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ARTICLE

Glycerol as feedstock in the synthesis of chemicals: a life cycle analysis for acrolein production

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Glycerol is an important bio-platform molecule, potentially usable for the synthesis of various chemicals and fuel additives, the synthesis of acrolein by dehydration being one of the most studied reactions. Through the application of Life Cycle Assessment (LCA) methodology we investigated the production of acrolein from glycerol, by comparing two alternative scenarios in which glycerol is obtained as a co-product either in triglyceride trans-esterification to FAME or in hydrolysis to fatty acids. Our results show how main impacts are not related to the energy involved in the two processes. In fact, the use of dedicated crops as a source of triglycerides in the biodiesel production entailed higher impacts in terms of land exploitation. On the other hand, beef tallow was assumed as a starting raw material in the production of fatty acids, and this involved some significant impacts associated with animal rearing. At the same time, however, avoiding the use of dedicated biomass ensured a lower global impact (in terms of single score). Lastly, in order to validate the model created, a sensitivity analysis using the Monte Carlo method was performed. The two routes from glycerol were also compared with the classical chemical route where acrolein is produced by propylene oxidation.

1. Introduction

In the coming decades, bio-based feedstocks are going to play a crucial role in the chemical and fuel industries, where their use is expected to grow and surpass that of fossil raw materials.¹ This sector, also known as bio-refineries, is expanding greatly and – in addition to the already well known environmental benefits – the coproduction of chemicals and biofuels may lead to a higher return on investment.² An important emerging sector will be "glycerchemistry",³ which consists of replacing oil with glycerol as a feedstock in several applications in the chemical industry, also as a solvent and fuel.⁴

Indeed, glycerol is widely studied as a feedstock due to its chemical characteristics and availability on the market. Nowadays, it is mainly generated as a co-product in processes which involve reactions with triglycerides, such as the production of fatty acids by hydrolysis, and the trans-esterification with methanol, which leads to the production of fatty acid methyl esters (FAME), also called biodiesel.⁵ Every year about 20Mt of fats and oils are processed by the chemical industries; this leads to a great abundance of glycerol on the market: in 2012 its production was estimated at about 1.2 Mt,³ and it is expected to rise to 1.54 Mt in 2015⁶ and around 2.5 Mt in 2020.⁷

As previously stated, glycerol's chemical and physical properties make it an extremely versatile compound, which can be used as a feedstock for the synthesis of a high number of

molecules (e.g. ethers, esters, carboxylic acids, ethylene glycol, epichlorohydrin, syngas, oligomers, polymers and many others).^{6,8,9,10,11}

The synthesis of acrolein by dehydration appears to be one of the most promising ways to valorize it,^{8,12} therefore companies' efforts are focused substantially in that direction.^{13,14,15} In fact, as shown in literature¹¹ acrolein produced starting from glycerol (with a purity grade around 92% wt) seems to have a good economic return and low raw material cost. Acrolein is an important drop-in chemical intermediate both in the industrial sector (e.g. acrylic acid)^{16,17,18} and in the agricultural field (methionine, annual world-wide production of around 0.5 Mt);¹⁹ nowadays it is commonly produced by partial propylene oxidation. Nevertheless, considering the issue of depletion of fossil fuels, glycerol use could become a competitive alternative.

Before being used as a feedstock, however, crude glycerol obtained as a co-product needs to be treated to remove impurities in organic synthesis, but due to the high price of these processes the availability of refined glycerol in Europe is now decreasing, with a corresponding increase in the non-upgraded glycerol, which is addressed to the renewable energy market or even to poorer markets (e.g. animal feed). This end of life results in a loss of a valuable product that could be exploited in different ways, to make the most of its great potential. As well known the 7th principle of Green Chemistry²⁰ encourages the use of renewable feedstock, in order to

minimize fossil resources consumption, and to mitigate the greenhouse gases emissions associated to them. For this reason the aim of this study was to evaluate – from a life cycle perspective – the potential impacts on human health and the environment of the use of glycerol as an alternative and renewable feedstock in the production of acrolein. In fact, the glycerol production and its usage represent nowadays a crucial topic for chemical industry, in particular for companies with the aim of achieving a more sustainable production.

For this reason, two main synthesis routes entailing glycerol generation as a co-product were compared: the transesterification process to produce biodiesel, and the production of fatty acid by triglycerides hydrolysis. This approach is able to identify both the environmental issues and the potential benefits connected with each production step considered in the study, and may be considered as a support for the companies involved in the chemical sector in achieving the target of sustainability promoted by the principles of Green Chemistry.²⁰ Furthermore, a comparison was carried out with the traditional acrolein production process starting from propylene.

2. Methods and materials

2.1 Introduction to the methodology

The Life Cycle Assessment (LCA) tool was used as a scientific approach to i) create models which simulate – as realistically as possible – the production chains considered, and ii) evaluate the potential environmental burdens associated with them. It is a standardized methodology,^{21,22} divided in four conceptual phases:

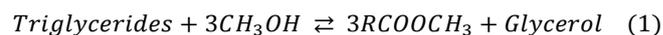
- the *goal and scope definition*, in which researchers define the aim of the study by identifying system boundaries (as geographical, technological and temporal) and the functional unit, which is necessary to refer each data and compare different scenarios;
- the *life cycle inventory (LCI)*, which represents the more time-consuming phase of the entire LCA, due to data search and utilization to create models as snapshot of the system boundaries;
- the *life cycle impact assessment (LCIA)*, in which an analysis method is chosen to evaluate each scenario created from a life cycle perspective and obtain results in terms of ecosystem quality, human health and resources consumption;
- the *results interpretation and improvement*; here the results obtained by LCIA are discussed to identify the worst scenario and the processes with higher contribution. In this way researcher are able to detect the crucial hot-spots that should be modified to improve the process.

There are two main reasons for the use of LCA. First, it is able to investigate different domains of the industrial sector, but unlike other tools it is recognized by the international community due to its standardization. Secondly, the application of LCA methodology to the chemical sector is rapidly expanding and involving different fields: industrial chemistry production,²³ the biofuels sector,^{24,25,26,27} the comparison between two processes with and without catalysts,²⁸ and an expanding sector such as that of bio-refineries.^{29,30} As is well-known, the effectiveness of an LCA study is strongly influenced by the quality of the input data used in the various systems considered. For this reason, in this work LCI was carried out using mostly primary data directly provided by two

Italian oleochemical companies and one French company; however, when not available, data were collected from literature such as patents, encyclopaedia, and the Ecoinvent³¹ database (v. 2.2). LCA was conducted using the software developed by PRé Consultants, SimaPro³² (v.7.3.3). ReCiPe 2008³³ (I/A, v 1.07) and IPCC 2007³⁴ (20a) were used as LCIA analysis methods, both able to predict results with a twenty-year time horizon. The decision to choose these two methods stemmed from the need to express results in terms of midpoint categories, as well as in the forms of the most consolidated way, using CO₂-equivalents. Scenario modelling and their comparisons were carried out using the same amount of acrolein produced (1kg) as a functional unit. A *from-cradle-to-gate* perspective was applied, considering the whole production chain for both scenarios: from raw material production (oil and fat) up to the synthesis of acrolein by glycerol dehydration, including the main intermediate stages such as triglycerides reaction processes and purification steps (if required). System boundaries are schematically depicted in **Figure 1** and **Figure 2**. Below a detailed description of each inventory is reported.

