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# Environmental sustainability evaluation of glycerol and propylene-based pathways to acrylic acid *via* different intermediates†

Yash Bansod, [a] Prashant Pawanipagar, [a] Kamran Ghasemzadeh[a] and Carmine D'Agostino *[a,b]

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This study investigates the cradle-to-gate life cycle assessment of four acrylic acid production routes. Acrylic acid, an important industrial chemical, is currently produced using fossil fuel-based propylene but it can be sustainably produced from biodiesel derived glycerol through different pathways that involve intermediates such as acrolein, allyl alcohol, or lactic acid. Environmental impacts, including global warming potential, water footprint, acidification, eutrophication, ozone layer depletion, photochemical smog, and human toxicity, are evaluated. Glycerol-based processes exhibit significant environmental impacts mainly due to the energy-intensive production of epichlorohydrin-derived glycerol. The total potential global warming for glycerol-based processes having intermediates allyl alcohol, lactic acid and acrolein, was $1.67 \times 10^5$, $1.80 \times 10^5$and $1.34 \times 10^5$ kg $CO_2$ eq. $FU^{-1}$ respectively, with epichlorohydrin-derived glycerol, whilst this value was $0.552 \times 10^5$ kg $CO_2$ eq. $FU^{-1}$ for the propylene-based process. However, changing the source of glycerol to purified crude glycerol from the biodiesel industry results in a considerable reduction of the environmental impact. A sensitivity analysis using the two-factor interaction (2FI) model showed that the global warming potential varies from $0.676 \times 10^5$ to $1.45 \times 10^5$ kg $CO_2$ eq. $FU^{-1}$ depending on the purification method used to purify crude glycerol and the glycerol content in the crude glycerol. It showed that a vacuum distillation purification process with 50% glycerol content had the least global warming values. This assessment provides insights into environmental performance trade-offs, guiding efforts towards more sustainable acrylic acid production and emphasizing the potential of using by-products from other industries to enhance the sustainability in chemical production processes.

## 1. Introduction

Acrylic acid is a highly valuable industrial chemical for the consumer product industry as it is used as a starting material for a variety of commodities. For example, acrylic polymers and co-polymers are currently used widely in a variety of industrial applications due to their chemical purity, stability, high heat resistance, sunlight resistance, excellent weathering, low-temperature performance, water resistance as well as hydrophobicity.[1] Acrylic acid along with its ester derivatives is used for superabsorbent polymer production, acrylic fibres, detergents, surface coatings, textiles, and adhesives, as well as in wastewater treatment and the leather industry.[2]

Valued at $14.6 billion in 2022, the global acrylic acid market is projected to grow at a Compound Annual Growth Rate (CAGR) of 4.8% between 2022 and 2032, potentially reaching $22.6 billion by the end of the period.[3] Currently, industries use fossil-fuel derived propene to produce acrylic acid by a two-step catalytic gas-phase oxidation. In the first step, propene is oxidized to acrolein over bismuth molybdate-based catalysts in the presence of a steam–air mixture at 300–370 °C and 1–2 bar. In the subsequent step, the acrolein is fed into a second reactor at 260–300 °C over MoVO-based catalysts to produce acrylic acid.[4] However, over the last decade, glycerol has attracted significant attention among researchers as a bio-based feedstock to produce acrylic acid since it is inevitably created in large quantities as a by-product in biodiesel manufacturing, whereby 100 kg of glycerol is created for each ton of biodiesel produced.[5]

Acrylic acid can be produced from glycerol *via* various intermediates such as allyl alcohol, lactic acid and acrolein as

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[a] *Department of Chemical Engineering, University of Manchester, Manchester, M13 9PL, UK. E-mail: carmine.dagostino@manchester.ac.uk*

[b] *Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali (DICAM), Alma Mater Studiorum – Università di Bologna, Via Terracini, 28, 40131 Bologna, Italy*

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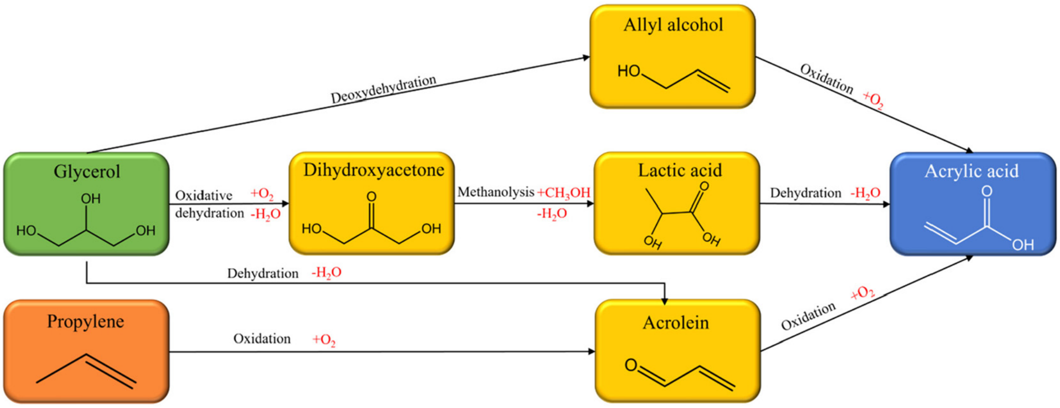

