

Article

From Fossil to Bio-Based Acrylic Acid: A Techno-Environmental Comparison of Propylene and Glycerol Pathways

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Abstract

The growing demand for acrylic acid, driven by its widespread use in polymers and specialty chemicals, raises concerns regarding the environmental impact of its conventional fossil-based production. In this context, the present study evaluates the techno-environmental performance of a glycerol-based acrylic acid route compared to the conventional propylene pathway. Process simulations were carried out using CHEMCAD for an annual capacity of 50,000 tons. The environmental impact is assessed through Life Cycle Assessment (LCA) methodology and LCA for Experts software, following the ReCiPe 2016 (H) impact method. The results show that the glycerol-based route requires higher raw material input (1.90 kg/kg acrylic acid) than the propylene pathway (0.84 kg/kg acrylic acid), yet generates slightly lower liquid wastes (3.25 kg/kg acrylic acid vs. 3.60 kg/kg acrylic acid). From an environmental standpoint, the glycerol route performs better in 12 of 16 impact categories. The conventional process is dominated by the propylene supply chain, contributing up to 62% of the global warming impact, while electricity demand ranks second in the glycerol-based route. Scenario analysis based on future European electricity mixes (EU-2030 and EU-2050) further reduces climate and fossil depletion impacts, although with increased mineral resource use. Overall, the results highlight the potential of glycerol as an alternative feedstock and the key role of electricity sourcing.

Keywords: acrylic acid production; glycerol valorization; process modeling and simulation; global warming potential; life cycle assessment

1. Introduction

In 2024, global CO₂ emissions increased by 0.8% compared to previous estimates, resulting in a record level of 37.8 Gt CO₂ and corresponding to an atmospheric concentration of 422.5 ppm [1]. According to the International Energy Agency (IEA), the industrial sector remained the largest contributor to emissions in 2022, accounting for roughly 38% of global fuel-combustion emissions when electricity and heat are allocated to end-use sectors [2]. Despite its significant contribution to greenhouse gas (GHG) emissions, the industrial sector also plays an important role in mitigating climate change by enabling the development of alternative solutions, such as lightweight polymers and building insulators [3].

The chemical industry is among the most energy-intensive industrial sectors, consuming roughly 10 million barrels of oil per day and around 300 billion cubic metres of natural gas globally. Despite this high energy demand, it ranks third in terms of direct CO₂ emissions, mainly because nearly half of its energy consumption is used as feedstock rather than as an energy source [4]. Within the chemical sector, the manufacture of bulk



Academic Editor: Constantinos V. Chrysikopoulos

Received: 20 April 2026

Revised: 28 May 2026

Accepted: 9 June 2026

Published: 7 July 2026

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and intermediate chemicals, including ammonia, methanol (MeOH), propylene, and others, are the key drivers in terms of energy use and GHG emissions [5]; therefore, to align with the goals of the Net-Zero Emissions (NZE) scenario, improving their sustainability has become a key priority [6].

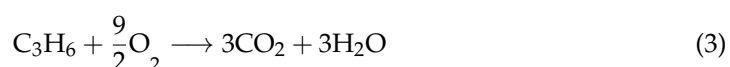
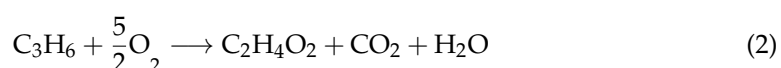
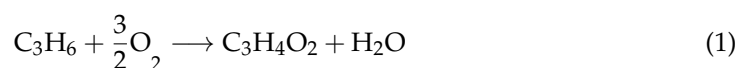
While the adoption of low-carbon electricity and improvements in energy efficiency are considered key strategies to cut CO₂ emissions, these measures alone are not sufficient to achieve deep decarbonization in so-called hard-to-abate sectors (e.g., chemicals, cement, iron and steel, etc.) [7]. A range of additional approaches has therefore been explored, including changes in fuels and feedstocks, and the integration of carbon capture and storage or utilization (CCS/CCU). However, achieving substantial emission reductions will require fundamental changes in how chemical products are manufactured [8].

In this context, there is a growing interest towards the use of alternative, renewable-based feedstocks aiming to reduce the environmental burden of chemical production [9]. Particularly, biomass utilization routes emerge as promising options since they enable fossil-resource substitution through renewable feedstocks with the potential to reduce overall environmental impacts [10]. Biomass conversion to value-added products, including biodiesel and platform chemicals, has gained significant interest across the scientific community as it contributes to the development of the circular economy. This approach is particularly relevant for the production of chemicals, where the feedstock selection shapes the overall environmental performance [11].

Among accessible alternative feedstocks, glycerol is markedly important due to its large-scale production as a by-product of the biodiesel industry, with every ton of biodiesel roughly 100 kg of glycerol are produced [12]. The continuous development of the biodiesel industry therefore resulted in massive amounts of glycerol [13], which ultimately hampers biodiesel economic viability if alternative utilization pathways are not found [14]. Therefore, the glycerol-chemistry topic recently gained significant consideration as diverse valorization pathways, including solketal [15], glycerol carbonate [16], 2,3-butanediol [17], acrolein [18], lactic acid [19], and acrylic acid [20], have been thoroughly investigated.

Acrylic acid is regarded as a key chemical building block due to its wide use in the production of super-absorbent polymers (SAP) and acrylate esters, which are further applied in coatings, adhesives, wastewater treatment, and personal care products [21]. Global production is currently estimated at 7.77–10.01 million tons per year and is expected to grow at an annual rate of approximately 5.2% until 2029 [22]. This increase is mainly driven by the demographic expansion and thriving economy, especially in regions such as China and India [23].

Nowadays, the main acrylic acid manufacturing route involves a two-step propylene oxidation process. Herein, propylene is firstly oxidized to acrolein in the presence of a steam–air mixture at temperatures above 300 °C, followed by further conversion to acrylic acid. The main chemical reactions involved in the conventional technology are [24]:



This conventional pathway achieves propylene conversions over 95% and acrylic acid yields in the range of 80–90%.

However, due to the fossil-based nature of propylene and concerns regarding limited resource availability, significant research efforts have focused on finding alternative feed-

stocks and improving process efficiency. For instance, Petrescu et al. investigated the application of Life Cycle Assessment (LCA) methodology to evaluate different propylene-based acrylic acid plant configurations, ultimately aiming to improve the overall environmental performance [25].

In contrast, several studies have explored bio-based production routes. Chu et al. developed and proposed a direct fermentative pathway for producing acrylic acid from glucose [26]. Similarly, Bhagwat et al. examined, through techno-economic and LCA, the production of acrylic acid via sugar fermentation using 3-hydroxypropionic acid (3-HP) as an intermediate [27]. Another study conducted by Brobbey et al. analyzed three process configurations for bio-based acrylic acid production using sugarcane-derived molasses as feedstock, focusing on lactic acid, 3-HP, and glycerol as intermediates. According to their findings, the lactic acid pathway showed the most promising performance from a techno-economic point of view [28]. Additionally, Okoro et al. assessed and compared two distinct acrylic acid production configurations based on the valorization of waste apple pomace. One pathway involves transforming waste apple pomace into lactic acid prior to obtaining acrylic acid, while the second route converts apple pomace into propylene, subsequently followed by acrylic acid production [29].