2.2 Triglycerides trans-esterification process

As reported in literature,³⁵ the use of vegetable oils as a diesel source was investigated long before the oil crisis of the 1970s and '80s. Rudolf Diesel himself, in his book *Liquid Fuel*, mentioned the use of peanut oil (also known as arachis oil) in a small diesel engine seen during the Paris Exposition in 1900.³⁵ However, the patent developed by Chavanne³⁶ in 1937 seems to have been the first example of what we now call biodiesel. Nowadays, biodiesel is considered the best candidate to replace fuels in diesel engines, despite the higher cost³⁷ and lower HHVs (higher heating values) than traditional fossil fuels.³⁸ Biofuel importance is related to: i) the possibility of applying it in a blend without involving any engine modification,³⁹ and ii) the benefits linked with its usage (e.g. greenhouse gases reduction).³⁸ Differently from Chavanne's work, which entailed the use of an acid catalyst, nowadays most industrial processes involve alkali-catalyst (NaOH or KOH) trans-esterification⁴⁰ conducted at 60°C under atmospheric pressure with a residence time of about 1 hour.³⁵ Catalyst usage is also necessary in order to enhance the solubility of alcohol in oils.⁴⁰ Triglycerides and an alcohol (methanol is the most used due to its low cost) are normally combined in a molar ratio of 1:3⁴¹ and then let react in continuous stirred tank reactors (CSTR).³⁵ Below, equation (1) represents the general reaction for the triglycerides trans-esterification process using methanol.



The process yield for glycerol is about 10 wt.%,⁷ producing empirically 1 ton of biodiesel and 100 kg of crude glycerol per each ton of vegetable oil treated.⁴¹ As previously stated, the crude glycerol, generally with a purity grade of 80-88%,⁷ needs to be refined before its industrial usage. Generally speaking, the purification procedures require more processing steps and energy in respect to those used after hydrolysis, as salts and methanol have to be separated, and involve subsequent distillation steps until glycerol is obtained with the desired purity grade. Depending on salt content, the equipment may also use ion exchange or thin-film distillation.⁴² As shown in **Figure 1**, the system boundaries for acrolein obtained by glycerol from the trans-esterification process scenario (hereafter called Scenario A) cover the entire production chain: biomass cultivation and harvesting, oil production process, and trans-esterification to obtain biodiesel and glycerol purification.

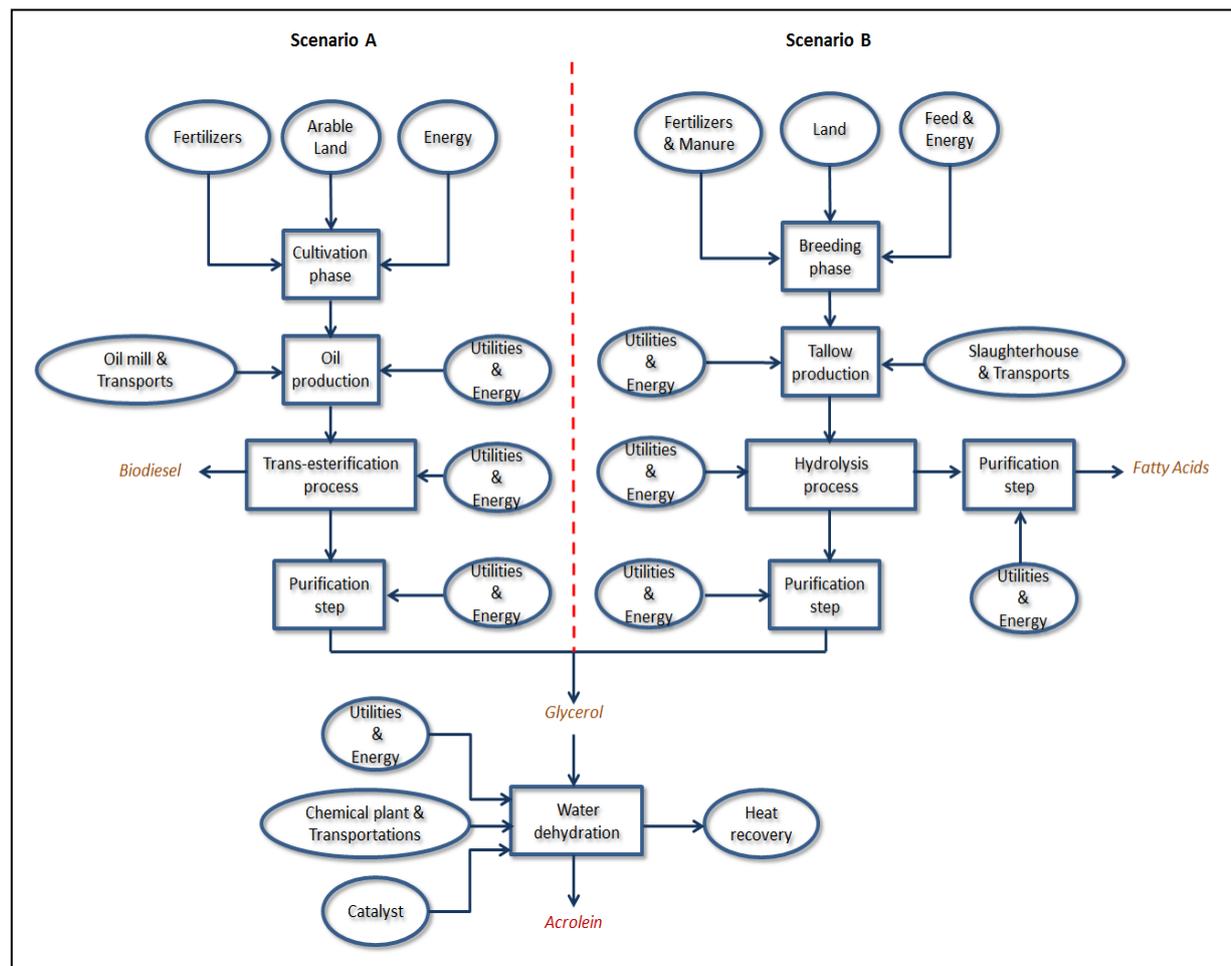


Fig. 1. System boundaries considered in LCA study for the bio-based scenarios.

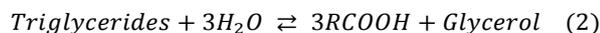
Obviously they also include the dehydration step to produce acrolein, which is common to both scenarios and is described separately in section 2.4. Rapeseed (*Brassica napus*) was chosen as representative of energy crops since it is the most common cultivation in Europe for obtaining biodiesel.^{28,43,44} Furthermore, Europe represents the World's biggest producer of biodiesel,^{24,45} with 178 thousand barrels/day in 2011⁴⁶ and thus rapeseed is now the dominant feedstock on a global scale.⁴³ Rape oil, at mill/RER U (Ecoinvent database) was chosen as the reference process to simulate both the rape cultivation and oil production phase. It includes all energy and mass flows used in rapeseed cultivation in Europe and all the utilities for treating seeds and extracting oil in an average European mill plant (included average seed transportation to the mill).³¹ All these information were used in order to create two distinct models able to simulate both the *Cultivation phase* and the *Oil production* step. For more details see **Table S1** reported as supplementary information. As shown in **Figure 1**, oil is then sent to the trans-esterification step. The default process considers that both plants are located in the same place (as in the case of hydrolysis). Spiga BD Srl, an Italian company which works in the field of biodiesel, glycerine, glycerine derivatives and renewable chemicals, provided the primary data needed to complete the life cycle inventory of trans-esterification and glycerol refining phases. The same operating

conditions (temperature and pressure) described earlier were assumed. As suggested by the company, around 122kg of glycerol are generated from 1005kg of triglycerides treated to produce one ton of biodiesel. Moreover, the latter does not need to be refined: thus further purification steps were not included in the system boundaries. The use of glycerol as the starting raw material prevents its downgrading for energy uses. For this reason a process avoiding glycerol burning was introduced in both scenarios. The energy produced by the combustion was modelled by using the average values for glycerol LHV (18.74MJ/kg) reported in literature.⁴⁷ No reliable information on emissions was available, however in order not to neglect this environmental load, average air emissions from the combustion of natural gas³¹ were used as proxy data. In addition, due to the fact that glycerol combustion would provide energy in the form of heat, the process includes this avoided energy recovery. Lastly, in order to take into account the environmental benefits connected with the production of biofuel, the model created for Scenario A assumed that biodiesel is used to replace the traditional fossil fuel and included the avoided extraction of the same diesel amount. However, all input and output flows considered in the modeling of Scenario A are listed in supplementary information, see **Table S1**.