**Fig. 1** Different pathways for producing acrylic acid from glycerol and propylene.

shown in Fig. 1.[6] The most common method to produce acrylic acid from glycerol is *via* acrolein as the intermediate. This glycerol to acrolein to acrylic acid pathway has been more widely studied compared to other routes through intermediates like allyl alcohol or lactic acid. One main reason is that the catalysts and process chemistry required to convert acrolein into acrylic acid in the second reaction step have already been well developed and optimized.[7] Generally, the first step *i.e.* the dehydration of glycerol to acrolein proceeds on an acid catalyst, whereas MoVO-based catalysts can be used for the second step of acrolein oxidation to acrylic acid due to its known high yield from the propylene-based process.[8]

Another potential pathway for converting glycerol to acrylic acid is by having allyl alcohol as the intermediate. There are several methods to convert glycerol to allyl alcohol such as gas phase transfer hydrogenation,[9] rhenium complex-catalysed deoxydehydration[10] and formic acid mediated deoxydehydration.[11] However, due to low efficiency and high costs of the former two approaches, conversion *via* the non-catalytic deoxydehydration reaction using formic acid as a mediator is the best choice.[11] Moreover, this pathway requires the use of a single catalyst. Li and Zhang (2016)[11] reported that MoVWO catalysts exhibit high catalytic activity for allyl alcohol oxidation to acrylic acid in *ca.* 90% yield, along with excellent stability over a longer period (>60 hours) under the optimal reaction conditions.

Another promising pathway to produce acrylic acid from glycerol is *via* a lactic acid intermediate. However, before glycerol can be converted to lactic acid, it must first be transformed into either dihydroxyacetone or pyruvaldehyde.[12] The dihydroxyacetone intermediate is usually preferred as the catalyst available for the glycerol to dihydroxyacetone conversion and has higher yield and stability compared to that used for conversion of glycerol to pyruvaldehyde.[13] Subsequently, dihydroxyacetone can be converted to lactic acid using other catalysts followed by dehydration of lactic acid to acrylic acid. It is clear that conversion of glycerol to acrylic acid through the lactic acid intermediate is a rather long process involving three reactions and three different catalysts. However, this sequential transformation has the advantage of yielding multiple commercially valuable chemicals. *i.e.* dihydroxyacetone, lactic acid and acrylic acid.

In spite of the additional complexity and required catalysts for the lactic acid route, a life cycle assessment (LCA) performed by Brobbey *et al.*, (2023)[14] indicates that the lactic acid pathway could reduce carbon emissions for acrylic acid production when sugarcane A-molasses are used as the feedstock. Brobbey *et al.*, (2023)[14] carried out techno-economic and environmental analysis of acrylic acid production using sugarcane A-molasses as the feedstock. It was reported that the production of acrylic acid from sugarcane A-molasses had the lowest carbon emissions when the process went through a lactic acid intermediate rather than 3-hydroxypropionic acid. In another work, Petrescu *et al.* (2016)[15] evaluated the environmental impacts of the acrylic acid production process from propylene with different fuels for steam generation. The lowest value for global warming was reported when biomass was used to generate the steam required by the process. Lari *et al.* (2018)[16] carried out an early-stage life cycle assessment and techno-economics analysis of various products including acrylic acid, allyl alcohol and lactic acid derived from glycerol. It was reported that the overall global warming of lactic acid, acrylic acid, and allyl alcohol was 12.16, 4.8 and 28 kg $CO_2$ eq. per kg product produced. As the reactors within the process simulations were modelled assuming that the conversion of the reactants occurs with the same performance observed in laboratory-scale experiments and no reaction kinetics was considered, the margin of error for these global warming values would be high.

Although environmental analysis and viability analysis of acrylic acid production from several feedstocks have been conducted, no studies have compared the environmental feasibility of utilizing glycerol as a feedstock *via* different intermediates. Moreover, whilst there are many studies in the literature focusing on material development and reaction conditions to maximise the yield of acrylic acid from glycerol, none of these studies have carried out an in-depth LCA of the glycerol to acrylic acid process *via* different intermediates.

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Given that the purpose and goal of valorising biodiesel-derived glycerol into acrylic acid is to not only bring economic benefit, but to also improve the biodiesel industry's sustainable footprint, this research work aims to investigate and quantify the environmental impacts of different pathways to produce acrylic acid from glycerol. In particular, three types of processes to produce acrylic acid from glycerol are modelled and assessed: (1) glycerol to acrylic acid *via* allyl alcohol, (2) glycerol to acrylic acid *via* lactic acid and (3) glycerol to acrylic acid *via* acrolein. A fourth acrylic acid production process was simulated based on current production methods *i.e.* propylene to acrylic acid *via* acrolein for comparison with the glycerol-based processes.