Focusing on the biofuel industry, Braga et al. explored a novel single-step oxidation-dehydration route for converting crude glycerol into acrylic acid [30]. Similarly, Sánchez-Gómez et al. investigated process intensification strategies based on reactive distillation configurations, demonstrating improved economic performance due to a reduced number of process units [31]. Sandid et al. conducted a techno-economic comparison between the conventional-based propylene approach and the alternative glycerol-valorization route for producing acrylic acid, ultimately emphasizing the increased capital cost associated with the propylene-based pathway [20]. Recently, Bansod et al. performed a cradle-to-gate environmental evaluation of four distinct acrylic acid production pathways, that imply intermediates such as acrolein, allyl alcohol, or lactic acid. The findings of their study point towards the energy-intensive glycerol production process as the main environmental hotspot, given the assumed epichlorohydrin-derived glycerol. In addition, the results showed considerable improvements when changing glycerol supply from epichlorohydrin towards purified crude glycerol from biodiesel industry [32]. Moreover, the authors (i.e., Bansod et al.) investigated via techno-economic analysis three glycerol alternative acrylic acid manufacturing routes, with allyl alcohol, lactic acid, and acrolein as intermediates, against the propylene-based method. The authors pointed out that the glycerol valorization route via acrolein to obtain acrylic acid was the only favourable pathway from an economic point of view, despite the increased payback period [33].

In spite of the growing interest in bio-based acrylic acid production, most existing studies have primarily focused either on process development or on techno-economic performance, with limited attention given to comprehensive environmental assessments. Although recent environmental analyses have provided valuable insights into glycerol-based acrylic acid production, a systematic techno-environmental assessment comparing the conventional propylene-based route against the emerging glycerol-based pathway under evolving electricity supply conditions remains insufficiently explored. To address this gap, the present study integrates process simulation with LCA using the ReCiPe 2016 methodology, thus enabling a broader and more up-to-date evaluation across multiple environmental impact categories. Beyond the comparative assessment, a detailed hotspot contribution analysis is performed to identify the dominant environmental drivers in key impact categories, including global warming potential (GWP) and human-toxicity-related impacts. In addition, the analysis considers future European electricity scenarios (EU-2030 and EU-2050), along with country-specific electricity mix evaluations to examine how

regional and ongoing energy system decarbonization may influence the environmental performance of the glycerol-based route.

2. Materials and Methods

The processes considered in this study, along with simplified process flow diagrams and the main modelling assumptions, are presented in Section 2.1. The LCA methodology applied to the examined scenarios is described in Section 2.2.

2.1. Process Modelling and Simulation

Process modelling and simulation was carried out by means of CHEMCAD process simulation software, version 7.1.2, developed by datacor [34]. The two examined scenarios are as follows:

Case 1: Acrylic acid production via conventional propylene oxidation process.

Case 2: Acrylic acid manufacture via glycerol dehydration, subsequently followed by acrolein oxidation.

Each of the abovementioned configurations is further described, while also presenting the process modelling assumptions.

Figure 1 illustrates the process flow diagram for the propylene oxidation to acrylic acid. As can be observed, the raw materials consisting of air (S1), low-pressure (LP) steam (S2), and propylene (S3) are mixed (MIX-1) and fed into the reaction unit (R-1), modelled as a kinetic reactor. The reactions occurring at this step were previously introduced in Section 1 as R1–R3.

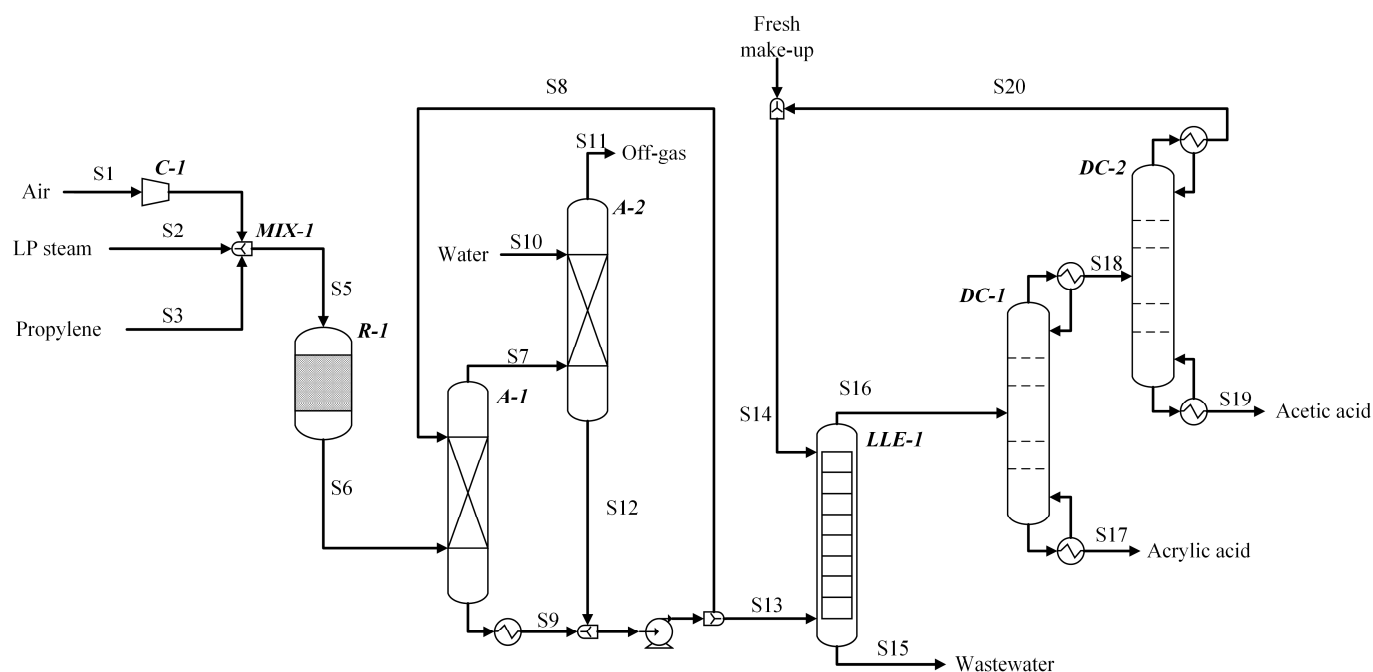
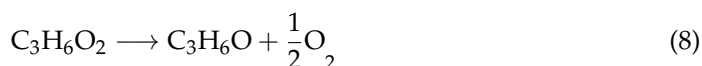


Figure 1. Schematic diagram for the acrylic acid production via propylene oxidation.

The reactor operates at 3.5 bar and 310 °C, achieving an 89% propylene conversion. The kinetic parameters, including activation energy and frequency factors, are further presented in Table 1. Subsequently, the outlet stream of the reactor (S6) is sent into the separation section. The separation section consists of two absorption units (A-1 and A-2), one liquid–liquid extraction unit (LLE-1), and two distillation towers (DC-1 and DC-2).



As can be observed, glycerol (S1), water (S2), and air (S3) are mixed (MIX-1) and fed into the reactor (R-1). The reaction unit is modelled as a kinetic reactor, and operates at 389 °C and 4 bar. It is assumed that glycerol achieves almost total conversion (99%). All kinetic parameters taken into account are given in Table 2. The outlet of the reactor enters the first distillation unit (DC-1) to separate the acrolein from the water–acetol mixture (S11). Acrolein is further mixed with air (S13) and fed into the oxidation reactor (R-2). The reaction unit is modelled as a stoichiometric reactor, assuming a reaction temperature of 375 °C and a pressure of 5 bar. Herein, 100% conversion of acrolein is considered. The reactor outlet is cooled to 40 °C to avoid any side reactions. Furthermore, the cooled acrylic acid stream (S18) enters a gas–liquid separation unit (F-1).

Table 2. Kinetic parameters for the glycerol-based acrylic acid production [20].