2.3 Triglycerides hydrolysis process

Despite the fact that a higher quantity of glycerol is commonly obtained as a co-product from FAME manufacturing,⁷ biodiesel

amounts produced in Europe during 2011 decreased by about 10% as compared to 2010.⁴⁸ This trend affects the availability of glycerol on the market; therefore triglycerides hydrolysis was investigated as an alternative route. Literature⁷ reports that fat splitting (followed by saponification) was the first source of glycerol in the past, until biodiesel production caught on. However, after a stagnant period, it is now considered to be the second major reserve of glycerol.⁷ Also, due to the synthesis of fatty acids, its industrial importance makes it a secure reserve process for glycerol production. In fact, today fat splitting using water is the most common way of obtaining synthetic fatty acids. This process occurs in homogeneous conditions in which water is dissolved in the lipid phase.⁴⁹ The total equilibrium for the direct hydrolysis process is reported below (2).



After the pre-treatment procedures to remove impurities and settle triglycerides sources (such as filtration under heat, acidification, and degassing), hydrolysis takes place in the presence of demineralized water as a splitting agent (to increase efficiency and prevent higher salt content).⁴⁹ Ernst Twitchell was the first scientist to attempt to improve the process performance by introducing the Twitchell reagent as a catalyst in 1898. Later, either different catalysts were used: lipases (cheaper due to lower process temperatures) or dibasic metal oxides (preferred over the acids, for corrosion prevention).⁴⁹ However, the majority of modern units operate without a catalyst in continuous splitting columns, in the presence of high pressure steam, to achieve higher temperature and pressure (average values are 210-260°C and 1.9-6.0MPa).⁴⁹ Fatty acids purity degrees obtained with the continuous processes splitting are generally higher than 98%; crude glycerol obtained achieves a purity grade of about 20% and needs to be at first concentrated up to about 90%, then purified (see procedure previously described, distillation or ion exchange).⁴⁹ As shown in **Figure 1**, the system boundaries for the production of acrolein starting from glycerol as a by-product of hydrolysis (Scenario B) cover the entire manufacturing chain: from the triglycerides source (beef tallow) up to the dehydration step to produce acrolein, also including the hydrolysis and purification procedures. As for the previous scenario, in this case, also, primary data regarding the triglycerides splitting and purification procedures were provided by SO.G.I.S. SpA. This oleochemical company synthesizes fatty acid starting mainly from animal fats or Palm Oil as triglycerides source. This raw material is obtained as a derivative from animal by-product of the meat production process and – as with other animal by-products – can be used in the industrial sector.⁵⁰ In particular, beef tallow was considered in the model. *Tallow, at plant/CH U* was taken as the reference process in the Ecoinvent database to describe average energy flows and other utilities (tap water, transportation, and infrastructure) involved in the production of tallow.³¹ *Beef (farm type 23)*⁵¹ was chosen as the reference process to describe all the inputs and outputs connected with animal rearing, such as, for example: the occupation of arable land dedicated to the growth of cows, the animal feeds, the use of artificial fertilizer and in part of manure as fertilizer, and all the energies usage during the breeding process. Given that tallow is considered a by-product, no mass flows and therefore no impacts related to animal rearing are included in the default process (*Tallow, at plant/CH U*)³¹. However, for the sake of prudence and considering that tallow has its own market price, an economical allocation was done by including the beef growth in the model. Therefore the amount of tallow obtained

from the mass balance (able to produce 1 kg of acrolein) was multiplied by an economic allocation factor of 1.02E-01 estimated from the ratio between the wholesale beef tallow price⁵² and the price of beef meat.⁵³ In this way, tallow impact is proportional to its market price. As previously stated, hydrolysis and purification were modelled by using information directly supplied by SO.G.I.S. SpA. According to this company, a production of around 90kg of glycerol (and 880kg of fatty acids) per ton of treated triglycerides was assumed. Also, inventory includes all the mass and energy flows involved in the fat splitting, as well as the utilities necessary for the purification step. In this case, the company suggests that refining procedures are necessary for both glycerol (from 20% to 99.5%) and fatty acids to reach market purity grade. As in the case of Scenario A, an avoided glycerol combustion was included in the model. Moreover, benefits deriving from fatty acids production starting from tallow were estimated by considering an avoided production of vegetable oil (*Rape oil, at oil mill/RER U*)³¹ necessary for the synthesis of the same amount of acids. All the life cycle inventory details for Scenario B are listed in supplementary information, see **Table S2**.

2.4 Glycerol dehydration process

Due to its importance as a chemical intermediate, mainly in the synthesis of acrylic acid and methionine, different acrolein production routes have been investigated in the past. In 1942, Degussa developed the first industrial synthesis process starting from acetaldehyde and formaldehyde through an aldol condensation reaction; this was subsequently replaced by partial propylene oxidation because of conversion and product separation problems.⁵⁴ Given the affordability of propylene, today the latter process is still the most widespread manufacturing synthesis process despite the investigation into other routes – such as the partial oxidation of propane and the biological one.⁵⁴ Nevertheless, the availability of a great abundance of glycerol as a co-product has led companies and research efforts to look into new synthesis procedures. Among these, the dehydration of glycerol is studied in depth in literature,^{55,56,57,58} due to the fact that it represents one of the most promising and easiest ways to valorize it.^{8,11,12} As reported in **Figure 1**, acrolein production represents the last step for both scenarios. The dehydration process generally occurs in a Packed Bed Reactor (PBR) at 280°C and 101kPa in the presence of an acid catalyst.⁵⁴ In this study, a heteropoly acid catalyst with an empirical structure of H₄SiW₁₂O₄₀/TiO₂ was taken into account.⁵⁵ Experimental data demonstrated⁵⁵ that it leads to a 79% yield and selectivity of acrolein, with a glycerol conversion of 100%. As already stated, acrolein is the main intermediate in the production of acrylic acid; therefore, some data regarding utilities consumption (e.g. electricity, natural gas, cooling and process water) as well as the amount of inert gas were assumed to be the same as the glycerol dehydration to acrylic acid and extrapolated from an internal report of a company.⁵⁹ Instead, general information regarding infrastructure (chemical plant), chemical auxiliary usage (e.g. hydroquinone as a stabilizing agent and ethyl acetate as a solvent for the extraction process) and average transportation, was assumed to be the same as for the process *Acrylic acid, at plant/RER U*.³¹ Moreover the same average catalyst consumption for the synthesis of acrylic acid was assumed (0.3g per functional unit)³¹ by modelling its structure on the basis of the already explained procedure reported in literature.²³ No information on regeneration and make-up, as well as on

industrial energy consumption for the catalyst production, was available because such information usually constitutes corporate know-how. Therefore they were not included, assuming that their contribution to the overall impact is negligible, as reported in literature.²³ The amount of water in the form of steam, inlet into the reactor (necessary to maintain the desired temperature), was estimated by using the molar ratio reported in literature.⁵⁵ In order to limit the energy cost associated to the dehydration phase and to avoid side reactions, a concentrated solution of 50 wt % in glycerol is recommended as inlet to the reactor.^{55,60} An energy recovery of half the heat exchanged in the reactor coils was assumed, calculating its amount through the enthalpy balance and the assumptions reported in literature:²³ half is recovered as heat and the rest as electricity (with a conversion efficiency of 31%). Lastly, the amount of steam for the purification steps of acrylic acid (reported in a previous study)⁶¹ was assumed to be the same as in the case of acrolein. As can be seen, because of the lack of data due to corporate confidentiality, it was only possible to model the dehydration process by using some proxy information, but it does not seem to affect the result of the study. Moreover, for the sake of prudence, it has been deliberately overestimated. A detailed description of the life cycle inventory for the dehydration process is shown in supplementary information, see **Table S3**.

