to produce acrylonitrile was chosen as a case study, comparing the environmental loads of the traditional process (SOHIO) with the alternative routes starting from propane on the base of the same amount of acrylonitrile produced (1 kg). Information reported on patents, and data collected on Ecoinvent 2.2 database were used to create each ammoxidation scenario in SimaPro 7.3.3 software. The system boundaries of the study include the main production stages on industrial scale: reaction flows, heat exchange, raw materials for catalyst manufacture, the main plant emissions and transportation phase. The comparison was carried out using ReCiPe 2008 method, expressing results in terms of midpoint impact categories, as: climate change (both damage on human health and on ecosystem), particulate matter formation, fossil fuel depletion and metal depletion. Results show how the alternative routes starting from propane seem to have higher potential impact than the traditional SOHIO process, due to the lower catalysts activity. Also, to quantify the environmental load of ammoxidation processes a comparison with other common chemical industrial productions was done. This simplified approach is able to show the environmental impacts of the ammoxidation scenarios in a broader industrial context.

1. Introduction

The application of the Life Cycle Assessment methodology to chemical processes is becoming an increasingly required approach, to meet the goal of a real sustainability, beyond the fulfilment of a single green chemistry criterion.

An interesting case study is represented by Acrylonitrile. Today it represents one of the most diffused organic chemicals produced on the world, about 6 Mt in 2010, mainly due to the synthesis of polymers: ABS (acrylonitrile-butadiene-styrene) and SAN (styrene-acrylonitrile).

Nowadays about 90 % acrylonitrile world production is synthesized by Innovence (Ineos) Technologies. The traditional process commonly called SOHIO (Standard Oil of Ohio) involves the propylene ammoxidation in the presence of ammonia and oxide-metal catalysts (1).

$$CH_2{=}CHCH_3 + NH_3 + 3/2O_2 \rightarrow CH_2{=}CHCN + 3H_2O \qquad (1)$$

Due to the higher price of propylene, which represents about 70 % of the entire production cost, there is an increasing interest on finding alternative ways to produce acrylonitrile, more economic than the traditional route. The most promising raw material seems to be propane, due to its lower price (difference between two chemicals was estimated about 1000 $/Mt in the 2012; Dow, 2011). For this reason propane ammoxidation has been deeply investigated as alternative ways to produce acrylonitrile (2).

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$CH_3CH_2CH_3 + 2O_2 + NH_3 \rightarrow CH_2{=}CHCN + 4H_2O$ (2)

Also, the use of propane could produce benefits from an environmental point of view, due to the fewer stages involved in the production of alkane. In fact, while propylene production is a two-step process, characterized by distillation and cracking stages, the propane production involves only the oil distillation. Therefore, the aim of the study is to investigate the acrylonitrile industrial production from a life cycle perspective, comparing the traditional SOHIO process with the alternative route starting from propane. The methodology applied is able to determine if the propane based process could represent a much more sustainable route than the conventional one, and also to quantify its potential sustainability if compared with other common chemical industrial productions.

2. Methods

Life Cycle Assessment (LCA) methodology consists in a software simulation able to evaluate the environmental load of a product, process or system during the entire life cycle. LCA general framework is defined by the ISO 14040 and 14044, which provide four conceptual phases: Goal and Scope definition, Life Cycle Inventory (LCI), Life Cycle Impact Assessment (LCIA), and Results Interpretation. Below a description for each phase is reported. The use of LCA methodology to investigate the industrial chemical sector is not new (e.g. Chinnawornrungsee et al., 2013), and its importance has been recently highlighted, because joined to energy and mass balances it was indicated as a method useful to investigate chemical industry, and to evaluate which process is better than other from environmental and economic point of view (Armor, 2011).

2.1 Goal and scope definition

The goal and scope definition represents the first stage of a LCA analysis in which researchers define the aim of the study by identifying the system boundaries and the reference unit for all flows. System boundaries for the ammoxidation reaction cover the main stage in the acrylonitrile production: mass and energy flows input and output from the reactor, the main air and water emissions, the heat transfer phase, the resources extracted and used for the catalyst production, the transports and the avoided impacts resulting from energy and mass recovery. No cut-off was applied in considering inputs and outputs to the system; however, the chemical plant infrastructure was not included in the system boundaries, due to the uncertainties associated to its estimation. As a functional unit the production of 1 kg of acrylonitrile was assumed.