Reaction	E_i [kcal/kmol]	A_i [kmol/m ³ Reactor h (kPa) ²]
R4	10.99	20.7
R5	12.73	12.1
R6	1.19	6.3×10^{-5}
R7	1.45	1.8×10^{-4}
R8	11.13	2.6

The gaseous phase consisting of nitrogen, oxygen, and small amounts of acrylic acid enters the absorption column (A-1), ultimately aiming to remove the acrylic acid from the non-condensable gases (S22). The liquid stream obtained at the bottom of the absorber is mixed with the liquid stream from the gas–liquid separation unit and further fed into the second distillation column (DC-2). This unit ultimately aims to separate the azeotrope of water–acrylic acid by using toluene as an entrainer. Toluene was selected as the entrainer due to its immiscibility with water and its suitability for efficient acrylic acid separation, as reported in previous solvent screening studies [23]. High-purity acrylic acid is obtained at the bottom (S26), while the top stream, consisting of a water–toluene mixture, is separated and toluene recycled within the system. The main process modelling and design assumptions for propylene and glycerol-based acrylic acid routes are presented in Table 3.

Table 3. Process modelling design assumptions for propylene- and glycerol-based acrylic acid routes.

Propylene-Based Acrylic Acid Production Route		
Unit Operation	Assumptions	
Reaction unit (R-1)	Reactor type	CSTR–kinetic
	Operation mode	Isothermal (310 °C)
	Pressure	3.5 bar
Absorption unit (A-1)	Number of stages	25
	Number of stages	25
Absorption unit (A-2)	Top pressure	1 bar
	Bottom pump pressure	2 bar
Liquid–liquid extractor (LLE)	Number of stages	31
	Top pressure	0.19 bar

Table 3. Cont.

Propylene-Based Acrylic Acid Production Route		
Unit Operation		Assumptions
Distillation column (DC-1)	Number of stages	31
	Feed stage	7
	Top pressure	0.07 bar
	Reflux ratio	1
Distillation column (DC-2)	Number of stages	30
	Reflux ratio	0.25
Pump's efficiency		75%
Compressor's efficiency		85%
Glycerol-Based Acrylic Acid Production Route		
Unit Operation		Assumptions
Reaction unit (R-1)	Reactor type	CSTR-kinetic
	Operation mode	Adiabatic
Distillation column (DC-1)	Number of stages	8
	Condenser type	Partial
	Top pressure	1 bar
	Bottom pump pressure	1.045 bar
	Reflux ratio	1.1
Reaction unit (R-2)	Reactor type	Stoichiometric
	Operation mode	Isothermal (350 °C)
Absorption unit (A-1)	Number of stages	6
	Top pressure	4.97 bar
	Bottom pressure pump	5 bar
Distillation column (DC-2)	Number of stages	12
	Condenser type	None
	Top pressure	0.3 bar
	Bottom pump pressure	0.37 bar
	Bottom product temperature	104 °C
Distillation column (DC-3)	Number of stages	14
	Condenser type	Total
	Top pressure	0.2 bar
	Bottom pump pressure	0.2 bar
Pump's efficiency		75%
Compressor's efficiency		85%

2.2. Life Cycle Assessment (LCA)

The development and use of goods, technologies, and services are associated with the consumption of natural resources, including mineral and fossil fuels, land and water use, as well as the generation of environmental emissions [35]. Environmental Life Cycle Assessment (LCA) is one of the most commonly applied techniques for assessing the

environmental effects of a certain process or product across its full lifespan, starting from initial resource/material extraction up to disposal treatment [36].

The principles and framework, as well as the requirements and guidelines of an LCA, are defined by the International Organization for Standardization (ISO) through ISO 14040:2006 [37] and ISO 14044:2006 [38]. Therefore, in accordance with the ISO methodology, an LCA study is required to include the following four stages: (i) Goal and scope definition, (ii) Life Cycle Inventory (LCI), (iii) Life Cycle Impact Assessment (LCIA), and (iv) Interpretation of the results. Each step is further described in more detail.

2.2.1. Goal and Scope Definition

The goal of the current research is to quantify and evaluate the environmental impacts associated with two alternative pathways for acrylic acid production. In particular, the conventional route based on propylene is compared with a more sustainable approach that utilizes glycerol, a by-product of the biodiesel production process. The target audience of this study includes professionals working in the chemical and petrochemical sectors, with particular emphasis on those involved in process design, sustainable production, and development of bio-based chemical routes.

The functional unit (FU) represents a measurable function of a product, which serves as a reference for quantifying input and output flows and, ultimately, for evaluating the performance of the system under study [39]. The reference flows associated with a given FU correspond to the quantities of products required to fulfil the defined system function and to deliver the specified FU. Hence, an annual production of 50,000 tons has been set as the system's function, while one kg of acrylic acid has been considered as the FU for the present study.

System boundaries establish a clear distinction between the processes included in the assessment and those that fall outside its scope [40]. Accordingly, four main approaches can be used to define these boundaries: (i) cradle-to-gate, (ii) gate-to-gate, (iii) gate-to-grave, and (iv) cradle-to-grave. Although the cradle-to-grave method would best describe the environmental impacts by also including end-of-life treatment, data availability constraints lead the present analysis to adopt a cradle-to-gate perspective. Therefore, as illustrated in Figure 3, the following subprocesses are covered within this analysis: (a) upstream processes: electricity generation, thermal power production, raw materials supply; (b) main process: acrylic acid manufacture; and (c) downstream processes: waste disposal and wastewater treatment.

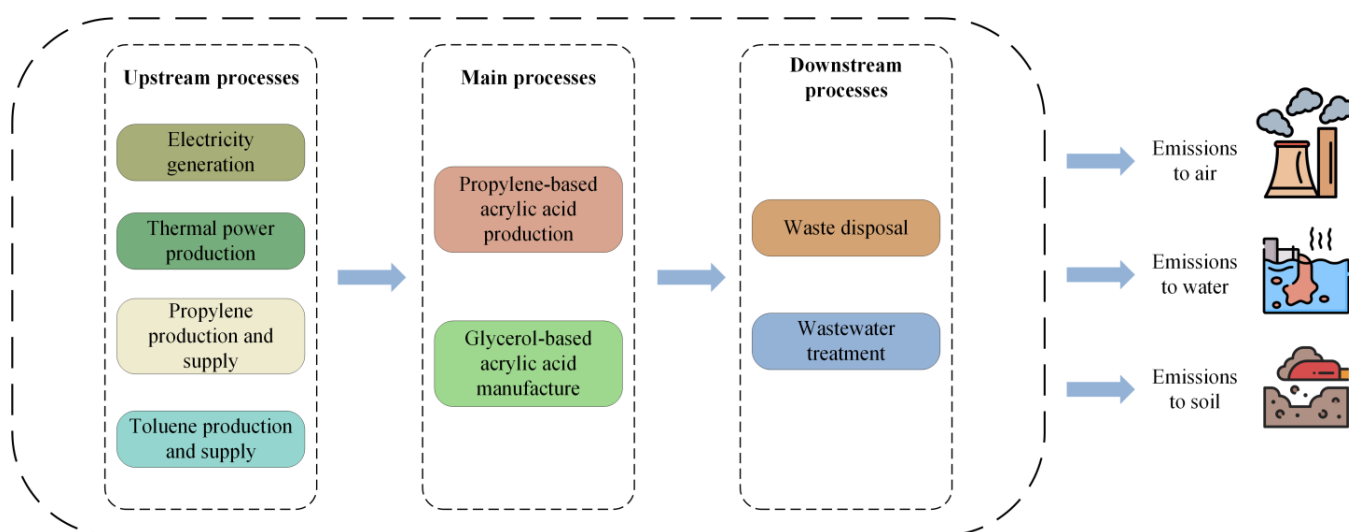


Figure 3. LCA system boundaries for the examined scenarios.

The geographical and temporal boundaries are key aspects to consider when defining the parameters of the analysis. The selection of plant site and its corresponding geographical context is determined by market circumstances and the product's definition. Establishing temporal boundaries is more challenging, as many stages of the product life cycle necessitate estimation due to their occurrence in the future. Therefore, the geographical and temporal boundaries of the system under study assume that the plant is located in Europe (EU), where biofuel production is well established and continues to grow, and has a lifespan of 25 years. This choice is based on the availability of reliable data and ensures that the system is modelled using European average conditions, thereby improving the representativeness of the results.