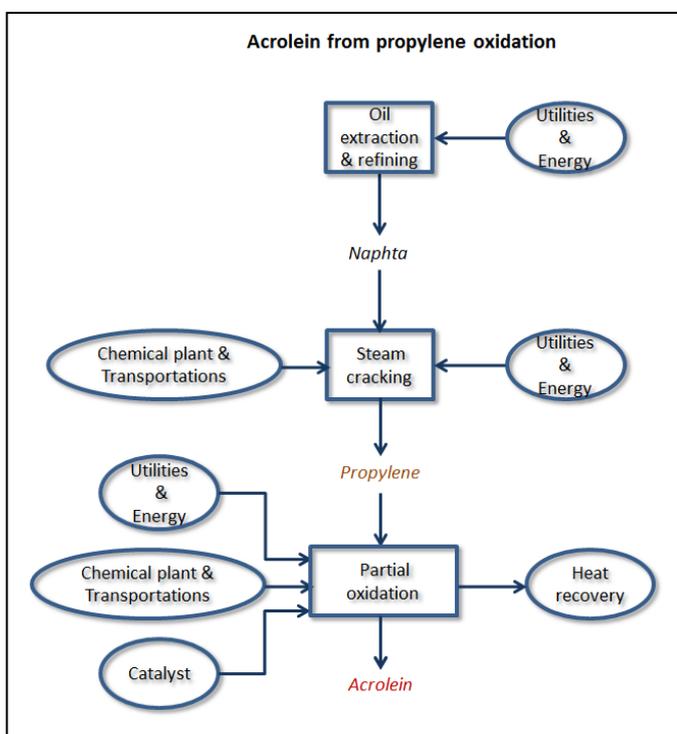


Fig. 2. System boundaries considered in LCA study for the scenario starting from propylene.

2.5 Acrolein from propylene oxidation

In 1959 Shell developed the first industrial synthesis of acrolein starting from propylene. The process was based on the vapour-phase oxidation of alkene using cuprous oxide as a catalyst. However, due to lower conversion of propylene, Sohio investigated a new class of catalyst based on bismuth molybdate.⁶² These multicomponent metal oxide systems are still used nowadays, conducting oxidation process in a tubular fixed-bed reactor operated at 300–320°C and inlet pressure of

150–250 kPa.⁶² Although the aim of the study was to evaluate the positive and negative aspects in the use of glycerol as renewable feedstock (as suggested by the Green Chemistry principles),²⁰ a system boundaries expansion was carried out in order to perform a comparison with the traditional route starting from propylene. In order to match the requirements in the quality of data common to a LCA studies, an internal report provided by a company⁶³ was used to complete LCI for the Acrolein from propylene oxidation scenario. As for the dehydration scenario, data regarding chemical plant, average transportation, and catalyst amount were collected from Ecoinvent database (*Acrylic acid, at plant/RER U*).³¹ On the other hand, the catalyst composition was evaluated from patent literature,⁶⁴ by assuming a yield of 75%⁶³ and a propylene conversion of 95%. Unreacted olefin was assumed to be released as CO₂, with a combustion efficiency of 100%. As in the case of glycerol dehydration, enthalpy balances²³ were applied to estimate the amount of energy dissipated and recovered for plant utilities. This process was taken into account as a reference scenario for a comparison with the two bio-based routes described above. System boundaries are depicted in **Figure 2**, while a detailed LCI description is reported in supplementary information, see **Table S4**.

3. Results and discussion

As previously stated, the LCIA phase was carried out using ReCiPe 2008³³ (v 1.07). This method makes it possible to estimate the impact categories indicators,³³ and is able to supply LCIA results in terms of midpoint impact categories; then the latter may be grouped into three endpoints based on i) Damages to Human Health, measured in disability-adjusted life years – DALYs, which represents the sum of years of life lost (YLL) and years life lives as disabled (YLD) due to the onset of a disease (e.g. cancer); ii) Ecosystem Quality, measured in potentially vanished fractions of species – species-yr, which represents the disappearance of the species in all compartments (terrestrial, freshwater and marine water) due to anthropogenic factors; iii) Resource Consumption, measured in terms of increased extraction costs – \$, which takes into account that each resource extraction will cause a cost increase. An Average Individualist (I/A) cultural perspective was selected with the aim of analysing the scenarios considered in a twenty-year time horizon. In fact, the other two available choices for the Hierarchic (H) and Egalitarian (E) methods use a time horizon perspective of 100 and 500 years, respectively, which in our opinion are too broad a range for this case study (mainly because of economic implications). Results were expressed by selecting six midpoint impact categories, according to their significance with relation to the aim of the study: agricultural land occupation, terrestrial eco-toxicity, metal depletion, fossil fuel depletion, and climate changes with damage both on human health and ecosystem quality. The software elaborates data from inventory phase and through a four-step procedure, which includes i) fate analysis; ii) effect analysis; iii) damage analysis and iv) normalization, is able to estimate the environmental loads associated to each LCI choice, expressing them in terms of midpoint impact categories. This visualization of results, reported in **Table 1**, is also called “characterization analysis”. Each impact category is related to a particular damage on Human Health, Ecosystem Quality and Resources Depletion, which is expressed with the units described above. However, in order to compare the two acrolein production scenarios showing which route is the preferable solution in terms of cumulative global impacts, it is necessary to sum up all

the above mentioned damages. The last step is v) weighting, in which the software converts damages in terms of score (Pt), also called “eco-indicator”. In this way, each impact category has the same unit (Pt) and a cumulative visualization called “ReCiPe 2008 single score” is possible. Results in terms of Pt are reported in **Figure 3**. As shown, acrolein produced by glycerol obtained as a co-product of triglycerides transesterification is less sustainable compared to the route based on hydrolysis.