## 2. Methodology

Sections 2.1 and 2.2 present the tools and methods employed in this research work. Section 2.2.1. discusses the goal and scope definition thereby defining system boundaries and the functional unit. Section 2.2.2. provides life-cycle inventory (LCI) primary data generated using Aspen plus simulations of four routes to acrylic acid namely – glycerol to acrylic acid *via* allyl alcohol (G-AA (*via* ALY)) and glycerol to acrylic acid *via* lactic acid (G-AA (*via* LAC)), glycerol to acrylic acid *via* acrolein (G-AA (*via* ACR)) and propylene to acrylic acid *via* acrolein (P-AA (*via* ACR)). Section 2.2.3. explains the unit operation of the four pathways in detail whereas Section 2.2.4. describes the methodology used in this study to perform the impact assessment.

### 2.1. Process design and simulations

Aspen Plus V12.1 was used to model the four process routes to acrylic acid (G-AA (*via* ALY), G-AA (*via* LAC), G-AA (*via* ACR) and P-AA (*via* ACR)). The NRTL-HOC package within Aspen software was used for performing the thermodynamic calculations for the G-AA (*via* ALY) and G-AA (*via* ACR) process whereas for the P-AA (*via* ACR) and G-AA (*via* LAC) process the UNIQUAC package was used. However, in the G-AA (*via* LAC) process, the thermodynamic calculations for the unit operations in stage one (glycerol to dihydroxyacetone) were performed using the SOLIDS package within the Aspen software.

The four processes were simulated assuming operation for 7920 hours/year and generating *ca.* 10000 kg $h^{-1}$ of acrylic acid (>99.5% wt.). Regarding raw materials, two types of glycerol were considered in the study, namely – (1) glycerol derived from epichlorohydrin and (2) glycerol derived from the biodiesel industry. However, the composition of crude glycerol from the biodiesel industry varies widely depending on the production process and feedstock used and generally contains impurities such as methanol, water, soap, fatty acid methyl esters (FAMEs), glycerides, free fatty acids (FFAs), ash and unseparated catalyst particles.[5] The processes associated with purification of crude glycerol are not modelled in this work but can be found elsewhere;[17–20] however, the environmental impacts associated with the purification processes are accounted for within this LCA.[21]

The reaction kinetics model used in the Aspen simulations for the reactors and reactive distillation columns are based on previous experimental studies and are given in Table 1.

### 2.2. LCA

This LCA study followed the ISO 14044, (2006)[28] methodology for estimating the environmental impacts of the four production pathways to acrylic acid. Fig. 2 shows the integration of different tools to estimate the potential environmental impacts associated with the four routes to acrylic acid production.

**2.2.1. Goal and scope definition.** The goal of this study is to perform the environmental impact assessment of four different production routes for acrylic acid to identify which is the most sustainable and environmentally friendly pathway. Specifically, the system boundaries, indicated by the red box in Fig. 3, encompass the collection of feedstocks, their transport to the plant, the acrylic acid production process, waste disposal, and storage of the final product. The transportation of feedstocks to the production plant and waste materials from the plant to waste management sites are also included in the analysis (denoted by 'T' in Fig. 3). The system inputs include the raw materials and energy required for acrylic acid production in the form of heat and electricity, while the system outputs comprise emissions, waste generated, and the functional unit amount of the product, *i.e.* acrylic acid. Given that this study focuses solely on acrylic acid production processes,

Table 1 Details about the reaction, kinetics and catalysts used in the reactors

| Reaction | Conversion pathway | Details in table (in the ESI†) | Ref. |
|---|---|---|---|
| Oxidation of allyl alcohol to acrylic acid using the MoVWO catalyst | Thermocatalytic conversion | Table S1† | 11 |
| Oxidative dehydration of glycerol to dihydroxyacetone using the carbon-based bismuth catalyst | Thermocatalytic conversion | Table S2† | 13 |
| Conversion of DHA to methyl lactate using H-USY zeolite | Thermocatalytic conversion | Table S3† | 22 |
| Hydrolysis of methyl lactate to lactic acid using D001 acidic cation-exchange resin | Reactive distillation | Table S4† | 23 |
| Dehydration of lactic acid to acrylic acid over K-exchanged ZSM-5 | Thermocatalytic conversion | Table S5† | 24 |
| Dehydration of glycerol to acrolein using alumina supported silicotungstic acid catalyst | Thermocatalytic conversion | Table S6† | 25 |
| Oxidation of acrolein to acrylic acid using molybdenum/vanadium mixed oxide | Thermocatalytic conversion | Table S7† | 26 |
| Oxidation of propylene to acrolein using the bismuth molybdate catalyst | Thermocatalytic conversion | Table S8† | 27 |
| Deoxydehydration of glycerol to allyl alcohol using formic acid | Non-catalysed acid mediator | — | 11 |