Furthermore, when conducting an LCA investigation, several aspects must be taken into consideration, particularly when data are limited or not readily available, which requires the use of assumptions. In this consideration, the assumptions considered in the LCA current study are presented in Table 4. Toluene production and supply was included within the system boundaries since it is used as an entrainer in the separation section, thus contributing to the overall material balance and environmental flow of the process.

Table 4. LCA assumptions considering upstream and downstream processes.

Process	Assumptions
Upstream processes	
Propylene supply chain ^a	The dataset covers all relevant process steps/technologies over the supply chain; Steam crackers are used to produce short olefins, such as ethylene and propylene, as well as hydrogen from naphtha. The feed stream is diluted with steam and then led through a furnace, where it is heated to a high temperature (around 850 °C) for a very short time. Temperature and residence time define the different yields of products. The product stream leaving the cracking furnace is quenched to prevent further reactions.
Toluene supply chain ^a	The dataset represents a regional consumption mix, combining different production routes, following a cradle-to-gate system boundary; Toluene production is modelled as a mix of aromatics derived from catalytic reforming and steam cracking (pyrolysis gasoline), with further separation and purification steps.
Downstream processes	
Electricity generation ^a	EU electricity mix consists of 21.24% natural gas, 20.93% nuclear, 15.98% wind power, 10.06% hydro power, 7.73% lignite, 6.98% photovoltaics, 6.74% hard coal, 3.56% biomass (solid), 2.08% biogas, 1.84% fuel oil, 1.60% waste-to-energy, 0.85% coal gases, 0.20% geothermal, 0.14% solar thermal, 0.07% peat.
Thermal energy generation ^a	Thermal energy produced in natural-gas-specific heat plants, considering national/regional-specific standards in regard to efficiency, firing technology, flue-gas desulfurization, NO _x removal and de-dusting.
Wastewater treatment ^a	Process water is sent to the wastewater treatment plant, modelled according to an average municipal wastewater treatment plant; GHG emissions from direct land use change are allocated to service for 20 years after the land use change occurs.

^a Pre-defined processes from the LCA for Experts software, based on primary and secondary data, used to cover the entire supply chain of the considered process/system.

Some factors are not considered in the present LCA, and therefore represent the main limitations of this investigation. These include: (i) construction and decommissioning of the facility; (ii) maintenance and repair activities; (iii) the development of transport infrastructure (e.g., roads, railways, and shipping) as well as transport vehicles; (iv) installation of unloading facilities; (v) labour-related human activities; and (vi) rare and unpredictable events, such as leaks or accidental spills. These aspects are not considered

in the present study as their inclusion would significantly expand the system limits. In addition, gathering such data is difficult, and previous studies proved that contributions from such elements are relatively small in terms of overall environmental impacts [41].

2.2.2. Life Cycle Inventory (LCI)

The Life Cycle Inventory (LCI) stage follows the Goal and scope definition and pertains setting up an inventory of input and output streams of a specific process over its entire life cycle [37]. Ultimately, the LCI represents a collection of several unit processes that are gathered within the system boundaries. It should account for all the input and output flows, from raw materials supply, resource utilization, up to the quantification of air, water, and soil pollutants. In addition, conventional LCA evaluates the overall material and energy exchanges linked to delivering a defined FU, typically focusing on processes that substantially influence the product's function and performance, respectively [42].

The datasets employed in an LCA investigation are generally classified into primary data (i.e., information obtained directly through interviews or on-site measurements) and secondary data (i.e., information derived from modelling and simulation activities, estimations, or previously published studies) [43]. The present analysis is based on both primary and secondary datasets. Background datasets for raw material supply and energy generation were obtained from the Sphera Managed Life Cycle Content databases and the Eco invent v3.8 database, which are based on primary industrial information [44]. The acrylic acid production process was modelled using literature-based data.

2.2.3. Life Cycle Impact Assessment (LCIA)

The third step of an LCA investigation is the Life Cycle Impact Assessment (LCIA) stage, which focuses on converting the LCI results into their potential environmental impacts by means of certain characterization factors. At this stage, various impact assessment methods can be selected to analyze the effects associated with air, water, and soil pollutants, addressing impacts on human health, climate change, ecosystem and/or resource use [45]. In the context of the current investigation, the environmental analysis was carried out using the LCA for Experts software, version 10.8, developed by Sphera® [46]. The ReCiPe 2016 impact assessment method, following the Hierarchist (H) cultural perspective, has been selected as the impact assessment method. The Hierarchist cultural perspective was chosen as it reflects the general scientific consensus, both in terms of the time horizon considered and the probability of the considered impacts. The ReCiPe 2016 framework quantifies both midpoint and endpoint impact categories along a cause–effect chain. Midpoint indicators are situated earlier in this chain and generally provide more detailed results with lower uncertainty, while endpoint categories appear at the final stage, thus making them more straightforward to interpret but exhibiting higher uncertainties [47]. Table 5 further presents the main midpoint impact categories assessed in the current study.

Table 5. Overview and description of midpoint environmental categories defined under the ReCiPe 2016 methodology.

Impact Category	Major Contributors
Global Warming Potential (GWP)	CO ₂ , CH ₄ , N ₂ O, NO ₂ , CFCs, HCFCs, HFCs
Freshwater Eutrophication Potential (FEP)	Nitrogen and Phosphorus compounds
Stratospheric Ozone Depletion Potential (ODP)	CFCs, HCFCs, halons

Table 5. Cont.

Impact Category	Major Contributors
Fossil Depletion Potential (FDP)	Depletion of fossil resources
Mineral Depletion Potential (MDP)	Depletion of mineral resources
Photochemical Oxidation Formation Potential ecosystem (POFP _{ecosystem})	Particulate matter, NMVOCs, NOx
Photochemical Oxidation Formation Potential human-health (POFP _{human-health})	
Human Toxicity Potential cancer (HTP _{cancer})	Toxic substances for human health
Human Toxicity Potential non-cancer (HTP _{non-cancer})	
Freshwater Ecotoxicity Potential (FETP)	Toxic substances with lethal concentrations in rodents and aquatic species
Terrestrial Ecotoxicity Potential (TETP)	
Marine Ecotoxicity Potential (METP)	
Particulate Matter Formation Potential (PMFP)	NH ₃ , NO _x , SO ₂
Terrestrial Acidification Potential (TAP)	SO _x , NO _x , HCl, HNO ₃ , H ₂ SO ₄ , H ₂ S
Water Depletion Potential (WDP)	Utilization of freshwater resources
Marine Eutrophication Potential (MEP)	Nitrogen-driven nutrients

3. Results

3.1. Process Modelling and Simulation Results

Prior to present the technical results, it is necessary to perform a comparison against literature studies to validate the developed models. Tables S1 and S2 in the Supplementary Materials File summarizes the model validation for both the propylene oxidation route and the glycerol dehydration followed by acrolein oxidation pathway. The main process streams corresponding to these scenarios are detailed in Tables S3 and S4.

The key technical performance indicators for the two investigated acrylic acid production routes are reported in Table 6. Concerning raw material consumption, the propylene-based route requires 0.84 kg propylene per kg of acrylic acid produced, whereas the glycerol-based pathway demands 1.90 kg glycerol per kg of product. Although this initially suggests a clear advantage for the propylene route, it should be noted that glycerol is a by-product of the biodiesel industry; thus, its valorization may offer additional systemic benefits. Both processes require LP steam and air, primarily for the operation within the fluidized bed reactor. However, the glycerol-based route entails an additional demand for these utilities upstream of the acrolein oxidation reactor.

Energy consumption in both scenarios stems from two primary sources: electrical and thermal. Electrical energy is primarily associated with the operation of pumps and compressors, while thermal energy is required for the reboilers of the distillation columns.