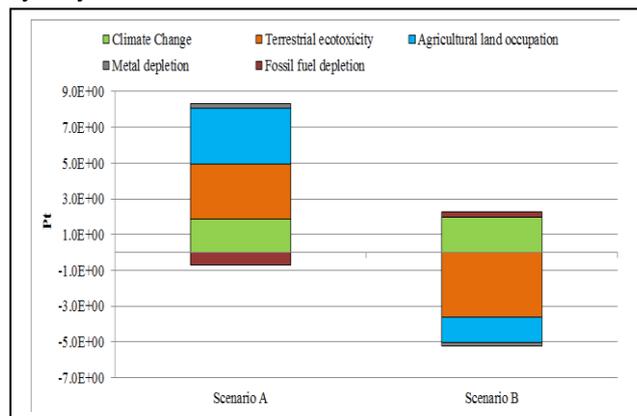


Fig. 3. Comparison between two acrolein production scenarios in terms of ReCiPe I/A – Single score

The lower sustainability of Scenario A is mainly due to significant impacts in terms of land occupation, terrestrial ecotoxicity and climate change (which includes process contributions to both human health and ecosystem damage categories), in spite of the benefits connected with an avoided fossil fuel consumption due to the avoided diesel extraction. This global negative trend is attributable to the high-intensity processes connected with the biomass growth phase as a source of triglycerides. On the other hand, Scenario B – based on hydrolysis – seems to have significant impacts on the climate change and the depletion of fossil fuels, which are related to the energy consumptions assumed in the scenario. In fact, both categories are strictly related to each other as well as to the energy need required by the system, for example during the very intensive phases of purification. In fact, as written previously in the description of LCI, the hydrolysis scenario implies a further purification stage than the trans-esterification scenario, in order to reach the market purity grade for fatty acids. This additional step leads to an increase of impacts related to energy use. Furthermore, although the just-mentioned negative effects are not negligible, the use of tallow as a substitute for vegetable biomass leads to potential environmental benefits in terms of avoided damage on land occupation and eco-toxicity. This cumulative representation shows a quick vision of the overall impacts of each scenario. However, considering only the figure above, it is not possible to clarify the environmental significance of each phase within both scenarios. Therefore, a contribution analysis was carried out in order to show the potential burdens on the environment which are associated with the system boundaries considered. To accomplish this, each scenario was split into its main phases and the analysis results are shown in terms of single score and characterization. The results from the analysis carried out for Scenario A (**Figure 4** and **Table 2**) show that the cultivation phase seems to contribute much more than the others to global impacts. As a confirmation of our previous suggestions, a detailed analysis conducted using the network tool provided by

the software revealed that about 100% of global contribution for both categories of agricultural land occupation and ecotoxicity is associated with the cultivation phase.

Impact category	Unit	Scenario A	Scenario B
Total Impact	Pt	8.6E+00	-3.8E+00
Agricultural land occupation	species-yr	1.5E-06	-6.4E-07
Terrestrial ecotoxicity	species-yr	1.4E-06	-1.7E-06
Climate change – Ecosystems	species-yr	3.7E-07	3.9E-07
Climate change – Human health	DALY	5.6E-05	5.9E-05
Fossil fuel depletion	\$	-4.6E-01	1.8E-01
Metal depletion	\$	1.6E-01	-1.5E-01

Tab. 1. Comparison between two acrolein production scenarios in terms of ReCiPe I/A – Characterization analysis

In particular, it was ascertained that the highest negative effect in terms of terrestrial eco-toxicity is related to the release of pesticides in soil, and that the exploitation of arable land contributes to its occupation. Also, as a confirmation of the scores reached in **Figure 4**, **Table 2** shows that the cultivation phase presents the highest negative load in terms of climate change. A contribution of approximately 77% was estimated for this impact category, associated with the energy consumptions during biomass growth. On the other hand the oil production phase has a contribution around 6% for the same category. Moreover, the trans-esterification, glycerol purification, and dehydration phases were estimated to make a non-negligible contribution to the same category (around 2-9% of the global impact) due to the energy flows involved. In particular, as previously described in the inventory analysis, mass and energy flows used to model the trans-esterification and purification processes were furnished directly by the company. For this reason the results may be considered a good simulation of the real case. Regarding the fossil fuel depletion category, the highest contribution is due to the cultivation phase (about 53%), followed by the trans-esterification process (22%), the oil production phase (10%), and the glycerol dehydration (7%) and refining (3%) phases. All these stages are energy-intensive, and industrial manufacturing involves higher consumption of fossil fuels for steam and electricity production. In particular, impacts regarding electricity generation are strictly related to the energy mix adopted by any country. In this case, according to the geographical system boundaries, an average energy mix for Italy was assumed (*Electricity, production mix IT/IT U*).³¹ Also regarding fossil fuel depletion, a contribution of about 5% was calculated due to the avoided glycerol combustion. This trend is related to the assumptions made during the inventory phase: it was considered that glycerol was commonly burned in the industrial sector in order to produce heat, and that in the case in which it is not incinerated (but recovered as a feedstock) the same energy amount should be produced by traditional fuels. On the other hand, the avoided emission of greenhouse gases from the combustion of glycerol helps to prevent, in part, the negative effects on climate change. However, the highest positive contribution to the environment and human health proves to be from the use of biodiesel in substitution for diesel. In fact, the

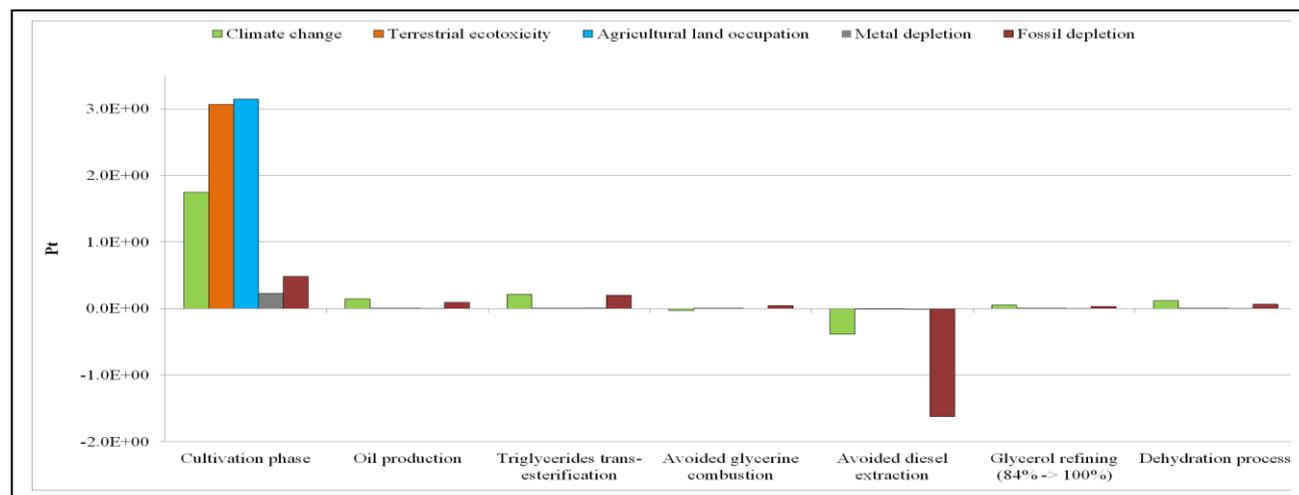


Fig. 4. Contribution analysis Scenario A – Acrolein produced by glycerol obtain as a co-product of triglycerides trans-esterification (ReCiPe 2008 I/A, Single score)

Impact category	Unit	Total	Cultivation phase	Oil product ion	Triglycerides trans-esterification	Avoided glycerine combustion	Avoided diesel extraction	Glycerol refining (84%→100%)	Dehydration process
Agricultural land occupation	species·yr	1.5E-06	1.5E-06	1.2E-10	2.1E-10	4.2E-11	-1.4E-10	6.5E-12	7.1E-11
Terrestrial ecotoxicity	species·yr	1.4E-06	1.4E-06	4.5E-11	7.9E-11	2.8E-11	-7.0E-10	1.3E-11	3.1E-11
Climate change Ecosystems	species·yr	3.7E-07	3.5E-07	2.9E-08	4.2E-08	-6.3E-09	-7.7E-08	9.8E-09	2.4E-08
Climate change Human Health	DALY	5.6E-05	5.2E-05	4.4E-06	6.4E-06	-9.5E-07	-1.2E-05	1.5E-06	3.6E-06
Fossil fuel depletion	\$	-4.6E-01	3.2E-01	6.2E-02	1.3E-01	3.0E-02	-1.1E+00	2.1E-02	4.2E-02
Metal depletion	\$	1.6E-01	1.5E-01	6.6E-03	1.1E-02	-6.1E-04	-1.4E-02	8.8E-04	4.7E-03