2.2 Inventory analysis

The inventory analysis is the second stage of a LCA, and it consists in a data collecting to create a model of the systems studied. This phase was conducted using SimaPro 7.3.3 software, and it resulted in the creation of five ammoxidation scenarios: the conventional SOHIO process starting from propylene, and the four alternative routes which involves propane ammoxidation: Asahi (the only alternative process industrially developed), Mitsubishi, BP propane poor and BP propane rich. Models were created using information reported on patents (e.g. selectivity, conversion, and yield). These data, in addition with those reported on Ecoinvent 2.2 database, were used to calculate the mass and energy balances for each ammoxidation scenario. Table 1 collects the main information used in the LCI phase. As shown each scenario involves the use of different catalyst systems and process specifications, this diversification necessarily affects all the mass and energy balances. Always these catalysts represent corporates know-how, so the companies do not furnish information about their production and regeneration on industrial scale. Therefore, considering data on the plant productivity and catalyst make-up (about 0.7 kg/t of acrylonitrile; IPPC, 2003), an amount of 1g of catalyst per kg of acrylonitrile produced was estimated for SOHIO process. Also, accordingly to estimated data from literature (Pavone and Schwaar, 1989) a catalyst consumption of 1.7g per kg of acrylonitrile was assumed for propane based scenario. See table below.

Table 1: Inventory analysis for the ammoxidation reaction scenarios

	SOHIO (Cavani et al., 2009)	**Asahi** (Hinago et al., 2000)	**Mitsubishi** (Ushikubo et al.,1992)	**BP poor** (Guttmann et al., 1988)	**BP rich** (Lynch et al., 1992)
Feed (molar ratio) $C_3\backslash NH_3\backslash O_2\backslash inert\backslash H_2O$	1\1.12\2.0\-\-	1.0\1.2\3.0\14.8\-	1\1.5\15\-\-	1\2\1.5\5.7\3	5\1\2.8\-\1
Catalyst composition	$Co_{4.5}\,Fe\,Ni_{2.5}\,Bi\,P_{0.5}\,K_{0.07}\,Mo_{12}\,O_{55}$	$Mo\,V_{0.33}\,Nb_{0.11}\,Te_{0.22}\,O_n$	$Mo\,V_{0.3}\,Nb_{0.12}\,Te_{0.23}\,O_n$	$V\,Sb_5\,W_{0.5}\,Te_{0.5}\,Sn_{0.5}O_x$	$V\,Sb_{1.4}\,Sn_{0.2}Ti_{0.2}\,O_x$
Catalyst support (wt%)	18	50	50	50	50
Catalyst amount (g)	1.0	1.7	1.7	1.7	1.7
Selectivity (%)	83	66	65	57	62
Yield (%)	81	59	60	39	9
C_3 Conversion (%)	98	90	91	69	14

2.3 Impact Assessment and Results Interpretation

Impact analysis was carried out using the ReCiPe 2008 method, which is able to express results in terms of midpoint categories as for example climate change (including both damage on human health and on ecosystem), particulate matter formation, fossil fuel depletion, and metal depletion (Goedkoop et al., 2012). These midpoint scores may further be grouped into three endpoints based on damages to human health (units of measurement: disability adjusted life years – DALYs), ecosystem quality (measured in potentially disappeared fractions of species – species·y), and resource consumption (in terms of increased costs of extraction – $). Below the main results of the study are reported.

Figure 1 shows the comparison between the five scenarios created, expressing results in terms of midpoint impact categories. Despite the production of propane has a lower global impact than the propylene, the comparison between the five ammoxidation processes shows different results. In fact, moving from the SOHIO process to the propane based scenarios, there is a growing trend regarding impact on climate change (both damage on human health and on ecosystem) and fossil fuel depletion categories which are closely related. This increase in impacts is mainly due to the different amounts of input and output substances of the models. The propane ammoxidation scenarios imply lower production yield (Table 1) involving higher extraction and consumption of organic feedstock than the traditional SOHIO process (for instance, in the case of the BP- rich scenario, the amount of propane used is more than ten times higher than the propylene in the SOHIO process). Also, alternative routes imply a large use of ammonia to run the processes (see the feed molar ratio in Table 1); this higher request involves large energy and fossil fuels consumption during its manufacturing. Besides, a large contribution for both climate change and fossil fuels depletion categories is linked with the energy consumption during the purification steps to obtain ammonium sulfate (produced by neutralization of unreacted ammonia). This stage required a lot of energy, in particular to evaporate and crystalize the salt. Even particulate matter formation increases in the same order, even though a more complete assessment for this category should consider a site-specific evaluation.