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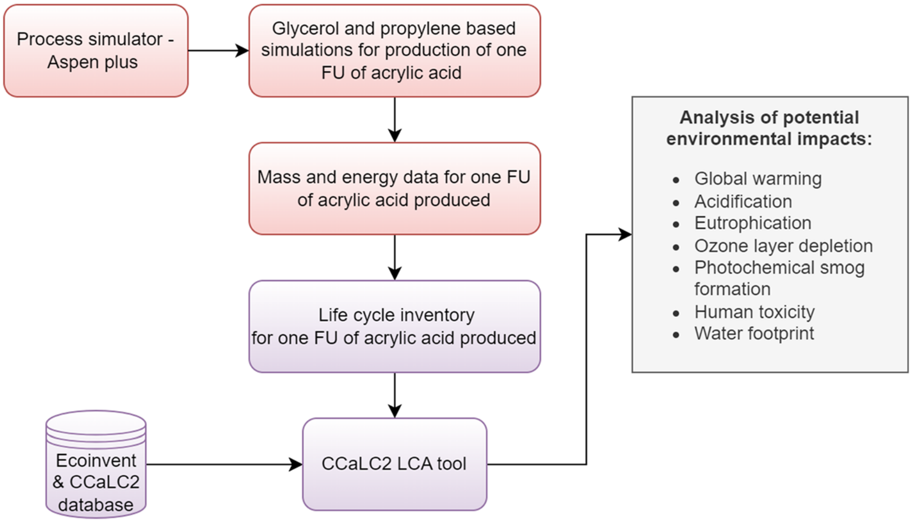

**Fig. 2** Integrated framework of the process simulation and LCA tool to estimate the potential environmental impacts associated with the four routes to acrylic acid production.

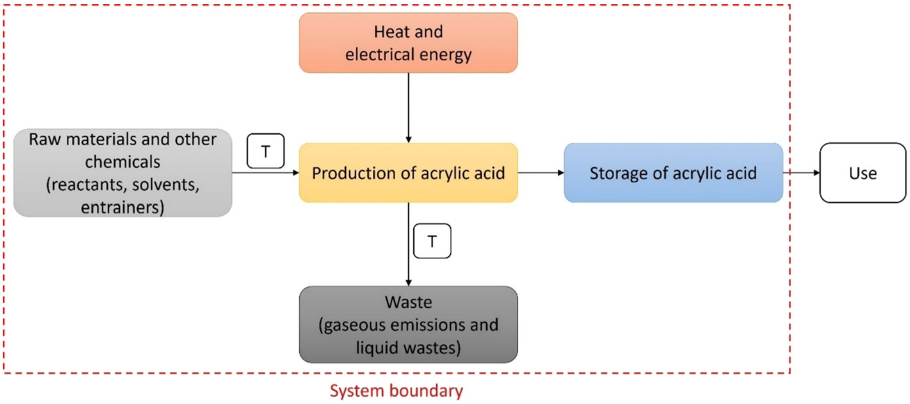

**Fig. 3** System boundary of the cradle-to-gate approach used for the four pathways to acrylic acid (T denotes transportation).

the 'use' and 're-use and/or recycle' aspects of the product have not been considered. Additionally, transport between the production and storage stages is excluded as it would be negligible relative to feedstock transportation impacts.

A functional unit of 10000 kg acrylic acid per hour was chosen to enable the comparison of the environmental impacts of different production routes on an equivalent output basis. This functional unit represents a practical industrial scale production level, providing reasonable environmental impact values per hour for comparison. The process feed flow rates were optimized in the simulations to give output equal to 10000 kg acrylic acid per hour for each production route, as listed in Tables S10–S13 (ESI†). For the sensitivity analysis, the glycerol feedstock was modelled as coming from three different purification processes,[21] representing realistic industrial sources.

To efficiently perform the LCA, the four processes – G-AA (*via* ALY), G-AA (*via* LAC), G-AA (*via* ACR), and P-AA (*via* ACR) were divided into simplified stages—two, three, two, and two stages respectively—as shown in the Aspen simulation diagrams in Fig. 4, 5, 6 and 7. This segmentation enables better comprehension while evaluating the environmental impacts related to different stages of the four acrylic acid production processes.

### 2.2.2. Inventory analysis

*2.2.2.1 Raw materials inventory.* Table 2 shows the inventory data for raw materials and their corresponding modelled materials within the Ecoinvent and $CCaCL_2$ database. 'glycerine from epichlorohydrin, at plant' was selected to represent the glycerol produced from hydrolysis of epichlorohydrin with caustic soda.[29] This allowed a better comparison of the potential environmental impacts when the source of the glycerol was changed to purified glycerol from the biodiesel industry. Formic acid in the G-AA (*via* ALY) process was represented by 'formic acid from methyl formate, at plant' as large-scale production of formic acid was done typically