Tab. 2. Contribution analysis Scenario A – Acrolein produced by glycerol obtain as a co-product of triglycerides trans-esterification (ReCiPe 2008 I/A, Characterization analysis)

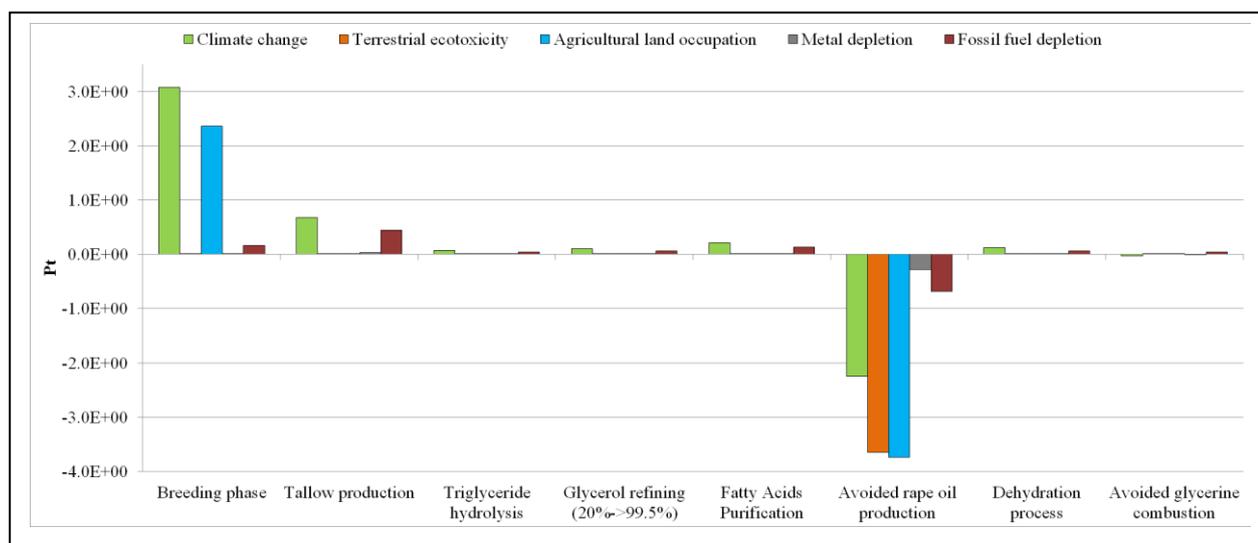


Fig. 5. Contribution analysis Scenario b – Acrolein produced by glycerol obtain as a co-product of triglycerides hydrolysis (ReCiPe 2008 I/A, Single score)

Impact category	Unit	Total	Breeding phase	Tallow product ion	Triglyceride hydrolysis	Glycerol refining (20%→99.5%)	Fatty Acids purification	Avoided rape oil production	Dehydration process	Avoided glycerine combustion
Agricultural land occupation	species·yr	-6.4E-07	1.1E-06	5.4E-10	1.2E-11	5.8E-11	2.4E-11	-1.7E-06	7.1E-11	4.2E-11
Terrestrial ecotoxicity	species·yr	-1.7E-06	1.2E-11	8.0E-11	2.2E-11	3.3E-11	6.5E-11	-1.7E-06	3.1E-11	2.8E-11
Climate change Ecosystems	species·yr	3.9E-07	6.1E-07	1.3E-07	1.4E-08	2.0E-08	4.2E-08	-4.5E-07	2.4E-08	-6.3E-09
Climate change Human Health	DALY	5.9E-05	9.2E-05	2.0E-05	2.2E-06	3.0E-06	6.3E-06	-6.7E-05	3.6E-06	-9.5E-07
Fossil fuel depletion	\$	1.8E-01	1.1E-01	2.9E-01	3.1E-02	4.1E-02	9.0E-02	-4.5E-01	4.2E-02	3.0E-02
Metal depletion	\$	-1.5E-01	9.7E-04	2.4E-02	5.8E-04	3.6E-03	1.6E-03	-1.8E-01	4.7E-03	-6.1E-04

Tab. 3. Contribution analysis Scenario B – Acrolein produced by glycerol obtain as a co-product of hydrolysis (ReCiPe 2008 I/A, Characterization analysis)

avoided diesel extraction leads to significant benefits regarding both the climate change and the fossil fuel categories. The relative contribution of each life cycle phase for Scenario A, both in terms of Impacts and Avoided impacts, is reported in **Table S5**. Results from the contribution analysis for Scenario B are shown in **Figure 5** and **Table 3**. The avoided use of rapeseed as a source of triglycerides entails several environmental benefits. First, the avoided burdens in terms of climate change (including damage to both human health and the ecosystem) and fossil fuels depletion are related to the lower energy consumption in the production of chemicals used as fertilizers. In particular, nitrogenous fertilizers produced by a synthesis starting from ammonia, whose manufacturing is highly energy-intensive, as well as the production of nitric acid, seem to be the major causes. Also, unlike in Scenario A, several advantages are linked to the avoided use of pesticides, and to the avoided occupation of arable areas which may be devoted to other agricultural activities. Moreover, the partial replacement of fertilizers with animal manure reduces the contribution of the breeding phase to the terrestrial ecotoxicity (around 4%), this latter category being highly influenced by both the release of substances and waste during the energy-consuming steps which characterize the tallow production (29%) and the other steps such as the fatty acids purification, that contributes for the 24%. However, even in this scenario the triglycerides supply is not without impacts. In fact, the phases of animal breeding and tallow production are the two steps with the highest environmental impacts along the entire manufacturing chain considered. As well known, animal rearing implies an intense use of resources and energy. In fact, despite the economic allocation of tallow, the breeding phase achieves the highest contribution in terms of agricultural land occupation (100%) and climate change (around 72%) categories. Also the contribution to the fossil fuel depletion is not negligible, around 17%. On the other hand, the intense energy consumption for the production of tallow is responsible for the highest contribution in terms of fossil fuel depletion (around 46%) and contributes for a 16% in terms of climate change category. Also, the energy consumption involved in the fatty acid purification stage is not so negligible as it contributes for 14% to the fossil fuel depletion and for 5% to the climate change category. Conversely, the energy used during hydrolysis and dehydration processes and for the glycerol refining procedure is not so

significant as far as the contribution to climate change (2-3%) and fossil fuel depletion (5-7%) are concerned. However, as for Scenario A, the impacts related to the production and purification of fatty acids and for glycerol refining should be considered a reliable approximation, since data were furnished directly by the enterprises. Also, it should be considered that the further purification stage of fatty acids increases the total impacts reached by Scenario B regarding both fossil fuel depletion and climate change categories of around 17% and 5% respectively. Moreover, this additional step entails an approximate 5% and 47% increases in impacts respectively on the same categories (fossil fuel depletion and climate change, including damage to both human health and the ecosystem), compared to results achieved by Scenario A for the same categories. As in the previous case, the contribution of each life cycle phase for Scenario B, both in terms of Impacts and Avoided impacts, is reported in **Table S6**. As shown by results, all energy consumptions involved in glycerol purification stage produce a contribution around 2% in terms of climate change and about 3-6% with regard to fossil fuel depletion (depending on the steps involved in refining). However, as reported in literature,⁶⁵ it seems not to be possible to avoid the glycerol purification stage, especially if glycerol is obtained as a co-product in the FAME process, due to the higher amount of impurities present in raw glycerol: water, salts deriving from basic medium neutralization, trace of methanol and NGOM (non-glycerin organic matter). A typical composition of various glycerol, produced at different industrial sites by transesterification was found in literature⁶⁵ and reported in **Table S7**. Basic compounds such as sodium and potassium salts might deactivate the acid catalyst used to dehydrate glycerol to acrolein, so prejudicing the entire process yield. Companies efforts are focusing on the developing of new technologies in order to solve this issue.^{65,66} Moreover, NGOM includes several different substances extracted during the seeds crush (e.g., lignocellulosic materials, such as phenolic compounds), that end up in the oil and finally in glycerine. This material contributes to coke formation and accelerates catalyst deactivation. Therefore, in order to reduce the content of these compounds, a glycerol distillation process is necessary. These issues could be solved by technology improvements that lead to new processes able to use crude glycerol as the feedstock for dehydration. Therefore, in order to verify how the global impact of the entire process could change avoiding the