Instead, results obtained for the metal depletion category are different from the previous case. As reported previously in the inventory analysis, the catalysts production is always confidential, so no detailed information about their manufacturing and make up on industrial scale were available. Nonetheless, we included the catalyst making in the model evaluating the potential impact of this step considering only the resources extraction for each system This evaluation is reported in the Figure 1 as impact on the metal depletion category. It can be noted that the relative impact is quite limited, compared to other categories. Furthermore, this category has not a regular trend, because it depends on the composition and the amount of each catalyst chosen in the model. In fact, each system seems to have different metal composition, and also the amount of catalyst per kg of acrylonitrile produced assumed by the alternative route is higher than the traditional (Pavone and Schwaar, 1989).

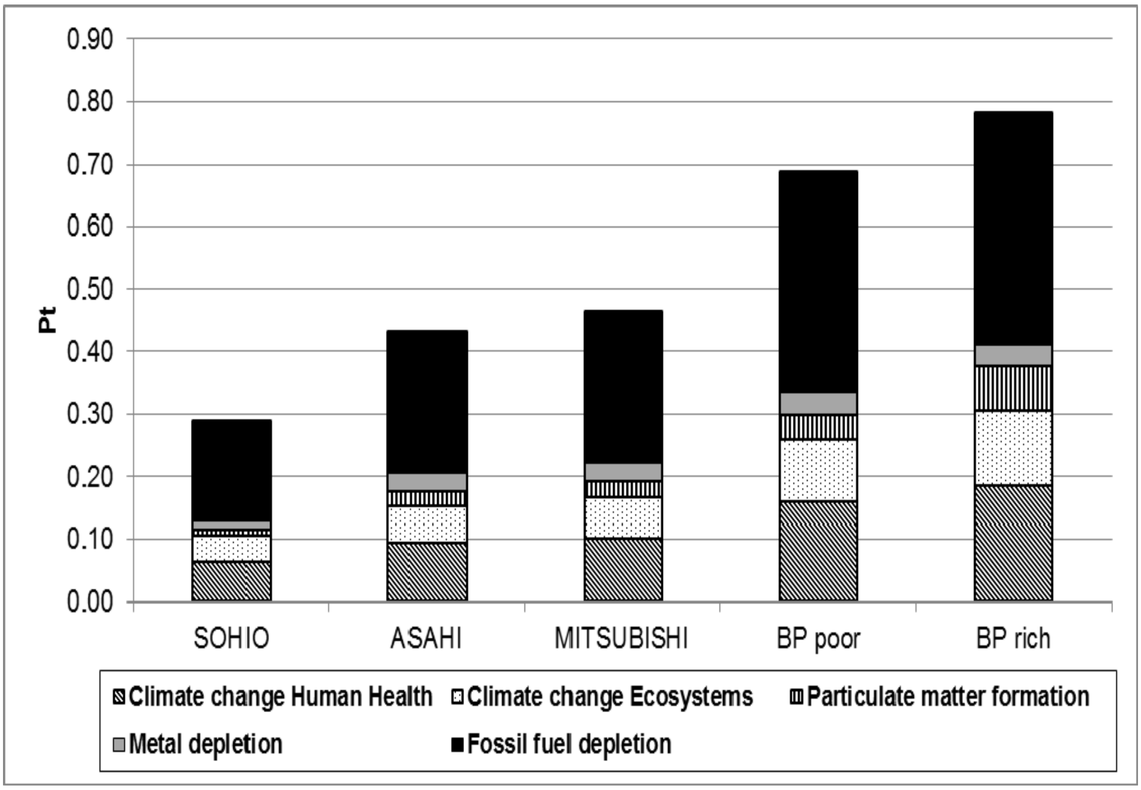

Figure 1: Five ammoxidation scenarios compared in terms of midpoint categories

Also, as reported in the introduction, to quantify the environmental sustainability of the ammoxidation reactions a comparison with other products was done. Six industrial productions were chosen as reference processes: the styrene production, the synthesis of maleic anhydride (both from benzene and from butane), the production of cumene, and the manufacturing processes for formaldehyde and acrylic acid, each of which was already contained in the Ecoinvent database. The comparison with the ammoxidation scenarios (SOHIO and Asahi) was done on the base of the same amount of synthesized product (1 kg).

This confrontation was not extended to the other ammoxidation processes, because they have not yet been industrially developed. The results of the comparison, expressed in terms of endpoint categories (damage on human health, ecosystem quality, and resources depletion), are reported in Figure 2. In this visualization, called ReCiPe single score, histograms show the overall results for each scenario, which were obtained from the cumulative sum of each damage category. The cumulative results give overall measures of the environmental performance for scenarios, and permit weighting the relevance of each endpoint category in the total load on the environment.