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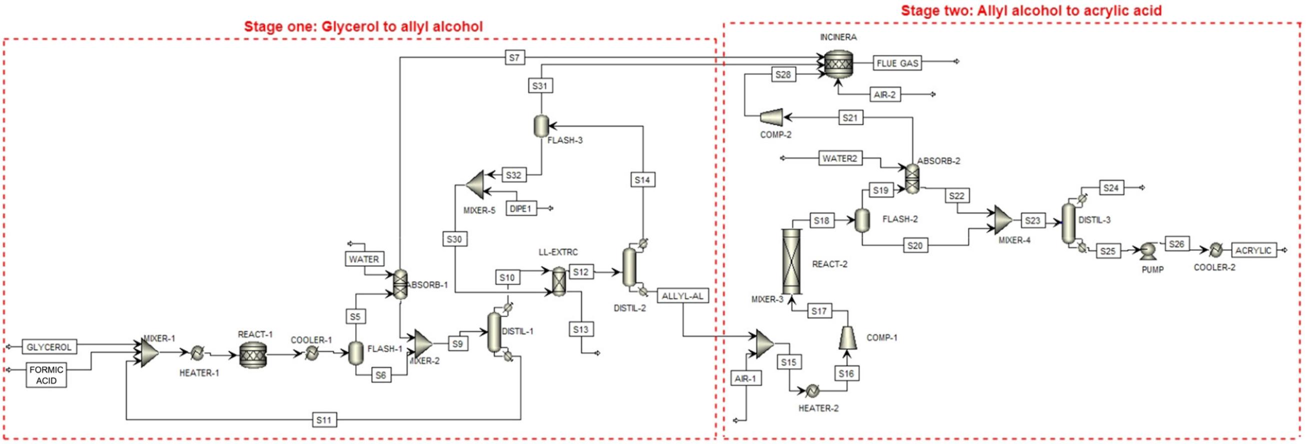

Fig. 4 Process simulation for glycerol to acrylic acid *via* allyl alcohol.

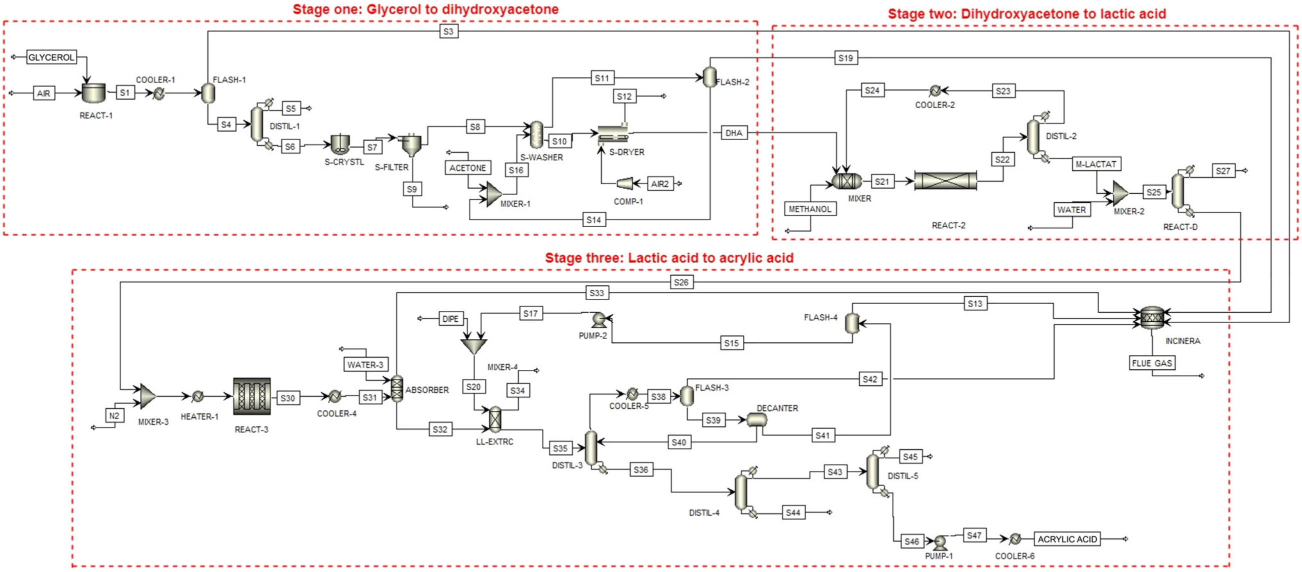

Fig. 5 Process simulation for glycerol to acrylic acid *via* lactic acid.