purification stage for glycerol, the LCIA phase was repeated for both scenarios, excluding the steps of glycerol refining. As expected, due to the low contribution of the purification stage, results reported in **Table S8** show that differences compared with the scores obtained previously (**Table 1**) were negligible. Moreover, the climate change category was also investigated using IPCC 2007.³⁴ This analysis method was developed by the Intergovernmental Panel on Climate Change (IPCC) which is able to assess the Global Warming Potential (GWP) while expressing results in terms of CO₂ equivalents. In agreement with the ReCiPe 2008 method, a perspective of a 20-year time horizon was chosen. Results from this study are shown in **Table 4**. In this table, IPCC confirms the scores achieved using ReCiPe 2008 as regards the climate change category (**Table 1**). Furthermore, this method is able to quantify the exact amount of CO₂ emitted or saved during each stage of the manufacturing process. Although the scores are quite similar, Scenario B achieves higher results (49.7 kg of CO₂ eq.) than the trans-esterification-based scenario (45.2 kg of CO₂ eq.). In fact, despite the high CO₂ savings due to the avoided use of vegetable biomass as a source of triglycerides (-54.7 kg of CO₂ eq.), the emissions associated with the animal rearing (70.0 kg of CO₂ eq.) and energy consumption involved in tallow production (16.6 kg of CO₂ eq.) contribute to increasing the global amount. On the other hand, the cultivation (42.5 kg of CO₂ eq.) and oil production phases (3.6 kg of CO₂ eq.) achieve higher results than the total CO₂ amount emitted by Scenario A (46.1 kg of CO₂ eq.); however, the use of biodiesel as a substitute for traditional fuels seems to produce several environmental benefits (-9.4 kg of CO₂ eq.) by reducing their global amount. Lastly, the metal depletion category was also investigated. It was introduced at first to verify the overall environmental impact associated with metal extraction for the production of catalyst systems which are used for the dehydration process. However, the contribution analysis conducted for both scenarios show that the catalyst assembly is not so significant for that category, which is mainly influenced by the consumption of metal in the form of salt used mainly as fertilizer (e.g. Ammonium Nitrate and Ammonium Nitrate Phosphate). In fact, the scores (Pt) achieved by both scenarios with regard to metal consumption are similar (**Table 1**) and, in both cases, the higher contribution (positive and negative) is due to phases which involve biomass cultivation (**Table 2** and **Table 3**). The rest may be attributable to the great quantity of infrastructure involved (e.g. chemical plant, oil mill, transportation). Therefore, catalyst contribution to the global impact seems to be negligible, even though, as previously described, the catalytic system was modelled using only proxy data regarding its amount of acrolein per kg (see paragraph 2.4). As stated above, in order to evaluate the environmental trends of both bio-based scenarios, a comparison with the traditional process for producing acrolein from the partial oxidation of propylene was also carried out using ReCiPe2008 as the test method. The results in terms of single scores are given in **Figure 6**. The radar chart is a quick representation to show scores achieved by each scenario for each impact category. The closer the line to the triangle vertex, the higher the score meaning a negative effect on the environment. This picture shows a considerable difference between bio-based scenarios and that starting from olefin. The latter seems to have lower impacts compared to the scores achieved by Scenario A. The avoided use of dedicated crops entails no impacts related to land exploitation, occupation, or the use of pesticides. Contrary to the common opinion, that attributes higher impacts on fossil fuel depletion and climate change to propylene partial oxidation (due to the use of oil as a raw material), the high energy consumption mainly related to

glycerol purification in bio-based scenarios greatly affects the results. In both categories (in particular the fossil fuel depletion) the impact of acrolein from partial oxidation is lower if compared with that of the two bio-based scenarios.

Scenario A	kg CO ₂ eq		Scenario B
Tot	45.2	49.7	Tot
Cultivation phase	42.5	70.0	Breeding phase
Oil production	3.6	16.6	Tallow production
Triglycerides	5.2	1.8	Triglycerides hydrolysis
trans-esterification	1.2	2.5	Glycerol refining (84%→100%)
Glycerol refining (84%→100%)	-0.8	-0.8	Glycerol refining (20%→99.5%)
Avoided glycerine combustion	-9.4	-54.7	Avoided glycerine combustion
Avoided diesel extraction	-	5.2	Avoided rape oil production
-	-	-	Fatty acids purification
Dehydration process	3.0	3.0	Dehydration process

Tab. 4 Global Warming Potential for both scenarios (IPCC 2007, 20a)

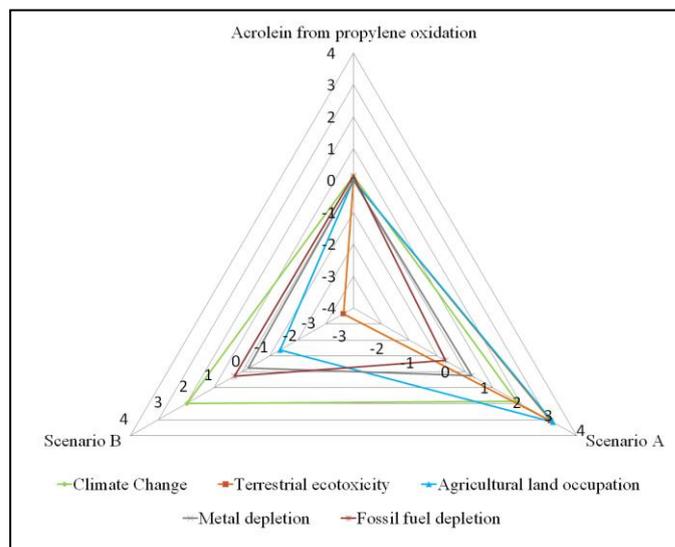


Fig. 6 Comparison between the three acrolein production scenarios, in terms of ReCiPe I/A – Single score (radarchart)

This trend is ascribable to both the massive consumption of fossil fuels that characterizes all the purification steps (e.g. glycerol, fatty acids) and to the triglycerides transformation (e.g. trans-esterification process) and the upstream stages: on one hand, the rapeseed cultivation and oil production, on the other hand the breeding and the tallow production. In fact, as previously reported, they represent the most intensive steps in terms of energy and resources requirement. The results in terms of characterization analysis are shown in **Table 5**. However, if the comparison is made considering the global impacts achieved by each process alone, Scenario B seems to be the most environmentally sustainable one due to the benefits associated with the avoided dedicated crops usage.