The comparison shows briefly how the SOHIO process seems to have global impact similar to the production of cumene and maleic anhydride from butane, and quite similar to the production of acrylic acid. Instead, it achieves higher impact than formaldehyde production and lower than styrene and maleic anhydride from benzene. On the other hand, the alternative route from propane seems to achieve the higher global impact, if compared with the six reference scenarios. This is mainly due to the result reached for the resources depletion category, which is influenced by the large consumption of fossil fuels, and the remaining is linked with the negative effects of particulate matter formation and the climate change categories.

However, these results should not be considered as an absolute, because the comparison was done using scenarios modelled using patents data with processes taken from database, but it could represent a simple tool able to show the environmental load in a broader industrial context, and to identify possible improvements.

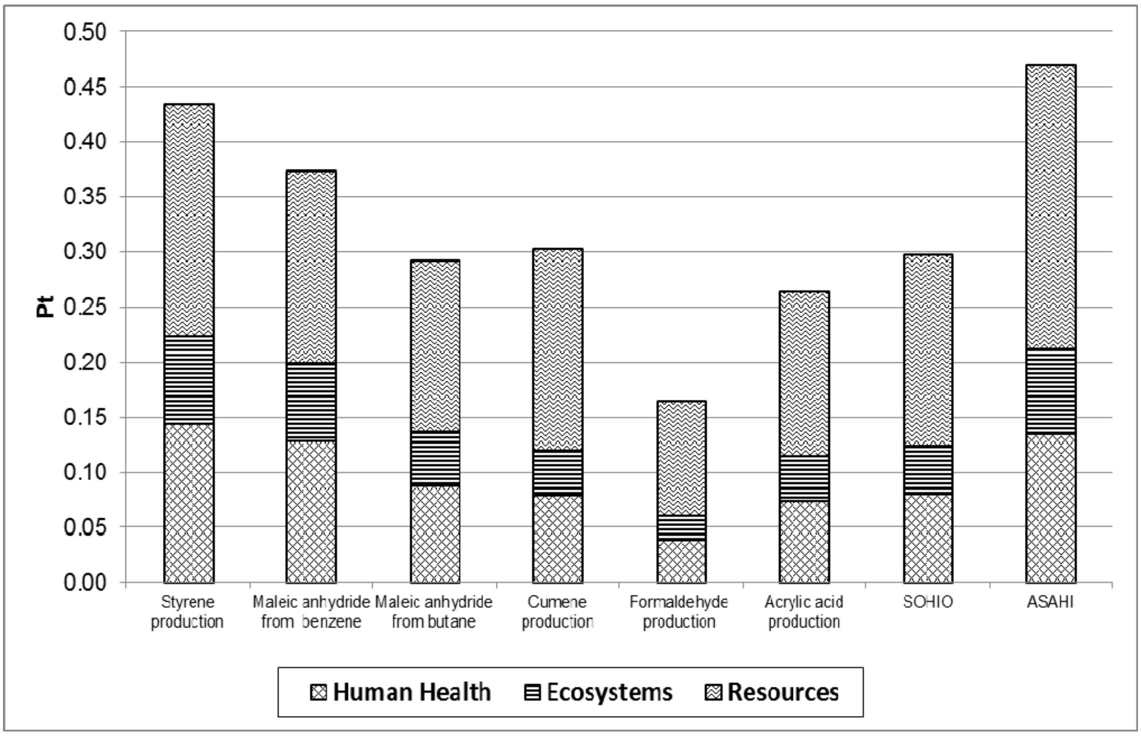

Figure 2: Comparison between ammoxidation scenario and other industrial production: ReCiPe single score

3. Conclusions

The study presents a scientific approach through which investigate the environmental footprint of the chemical production sector. In particular, different industrial processes were compared, focussing in particular on the acrylonitrile production, following two different routes: propylene ammoxidation (SOHIO process), and the less expensive alternative routes that use propane as the precursor. As shown by results, alternative processes starting from propane generally seem to have higher impacts especially in terms of fossil fuel depletion, and climate change categories.

In general, it can be concluded that LCA answers well the need for quantitatively assessing the environmental sustainability of an industrial process in a life cycle perspective.

Compared to other common chemicals, the traditional process of acrylonitrile production shows similar global impacts, while the alternative route from propane seems to result in higher environmental loads.

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