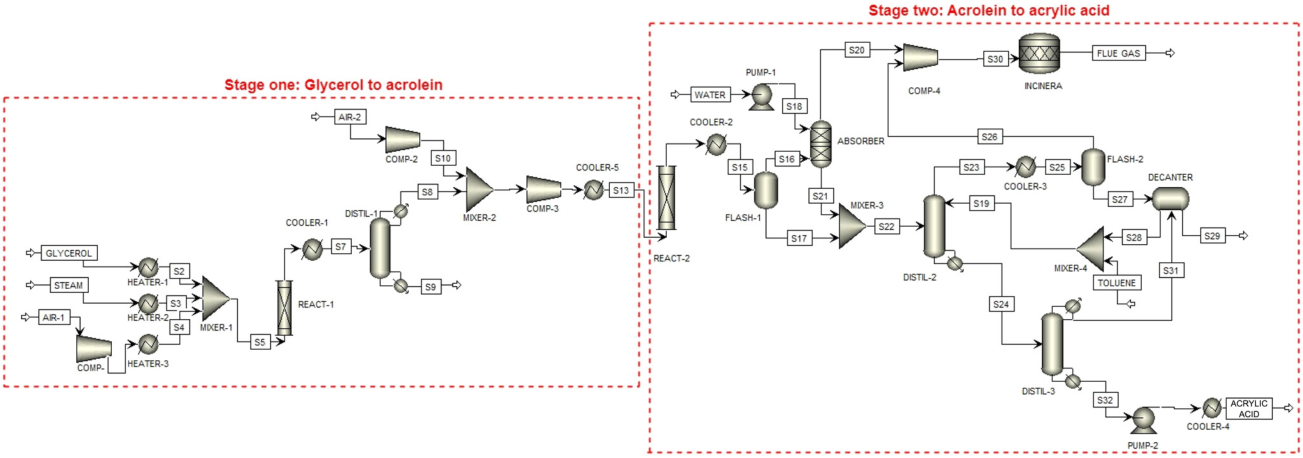

Fig. 6 Process simulation for glycerol to acrylic acid *via* acrolein.

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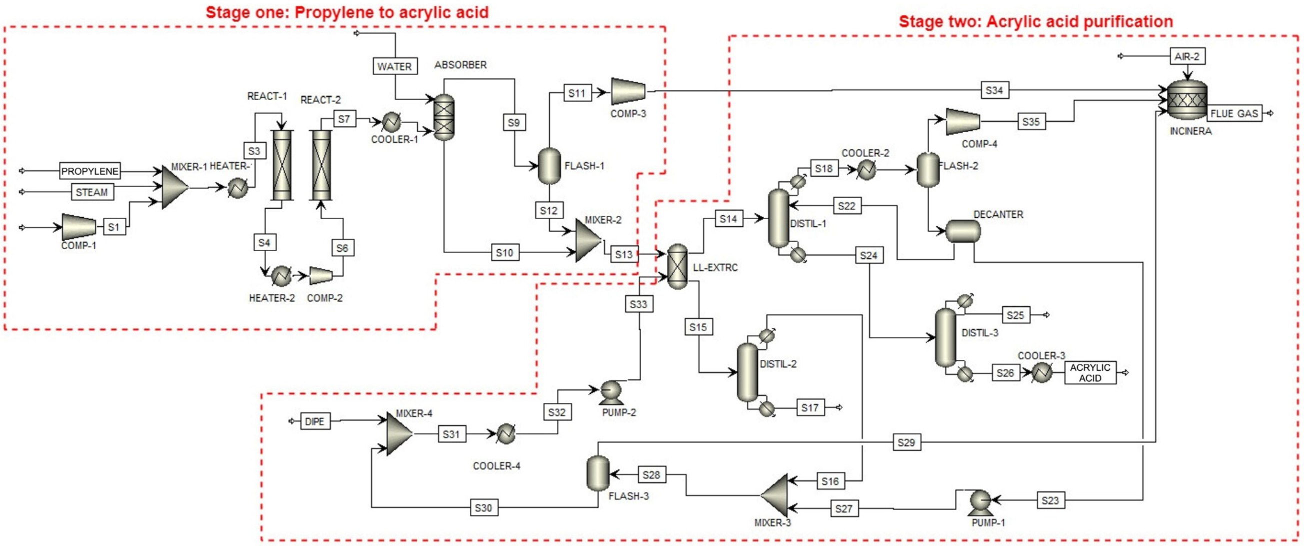

**Fig. 7** Process simulation for propylene to acrylic acid *via* acrolein.

**Table 2** Raw materials life-cycle inventory data associated with the four processes to produce acrylic acid

| Process name | Production stage | Raw material | Modelled CCaLC2 raw material | Amount (kg/FU) | Database |
|---|---|---|---|---|---|
| G-AA (*via* ALY) | Stage one | Glycerol | Glycerine, from epichlorohydrin, at plant | 17 339.99 | Ecoinvent |
| | | Formic acid | Formic acid, from methyl formate, at plant | 8666.16 | Ecoinvent |
| | | Diisopropyl ether | Diisopropyl ether, at plant | 3228.90 | CCaLC2 |
| G-AA (*via* LAC) | Stage one | Glycerol | Glycerine, from epichlorohydrin, at plant | 26 940.26 | Ecoinvent |
| | | Acetone | Acetone, at plant | 425.37 | Ecoinvent |
| | Stage two | Methanol | Methanol, from synthetic gas, at plant | 5062.66 | Ecoinvent |
| | Stage three | Nitrogen | Nitrogen, from cryogenic air separation | 22 410.78 | Ecoinvent |
| | | Diisopropyl ether | Diisopropyl ether, at plant | 644.72 | CCaLC2 |
| G-AA (*via* ACR) | Stage one | Glycerol | Glycerine, from epichlorohydrin, at plant | 20 160.78 | Ecoinvent |
| | | Steam | Steam, for chemical processes, at plant | 20 049.21 | Ecoinvent |
| | Stage two | Toluene | Toluene, liquid, at plant | 768.84 | Ecoinvent |
| P-AA (*via* ACR) | Stage one | Propylene | Propylene, at plant | 9758.91 | Ecoinvent |
| | | Steam | Steam, for chemical processes, at plant | 16 759.54 | Ecoinvent |
| | Stage two | Diisopropyl ether | Diisopropyl ether, at plant | 3283.12 | CCaLC2 |