The glycerol-based route exhibits a significantly higher electrical demand, approximately 4.6 times that of the propylene-based process. Conversely, the propylene route requires substantially more thermal energy, with an increase of about 3.8 times compared to the glycerol pathway.

Table 6. Technical performance indices in the examined acrylic production scenarios.

Propylene Oxidation Towards Acrylic Acid Production		
Key Performance Indicator	Unit of Measure	Value
Propylene specific consumption	kg propylene/kg acrylic acid	0.84
LP Steam specific consumption	kg LP steam/kg acrylic acid	2.83
Air specific consumption	kg air/kg acrylic acid	6.17
Electricity consumption	kWh/kg acrylic acid	0.32
Thermal power consumption	MJ/kg acrylic acid	5.41
CO ₂ specific emissions (on-site)	kg CO ₂ eq./kg acrylic acid	0.47
CO ₂ specific emissions (off-site)	kg CO ₂ eq./kg acrylic acid	0.06
Wastewater	kg wastewater/kg acrylic acid	3.60
Glycerol Dehydration Towards Acrylic Acid Production		
Key Performance Indicator	Unit of Measure	Value
Glycerol-specific consumption	kg glycerol/kg acrylic acid	1.90
LP Steam specific consumption	kg LP steam/kg acrylic acid	1.94
Air specific consumption	kg air/kg acrylic acid	19.31
Electricity consumption	kWh/kg acrylic acid	1.48
Thermal power consumption	MJ/kg acrylic acid	1.42
CO ₂ specific emissions (on-site)	kg CO ₂ eq./kg acrylic acid	0.48
CO ₂ specific emissions (off-site)	kg CO ₂ eq./kg acrylic acid	0.26
Wastewater	kg wastewater/kg acrylic acid	3.25

To estimate off-site CO₂-specific emissions, a carbon intensity of 0.174 kg CO₂ eq./kWh produced was adopted based on data from the IEA [48]. The results indicate that on-site emissions are comparable for both routes; however, the glycerol-based process leads to high overall emissions due to its increased electricity consumption.

Regarding wastewater generation, the propylene-based process produces 3.6 kg of wastewater per kg of acrylic acid, whereas the glycerol-based route results in a slightly lower value of 3.25 kg per kg of product.

3.2. Life Cycle Assessment Results

The interpretation phase aims to support conclusions and recommendations by accounting for the study limitations and results of the LCI and LCIA. The outcomes should be presented clearly to ensure they are easily understood by the target audience. Table 7 presents the LCA impact scores for the two investigated scenarios, while considering the previously mentioned assumptions and limitations. As can be observed, all impact results are reported per kg of acrylic acid produced to ease and ensure a fair comparison of the two scenarios.

Overall, the environmental impact results indicate that the glycerol-based acrylic acid production route performs better than the conventional propylene pathway. Case 2 shows lower impact scores in twelve out of the sixteen reported impact categories. In contrast, the traditional acrylic acid production route (i.e., Case 1) performs better in four environmental indicators, namely HTP_{non-cancer}, FETP, TETP, and METP. The most pronounced difference between the two pathways is observed for the FETP impact category, where the propylene-based scenario yields a result that is approximately 25 times lower. This difference is mainly linked to the wastewater treatment process. In addition, Case 1 shows a GWP impact

score that is about twice as high, primarily due to the propylene supply chain, followed by emissions from the main production process (see Figure 3).

Table 7. LCA results for the two acrylic acid production scenarios according to the ReCiPe 2016 impact assessment method.

KPI	Units	Case 1	Case 2
GWP	kg CO ₂ eq./kg _{product}	2.55	1.15
FEP	kg P eq./kg _{product}	8.85×10^{-5}	8.06×10^{-5}
ODP	kg CFC-11 eq./kg _{product}	3.70×10^{-7}	2.18×10^{-7}
FDP	kg oil eq./kg _{product}	1.48	3.30×10^{-1}
MDP	kg Cu eq./kg _{product}	9.71×10^{-4}	7.28×10^{-4}
POFP _{ecosystem}	kg NO _x eq./kg _{product}	3.15×10^{-3}	7.26×10^{-4}
POFP _{human-health}	kg NO _x eq./kg _{product}	2.97×10^{-3}	7.11×10^{-4}
HTP _{cancer}	kg 1,4-DB eq./kg _{product}	4.80×10^{-2}	1.30×10^{-2}
HTP _{non-cancer}	kg 1,4-DB eq./kg _{product}	1.56	1.61
FETP	kg 1,4-DB eq./kg _{product}	4.09×10^{-3}	1.05×10^{-1}
TETP	kg 1,4-DB eq./kg _{product}	2.80×10^{-1}	7.80×10^{-1}
METP	kg 1,4-DB eq./kg _{product}	6.81×10^{-3}	9.22×10^{-3}
PMFP	kg PM _{2.5} eq./kg _{product}	7.77×10^{-4}	2.72×10^{-4}
TAP	kg SO ₂ eq./kg _{product}	2.40×10^{-3}	8.87×10^{-4}
WDP	m ³ /kg _{product}	3.43×10^{-3}	3.33×10^{-3}
MEP	kg N eq./kg _{product}	2.35×10^{-4}	2.12×10^{-4}

Case 1—propylene-based acrylic acid production; Case 2—glycerol-based acrylic acid production.

Freshwater eutrophication potential (FEP) reflects the nutrient levels in freshwater systems, mainly related to nitrogen and phosphorus, and is reported in kg of P eq. per kg of product. As can be observed in Table 7, the glycerol-based pathway records a similar FEP score to the conventional acrylic acid approach (i.e., 8.06×10^{-5} vs. 8.85×10^{-5} kg P eq./kg_{product}, respectively). In both cases, the impact is dominated by the wastewater treatment stage, which contributes over 90% of the total score. Regarding the ODP impact indicator, Case 2 shows a value roughly 1.7 times-fold lower than Case 1. Since the propylene supply accounts for about 74% of the total ODP in Case 1, this result highlights that replacing propylene with an alternative feedstock such as glycerol can reduce emissions associated with ozone layer depletion.

Fossil depletion is directly linked to the extraction of fossil fuel resources, thus the 4-times larger impact in Case 1 as compared to Case 2 is mainly due to the propylene supply. This sub-process contributes by roughly 87% of Case 1 total impact score, and it is followed by the thermal energy production which contributes by 0.15 kg oil eq./kg_{product} of the total of 1.48 kg oil eq./kg_{product}. In the glycerol-based acrylic acid production, the largest contribution to FDP impact stems from the electricity generation and supply, which contributes by approximately 0.22 kg oil eq./kg_{product}, being followed by the toluene supply with roughly 0.07 kg oil eq./kg_{product}.

A similar trend is observed when examining the MDP impact indicator in Case 1, which relates to the extraction of ore grades. The propylene supply is the main contributor, accounting for approximately 7.37×10^{-4} kg Cu eq./kg_{product} out of a total of 9.71×10^{-4} kg Cu eq./kg_{product}. Electricity generation and thermal power requirements rank second and third, with contributions of 15.62% and 8.36% of the total impact score, respectively. In contrast, in Case 2, electricity demand, and thus electricity generation, provides the largest contribution with a share of over 95% of the overall impact.

Furthermore, Case 1 shows impact scores that are about 4 times higher for both POFP_{ecosystem} and POFP_{human-health} compared to the glycerol-based alternative. This

difference is mainly driven by the raw material supply chain. In particular, propylene supply accounts for nearly 90% of the total impact in both categories, resulting in 2.82×10^{-3} kg NO_x eq./kg_{product} and 2.65×10^{-3} kg NO_x eq./kg_{product}, respectively. In contrast, glycerol is regarded as a by-product of the biodiesel industry; therefore, its utilization adds value as it overcomes one of the main drawbacks of biodiesel production, namely the large-scale accumulation of glycerol [49].