Impact category	Unit	Amount
Total impact	Pt	3.1E-01
Agricultural land occupation	species·yr	9.3E-11
Terrestrial ecotoxicity	species·yr	5.8E-12
Climate change – Ecosystems	species·yr	2.9E-08
Climate change – Human health	DALY	4.3E-06
Metal depletion	\$	9.9E-03
Fossil fuel depletion	\$	9.0E-02

Tab. 5. Acrolein production from propylene partial oxidation, ReCiPe I/A – Characterization analysis

3.1 Sensitivity analysis

Lastly, in order to evaluate the robustness of the models created, a sensitivity analysis was carried out using the Monte Carlo statistical method. Data uncertainties were evaluated by combining the pedigree matrix developed by Weidema and Wesnaes⁶⁷ with the method previously reported in literature.⁶⁸ A lognormal statistical distribution with a 95% confidence interval was assumed; by performing an iterative calculation of 1000 simulations, both of the bio-based acrolein production scenarios were compared using ReCiPe2008 as the analysis method. The results of the sensitivity analysis are shown below, in **Figure 7** and **Table 6**. On the *y-axis* the six midpoint impact categories are reported, while the *x-axis* shows the frequency in terms of percentage. The frequency indicates how many times a scenario shows impacts higher than the other one for a particular impact category. Frequency equal to 100% (or -100%) means that for all the 1000 iterations the results are confirmed; on the other hand a frequency of 0% means that this situation does not occur. Green bars stand for the case in which Scenario A attains higher environmental impacts than B; red bars, on the other hand, indicate the opposite. As can be seen, the Monte Carlo method confirms the results obtained previously in the LCIA. 100% frequency was achieved for fossil fuels and metal depletion as well as for the impact categories related to land exploitation (agricultural land occupation and terrestrial ecotoxicity). Furthermore, higher frequencies (62-63%) were achieved by both climate change categories, thus confirming results robustness.

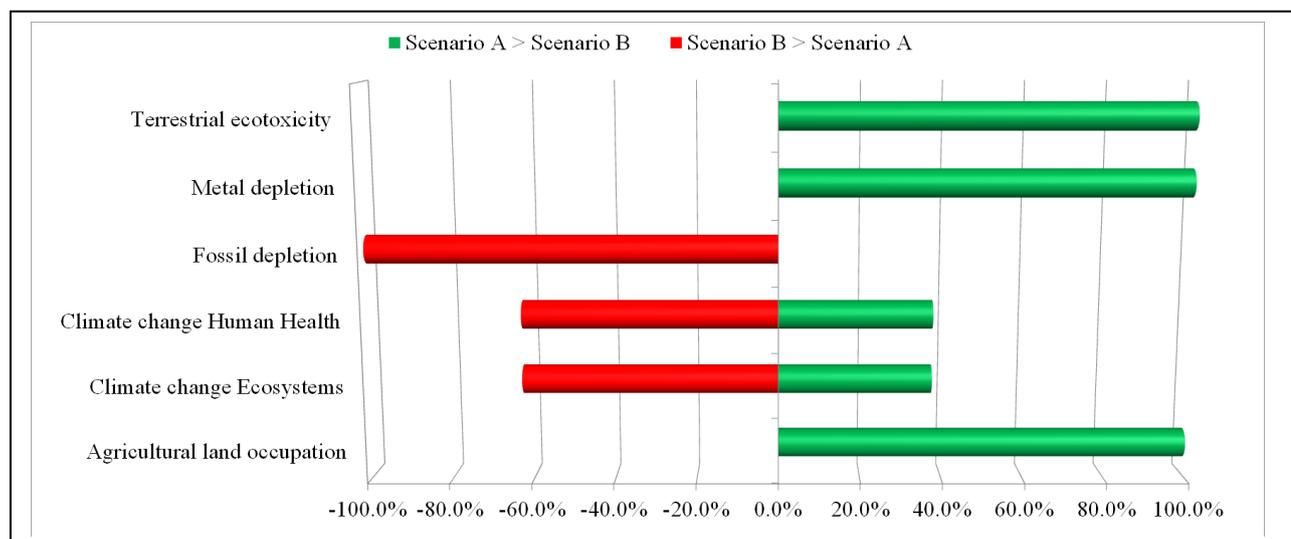


Fig. 7 Monte Carlo analysis – comparison between two bio-based acrolein scenarios, in terms of ReCiPe impact categories

Impact category	A > B	B > A
Agricultural land occupation	100%	0%
Climate change – Ecosystems	38%	63%
Climate change – Human health	38%	62%
Fossil fuel depletion	0%	100%
Metal depletion	100%	0%
Terrestrial ecotoxicity	100%	0%

Tab. 6. Monte Carlo analysis – comparison between two bio-based acrolein scenarios, in terms of ReCiPe impact categories

4. Conclusions

This work presents a life cycle assessment “from cradle to gate” for the production of 1kg of acrolein starting from glycerol generated as an industrial co-product. Two main industrial alternatives for the production of feedstock were compared: triglycerides trans-esterification and hydrolysis, which led respectively to the production of biodiesel and fatty acids as the main products. The aim of the study was to verify, from a life-cycle perspective, the environmental sustainability associated with the application of a principle of Green Chemistry, i.e. the use of renewable feedstocks,²⁰ by evaluating the possibility of using glycerol as a valuable chemical raw material instead of downgrading it for energy uses. Inventory analysis, which includes the main stages of the manufacturing chain (from source of triglycerides up to dehydration to obtain acrolein, also including the intermediate stages which lead to glycerol production and purification) was carried out using the data supplied by two companies (regarding the trans-esterification and hydrolysis processes and purification procedures) and extracted from literature (also including patents). The results show that the acrolein produced from glycerol and obtained as a co-product in biodiesel production seems to be less sustainable in terms of global impacts if compared with the hydrolysis-based scenario. However, contribution analysis indicates that the higher significance is not associated with the industrial consumptions, but with the triglycerides supply.

Due to the land occupation and exploitation, the vegetable source of triglycerides seems to have higher environmental loads. Nevertheless, if rapeseed is substituted (even in part) by a marginal cultivation which does not require the use of pesticides and does not subtract space from agricultural cultivation, lower impacts could be achieved. For example, as suggested by literature,⁶⁹ marginal lands could be exploited for the cultivation of *Jatropha curcas* and castor beans, which however need higher quantity of freshwater.⁶⁹ In addition, it should be considered that, although the cultivation phase represents the more stressful step for the environment,²⁵ it could be also influenced by many variables connected to different agricultural practices (e.g. higher or lower use of fertilizers) or different soil characteristics, typical of each geographical area.²⁵ On the other hand it is not possible to feed the entire glycerol industry using only tallow as the source of triglycerides (despite the fact that meat consumption is increasing due to the world's population growth). Moreover, this source is not without impacts, due to the significant environmental loads associated with both animal rearing and tallow production. For this reason, alternative routes should be pursued. Literature² points out the increasing attention to the use of biomass waste as a possible source for bio-based industry. This solution could be an interesting opportunity, considering that in 2012 the European production of organic waste was estimated to range between 118 and 138 million tonnes, with an estimated increase of 10% expected by 2020.⁷⁰ Also, this alternative could be even more advantageous for the Italian case study, thanks to its contribution to the reduction of CO₂ emissions: in Italy, in fact, the average percentage of organic waste not recovered (composted) amounts to around 60-70% of the total production.⁷⁰ Anyway, it should be considered that the use of alternative raw materials for the production of biofuels and chemicals in Europe will also be affected by EU and national fiscal incentives policies. In conclusion, this study highlights the importance of the application of LCA methodology as an assessment tool for evaluating the potential impacts associated with the industrial chemical sector. However, as commonly remembered in LCA studies, results should be considered valid only within the system boundaries concerned in the study. Further considerations regarding possible changes due to future trends could be estimated by an extension of the system boundaries to include economic and social variables also, but this would clearly go beyond the aim of this study.

Notes and references

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Three synthetic routes to obtain acrolein are compared, from a life cycle point of view: one by propylene oxidation and two by the dehydration of glycerol, obtained as a co-product either in triglyceride transesterification to FAME or in hydrolysis to fatty acids