through the hydrolysis of methyl formate. 'Methanol from synthetic gas, at plant' was chosen to represent the methanol used in the G-AA (*via* LAC) process as it refers to a full-methanol steam reforming process to obtain a 2.2 : 1 $H_2:CO$ ratio of the syngas for the sole production of methanol. 'Nitrogen from cryogenic air separation' was selected to represent the source of nitrogen as it is the common method of generating nitrogen from air. Other solvents such as acetone, toluene and diisopropyl ether are also present in the Ecoinvent and $CCaCL_2$ database and their equivalent modelled materials are shown in Table 2.

*2.2.2.2 Energy inventory.* Table 3 provides the life cycle inventory for energy, detailing the energy sources utilized in each stage of the four acrylic acid production processes as well as the quantities per functional unit. The energy required for the heat exchangers and reactors was sourced from the heat of 'steam-natural gas, UK' whereas the energy required for the pumps, compressors and the solid dryer was obtained from 'electricity, high voltage, production, UK, at grid'. For heat requirements of reboilers of distillation columns, 'natural gas burned in an atmospheric boiler' was the suitable choice for its source of energy.

*2.2.2.3 Transportation inventory.* Transportation of the raw material to the production stage as well as from the production to the waste management stage was denoted by 'T' as shown in Fig. 3. The location of the acrylic acid plant is significant for the LCA study, as the raw materials must be transported onto the site and the emissions associated with the transport will be included as part of the LCA. Stanlow, in the UK, was selected for the acrylic acid production plant as it has both the biodiesel industry[30] for sourcing glycerol and propylene refinery[31] for sourcing propylene. To simplify the LCA calculations of the environmental impact, the raw material storage facilities and waste management hubs are assumed to be located within 100 km of the acrylic acid production site. This radial constraint likely overestimates the real-world environmental impacts of the glycerol purification process. At the stated 240 tonnes per day output of acrylic acid based on the functional unit, a 40-tonne

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**Table 3** Energy consumption life-cycle inventory data associated with the four processes to produce acrylic acid

| Process name | Stage | Purpose | Energy type | Energy needed (MJ $h^{-1}$) | Database |
|---|---|---|---|---|---|
| G-AA (*via* ALY) | Stage one | Heat required for heat exchanger (HEATER-1) and reactor (REACT-1) | Steam – natural gas, UK | 227 790.29 | CCalC2 |
| | | Heat required for reboilers of the distillation columns (DISTIL-1 and DISTIL-2) | Natural gas, burned in boiler atmospheric burner non-modulating | 308 371.38 | Ecoinvent |
| | Stage two | Heat required for heat exchanger (HEATER-2) | Steam – natural gas, UK | 8177.52 | CCalC2 |
| | | Electricity required for pump (PUMP) and compressor (COMP-1) | Electricity, high voltage, production, UK, at grid | 7529.25 | Ecoinvent |
| | | Heat required for reboilers of the distillation columns (DISTIL-3) | Natural gas, burned in boiler atmospheric burner non-modulating | 57 793.79 | Ecoinvent |
| G-AA (*via* LAC) | Stage one | Electricity required for compressor (COMP-1) and solid dryer (S-DRYER) | Electricity, high voltage, production, UK, at grid | 311.84 | Ecoinvent |
| | | Heat required for reboiler of the distillation column (DISTIL-1) | Natural gas, burned in boiler atmospheric burner non-modulating | 94 638.12 | Ecoinvent |
| | | Heat required for flash drum (FLASH-2) | Steam – natural gas, UK | 33.56 | CCalC2 |
| | Stage two | Heat required for reboilers of the distillation columns (DISTIL-2 and REACT-D) | Natural gas, burned in boiler atmospheric burner non-modulating | 66 629.77 | Ecoinvent |
| | Stage three | Heat required for heat exchanger (HEATER-1) and reactor (REACT-3) | Steam – natural gas, UK | 99 548.83 | CCalC2 |
| | | Electricity required for pump (PUMP-1) | Electricity, high voltage, production, UK, at grid | 3.58 | Ecoinvent |
| | | Heat required for reboilers of the distillation columns (DISTIL-3, DISTIL-4 and DISTIL-5) | Natural gas, burned in boiler atmospheric burner non-modulating | 82 752.30 | Ecoinvent |
| G-AA (*via* ACR) | Stage one | Heat required for heat exchanger (HEATER-1, HEATER-2 and HEATER-3) | Steam – natural gas, UK | 54 276.45 | CCalC2 Energy |
| | | Electricity required for compressors (COMP-1, COMP-2 and COMP-3) | Electricity, high voltage, production, UK, at grid | 32 952.39 | Ecoinvent |
| | | Heat required for reboiler of the distillation column (DISTIL-1) | Natural gas, burned in boiler atmospheric burner non-modulating | 26 764.88 | Ecoinvent |
| | Stage two | Electricity required for pump (PUMP-1 and PUMP-2) and compressor (COMP-4) | Electricity, high voltage, production, UK, at grid | 8004.28 | Ecoinvent |
| | | Heat required for reboilers of the distillation columns (DISTIL-2 and DISTIL-3) | Natural gas, burned in boiler atmospheric burner non-modulating | 18 292.40 | Ecoinvent |
| P-AA (*via* ACR) | Stage one | Heat required for heat exchanger (HEATER-1 and HEATER-2) | Steam – natural gas, UK | 28 398.07 | CCalC2 energy |
| | | Electricity required for compressors (COMP-1 and COMP-2) | Electricity, high voltage, production, UK, at grid | 30 678.92 | Ecoinvent |
| | Stage two | Electricity required for pump (PUMP-1 and PUMP-2) and compressor (COMP-4) | Electricity, high voltage, production, UK, at grid | 213.00 | Ecoinvent |
| | | Heat required for reboilers of the distillation columns (DISTIL-1, DISTIL-2 and DISTIL-3) | Natural gas, burned in boiler atmospheric burner non-modulating | 49 686.83 | Ecoinvent |
| | | Heat required for flash drum (FLASH-2) | Steam – natural gas, UK | 2273.34 | CCalC2 energy |