Terrestrial ecotoxicity reflects the impact of harmful compounds on terrestrial ecosystems and sediments. As expected, the value of 2.80×10^{-1} kg 1,4-DB eq./kg_{product} in Case 1 is largely dominated by the propylene supply. However, the glycerol-based approach results in even higher effects, reaching 7.80×10^{-1} kg 1,4-DB eq./kg_{product}. This is mainly due to the main acrylic acid production process, which contributes 6.19×10^{-1} kg 1,4-DB eq./kg_{product}, followed by toluene supply and electricity generation, each accounting for around 10% of the total. A similar pattern is observed when looking at the METP impact category. In Case 1, wastewater treatment generates about 4.49×10^{-3} kg 1,4-DB eq./kg_{product}. Nevertheless, Case 2 records a 1.35-fold higher value, mainly due to contributions from the main production process (i.e., 51.55% of the total share) and wastewater treatment (i.e., 44.77% of the total share).

Additionally, in Case 1, more than 90% of the total PMFP impact is attributed to the propylene supply chain (i.e., 7.02 kg PM_{2.5} eq./kg_{product}), while only 5.5% stem from the electricity supply. In contrast, in Case 2, approximately 72.2% of the PMFP impact score is directly related to the electricity requirements, with the toluene supply chain contributing roughly 25% to the total share.

In line with the previous results, over 90% of the total TAP impact score in Case 1 is driven by the propylene supply, while around 6% are attributed to the electricity generation. On the opposite, the glycerol-based pathway is dominated by the electricity supply, which adds 6.65×10^{-3} kg SO₂ eq./kg_{product} to the overall score. Toluene supply and thermal energy requirements rank second and third, with contributions of 22.15% and about 2.80% of the total share, respectively.

Water depletion potential is directly linked to process water consumption. In Case 1, propylene supply contributes 5.91×10^{-3} m³/kg_{product}; however, the overall impact score is significantly reduced due to negative contribution from wastewater treatment (i.e., -3.6×10^{-3} m³/kg_{product}). Similarly, in Case 2, electricity generation ranks first with a contribution of 5.08×10^{-3} m³/kg_{product}, yet a negative contribution of -3.24×10^{-3} m³/kg_{product} due to wastewater treatment aids in shaping the overall water consumption score.

Details and discussion on the sub-processes with the highest influence over the GWP, as well as HTP_{cancer} and HTP_{non-cancer} impact categories, are further provided.

Figure 4 displays the detailed distribution of the GWP impact for the two acrylic acid production routes. In the conventional scenario, the propylene supply chain accounts for the largest share, at around 62% of the total, followed by the main acrylic acid production process and thermal energy generation, contributing 18.28% and 15.21%, respectively. This suggests that reducing GWP in this case should primarily focus on the propylene supply chain, while also targeting improvements in the main process. Additional efforts should address thermal energy generation, such as using lower-carbon alternatives.

On the opposite, the GWP distribution for the glycerol-based acrylic acid route shows that the main production process and electricity generation rank first and second, with shares of approximately 44% and 42%, respectively. Thermal energy generation and the toluene supply chain also contribute to the overall impact, although to a lesser extent. These results highlight that the main hotspots in this case are the production process and electricity use, suggesting that future improvements should focus on reducing process emissions and increasing the share of renewable electricity.

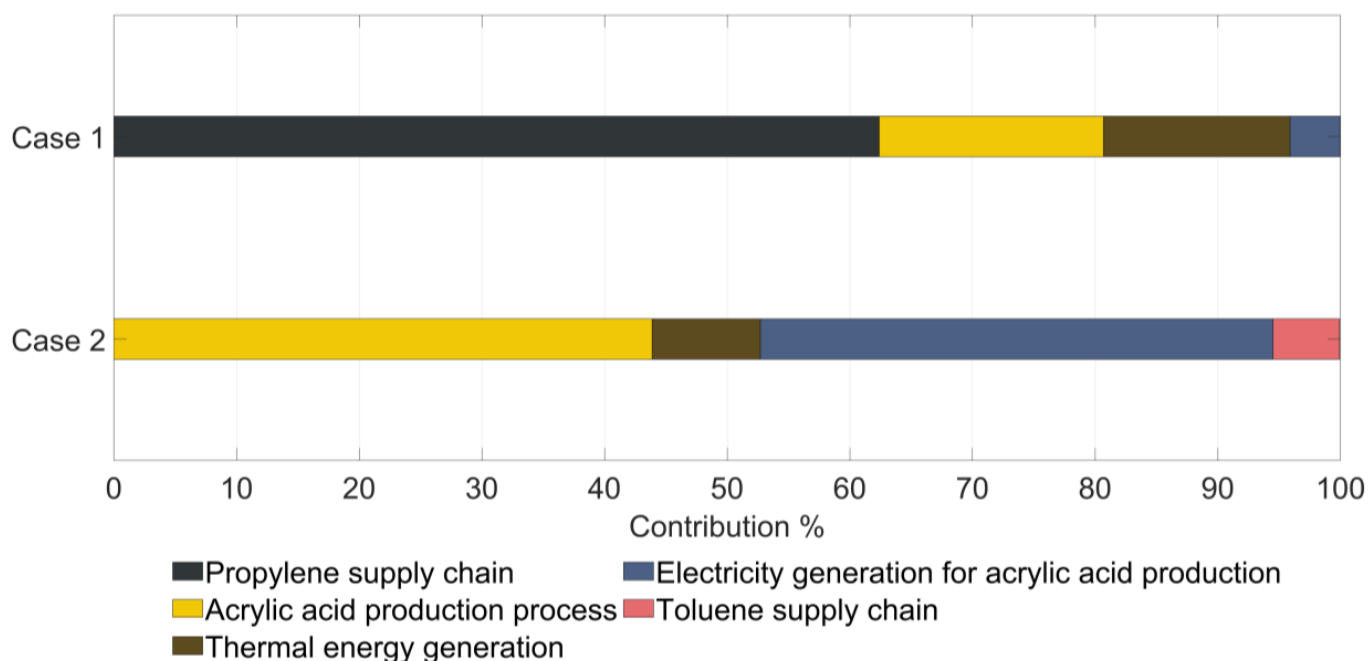


Figure 4. Detailed distribution of the GWP impact indicator for the investigated scenarios.

The detailed distribution of the HTP_{cancer} impact indicator is presented in Figure 5. In line with previous findings, the propylene supply ranks as the main contributor in Case 1, accounting for 3.56×10^{-2} kg 1,4-DB eq./kg_{product} of a total of 4.80×10^{-2} kg 1,4-DB eq./kg_{product}. The wastewater treatment process ranks second, with a contribution of 26%. In Case 2, wastewater treatment becomes the largest contributor, accounting for over 90% of the total impact, followed by electricity generation with a roughly 6.7% share. These results indicate that the conventional route is mainly influenced by the raw material supply chain, whereas the glycerol-based route is driven by wastewater treatment and electricity use. Therefore, reducing HTP_{cancer} impacts in Case 2 would require a focus on minimizing liquid waste streams, along with improvements in electricity sourcing.

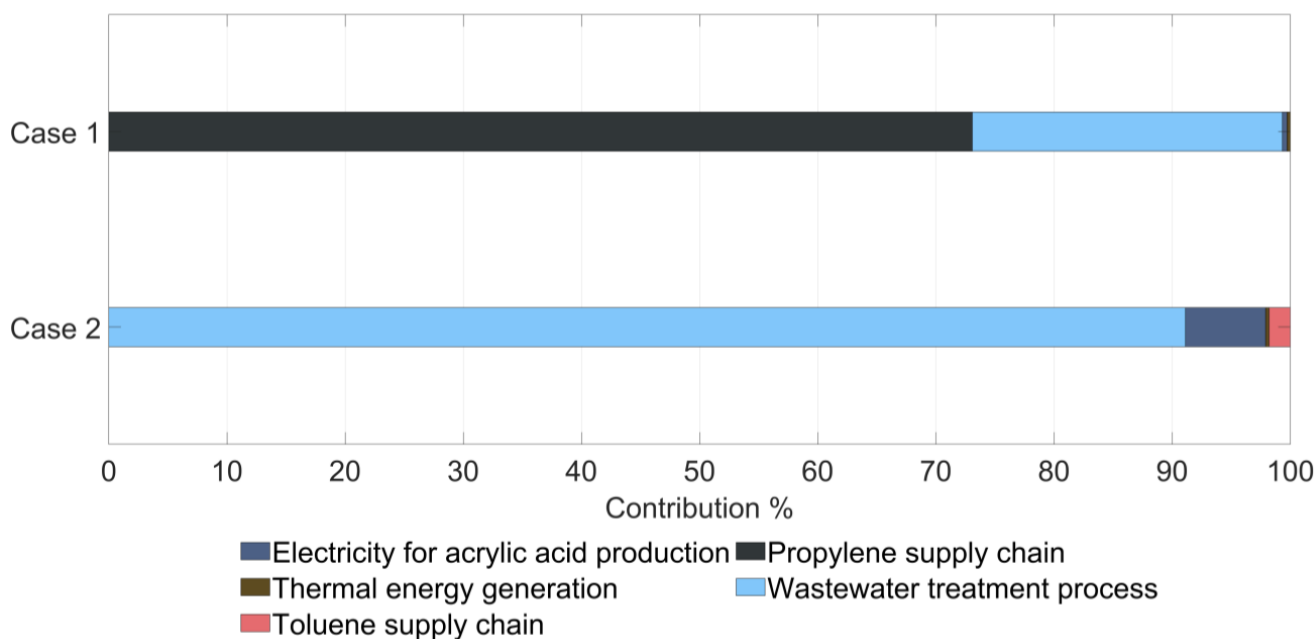


Figure 5. Detailed distribution of the HTP_{cancer} impact category in the investigated scenarios.

Figure 6 depicts the distribution of the $HTP_{non-cancer}$ impact indicator. As can be observed, in both Case 1 and Case 2, the results are primarily driven by the wastewater treatment process, with shares of 83.12% and 72.34%, respectively. This suggests that further improvements in both scenarios should focus on reducing wastewater generation and discharge. In Case 1, propylene supply is the second-largest contributor, accounting for nearly 17% of the total impact. In Case 2, the main production process ranks second, contributing about 27%.

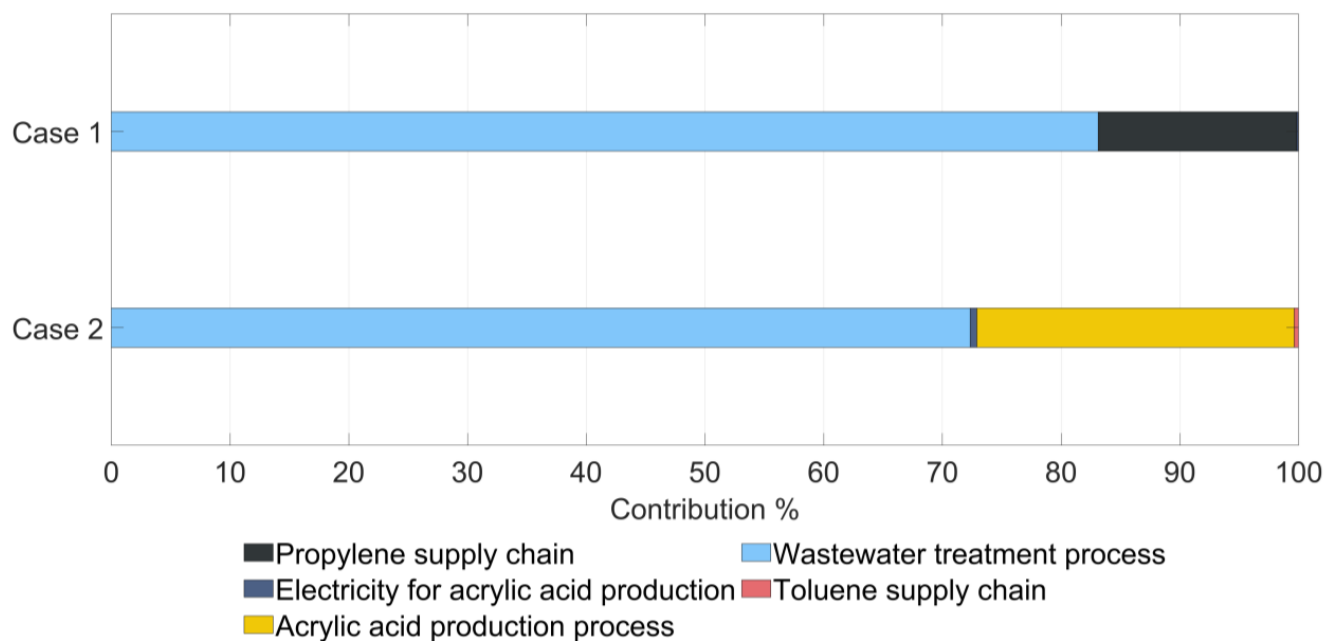


Figure 6. Detailed distribution of the $HTP_{non-cancer}$ impact category in the investigated scenarios.

As shown previously, electricity generation has a significant influence on the environmental performance of the glycerol-based acrylic acid production route. In this context, and considering the projected transition of the European electricity mix towards a higher share of renewable sources, a scenario analysis was performed to evaluate the effects of reduced fossil-based electricity while increasing the share of renewables. Two scenarios were considered, corresponding to the EU-2030 and EU-2050 electricity systems. The datasets were obtained from the Sphera Managed Life Cycle Content database, which considered established energy pathways, including the Stated Policies (STEPS), Announced Pledges (APS), and Sustainable Development scenarios (SDS). These scenarios reflect the ongoing decarbonization of the European electricity sector and allow for assessing its influence on the overall environmental system performance.

Table 8 presents the environmental impact scores for Case 2 (base case), along with the EU-2030 and EU-2050 electricity scenarios. A comparison between the base case and the EU-2030 scenario shows a clear reduction in environmental impacts, with 14 of a total of 16 impact categories presenting lower values. This trend becomes more pronounced in the EU-2050 scenario, where further improvements are observed due to the higher share of renewable electricity. In particular, the GWP impact decreases significantly, reaching nearly a 1.5-fold reduction compared to the base case. This reduction is mainly driven by the decreasing contribution of fossil-based electricity, which plays a dominant role in the overall environmental performance of the glycerol-based route.

However, not all impact categories follow this trend. The MDP indicator shows an increase in both future scenarios, with the highest value recorded in the EU-2050 case. This is directly linked to the higher share of renewable technologies, especially wind and

solar power. While these technologies reduce emissions during operation, they require substantial material inputs within the construction stage. As these upstream processes are accounted within the LCI, this transition towards renewable energy results in increased MDP scores. In addition, several impact categories, including FEP, METP, and MEP, show minor variations across the examined scenarios, thus indicating a lower sensitivity to changes in the electricity supply. As observed, the LCA results highlight a trade-off between impact categories, where reductions in climate-related impacts are accompanied by an increase in the use of mineral resources.

Table 8. LCA results for the glycerol-based acrylic acid production case in the announced EU-2030 pledged electricity scenario.

KPI	Units	Case 2—Base Case	Case 2—EU 2030 Pledge	Case 2—EU 2050 Pledge
GWP	kg CO ₂ eq./kg _{product}	1.15	0.85	0.76
FEP	kg P eq./kg _{product}	8.06×10^{-5}	8.05×10^{-5}	8.04×10^{-5}
ODP	kg CFC-11 eq./kg _{product}	2.18×10^{-7}	1.51×10^{-7}	1.25×10^{-7}
FDP	kg oil eq./kg _{product}	3.30×10^{-1}	2.37×10^{-1}	1.85×10^{-1}
MDP	kg Cu eq./kg _{product}	7.28×10^{-4}	7.96×10^{-4}	8.33×10^{-4}
POFP _{ecosystem}	kg NO _x eq./kg _{product}	7.26×10^{-4}	4.98×10^{-4}	4.26×10^{-4}
POFP _{human-health}	kg NO _x eq./kg _{product}	7.11×10^{-4}	4.86×10^{-4}	4.14×10^{-4}
HTP _{cancer}	kg 1,4-DB eq./kg _{product}	1.30×10^{-2}	1.27×10^{-2}	1.30×10^{-2}
HTP _{non-cancer}	kg 1,4-DB eq./kg _{product}	1.61	1.60	1.60
FETP	kg 1,4-DB eq./kg _{product}	1.05×10^{-1}	1.05×10^{-1}	1.05×10^{-1}
TETP	kg 1,4-DB eq./kg _{product}	7.80×10^{-1}	7.76×10^{-1}	7.64×10^{-1}
METP	kg 1,4-DB eq./kg _{product}	9.22×10^{-3}	9.18×10^{-3}	9.17×10^{-3}
PMFP	kg PM _{2.5} eq./kg _{product}	2.72×10^{-4}	2.58×10^{-4}	2.39×10^{-4}
TAP	kg SO ₂ eq./kg _{product}	8.87×10^{-4}	8.40×10^{-4}	7.74×10^{-4}
WDP	m ³ /kg _{product}	3.33×10^{-3}	0.58×10^{-3}	0.16×10^{-3}
MEP	kg N eq./kg _{product}	2.12×10^{-4}	2.09×10^{-4}	2.09×10^{-4}

Given the large influence of the electricity generation on the environmental performance of the glycerol-based acrylic acid production scenario in the Base case, as well as under the EU-2030 and EU-2050 electricity mix scenarios, and considering that the use of an average EU grid mix may cover up important regional variability, three alternative country-specific scenarios were evaluated. Electricity mixes representative of Poland, France, and Germany have been considered. The composition of each specific electricity mix is presented in Table S5, while the detailed environmental impact results are provided in Table S6, Supplementary Materials File. Overall, the results show that the environmental performance of the glycerol-based pathway is strongly influenced by the regional electricity mix composition, with low-carbon grids resulting in considerably lower climate-related impacts, while trade-offs across other impact indicators remain.

4. Conclusions

The present investigation focused on comparing the conventional propylene oxidation-based acrylic acid production route (Case 1) against more sustainable alternatives based on glycerol dehydration, subsequently followed by acrolein oxidation (Case 2).

From a technical perspective, the propylene-based route displays lower raw material specific consumption (e.g., 0.84 kg propylene/kg acrylic acid vs. 1.90 kg glycerol/kg acrylic acid) and reduced electricity requirements (e.g., 0.32 kWh/kg acrylic acid vs. 1.48 kWh/kg acrylic acid). In contrast, the glycerol-based pathway benefits from lower thermal energy needs (e.g., 5.41 MJ/kg acrylic acid vs. 1.42 MJ/kg acrylic acid), while generating slightly reduced wastewater streams. While the approximately 2.2 times higher glycerol consumption may appear as a drawback, its source as a by-product of the biodiesel

industry offers an opportunity for valorization and improved resource efficiency at a broader system level.

From an environmental point of view, the glycerol-based alternative route outperforms the conventional pathway across most impact categories, except $\text{HTP}_{\text{non-cancer}}$, FETP, TETP, and METP. This is mainly driven by the reduced dependence on fossil resources. In particular, Case 1 records a GWP score that is about twice as high as that obtained in Case 2 and this is primarily due to the propylene supply chain, which contributes by a share of 62% to the total score. The $\text{HTP}_{\text{cancer}}$ impact distribution shows that whether the traditional approach is significantly influenced by the raw material supply and sourcing, most of the impact in the sustainable approach may be attributed to the wastewater treatment process (e.g., 1.19×10^{-2} kg 1,4-DB eq./kg_{product}) and to electricity generation (e.g., 8.81×10^{-4} kg 1,4-DB eq./kg_{product}); therefore, clearly highlighting the environmental hotspots.

The high electricity requirements in Case 2 result in increased indirect emissions, thus emphasizing the strong influence of electricity supply on the overall environmental profile. This was further confirmed through a scenario analysis, where the use of future European electricity mixes (EU-2030 and EU-2050), based on established energy transition scenarios, resulted in significant improvements, particularly in terms of climate change and fossil depletion impacts. At the same time, the results reveal important trade-offs. The transition towards green electricity and the increased share of renewables contribute to a reduction in GHG emissions, yet it also results in higher MDP impacts due to the material requirements of the renewable technologies. Furthermore, the country-specific evaluation further confirms that regional electricity mix composition significantly affects the environmental performance of the glycerol-based route, with low-carbon grids substantially improving climate-related impacts.

Overall, the results show that the glycerol-based pathway represents a promising alternative to the conventional process, especially under future low-carbon electricity conditions. Nevertheless, its performance remains strongly dependent on electricity sourcing. Therefore, further improvements should focus on reducing electricity demand while increasing process efficiency. At the same time, the findings highlight that future progress in sustainable chemical production is closely linked to the decarbonization of the energy sector, while also requiring careful consideration of material resource use. The outcomes of the current study provide valuable insights into the glycerol economy and underline the need to evaluate sustainable production routes in the broader context of both energy and resource systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cleantechnol8040101/s1>, Table S1: Model validation for the propylene route; Table S2: Model validation for the glycerol-based pathway; Table S3: Main input and output streams for the propylene-based scenario; Table S4: Main input and output streams for the glycerol-based scenario; Table S5: Electricity generation mix assumptions considered in the country-specific analysis; Table S6: LCA results for the glycerol-based acrylic acid production pathway under EU-average and alternative country-specific scenarios.

Author Contributions: S.C.G., software, visualization, LCA analysis, review and editing the final manuscript version; L.P. supervision, conceptualization, methodology, provided guidance on the simulations and LCA and revised the manuscript. F.-A.B. investigation, data curation, performed simulations, validated the simulation results, write the original draft; C.-C.C. methodology, software, supervised and reviewed the work. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

IEA	International Energy Agency
GHG	Greenhouse gas
MeOH	Methanol
NZE	Net-Zero Emissions
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
SAP	Super-absorbent polymer
LCA	Life cycle assessment
3-HP	3-hydroxipropionic acid
S	Stream
R	Reactor
MIX	Mixer
A	Absorber
LLE	Liquid-liquid extractor
DC	Distillation column
F	Gas-liquid separator
E_i	Activation energy
A_i	Pre-exponential factor
CSTR	Continuous stirred tank reactor
ISO	International Organization for Standardization
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
FU	Functional unit
EU	Europe
H	Hierarchist
GWP	Global warming potential
FEP	Freshwater eutrophication potential
ODP	Stratospheric ozone depletion potential
FDP	Fossil depletion potential
MDP	Mineral depletion potential
$POFP_{\text{ecosystem}}$	Photochemical oxidation formation potential ecosystem
$POFP_{\text{human-health}}$	Photochemical oxidation formation potential human-health
HTP_{cancer}	Human toxicity potential cancer
$HTP_{\text{non-cancer}}$	Human toxicity potential non-cancer
FETP	Freshwater ecotoxicity potential
TETP	Terrestrial ecotoxicity potential
METP	Marine ecotoxicity potential
PMFP	Particulate matter formation potential
TAP	Terrestrial acidification potential
WDP	Water depletion potential
MEP	Marine eutrophication potential
LP	Low-pressure
PM	Particulate matter
STEPS	Stated policies
APS	Announced pledges
SDS	Sustainable development scenarios

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