truck is reasonably justified for transport given the raw material and waste quantities. Return trips with empty trucks are included in the life cycle assessment, as the same vehicle that delivers raw materials to the site must return. As per the CCaLC database, the modelled 40-tonne truck has a carbon footprint of $4.402 \times 10^{-5}$ kg $CO_2$ eq. per kg per km at an 85% utilization ratio. Further information on the transportation of raw materials and wastes is provided in Table S14 (ESI†).

*2.2.2.4 Storage and waste inventory.* Acrylic acid is a toxic, colourless, flammable, and highly corrosive liquid with a freezing point of 13 °C. It must be stored either in stainless steel or polyethylene containers. Since, acrylic acid is unstable, to prevent unwanted polymerization during the storage it is mixed with 200 ppm monomethyl ether of hydroquinone. Freezing of acrylic acid can lead to uneven distribution of the inhibitor, hence, it must be stored in a temperature range of 18 to 25 °C. Also, storing acrylic acid at high temperatures (>25 °C) for longer periods could lead to exothermic polymerization.[32] To meet the periodic market demand for acrylic acid, the storage capacity and refrigeration requirements for the acrylic acid product was determined to estimate the environmental impacts for including them in the LCA. Based on an annual production of 7920 hours, acrylic acid output in one-month corresponds to 660 hours of production. Storage containers and refrigeration units were sized to

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handle 60% of the maximum acrylic acid volume per month, using 10 $m^3$ units. Following Evans *et al.* (2014),[33] the total annual energy consumption (kW h per year) by electricity with the volume of refrigerated storage as shown in eqn (1).

$$\text{Energy usage per year (kW h per year)} = 480.28 \times (\text{volume of refrigeration unit})^{0.7864} \quad (1)$$

Table 4 shows waste streams from various units within the processes with their corresponding modelled CCaLC2 waste. Waste streams within the four processes having lower concentrations of organic impurities (<5%) in water were modelled as 'Wastewater treatment – industrial,1' within the CCaLC2 database whereas waste streams having slightly higher concentrations of organic impurities (<5% and >10%) in water as 'Wastewater treatment – industrial,3'. One of the waste streams was composed entirely of glyceraldehyde and due to the biodegradable nature of the compound, it was modelled as 'landfill – biodegradable waste' whereas another waste stream was sent to hazardous waste incineration facility as this waste stream also contained few toxic organic impurities (<10%) along with glyceraldehyde.

### 2.2.3. System description

#### *2.2.3.1. Glycerol to acrylic acid via allyl alcohol. Stage one: glycerol to allyl alcohol*

A systematic flow sheet combining all the unit operations for the G-AA (*via* ALY) process is illustrated in Fig. 4. The process started by heating the mixture of glycerol and formic acid to 235 °C before flowing it to the first reactor (REACT-1) where formic acid mediated the formation of allyl alcohol. The product stream (S3) containing allyl alcohol and unreacted reactants was cooled down using a heat exchanger (COOLER-1) to prevent the occurrence of any side reactions. The cooled product stream was then flashed out in the flash drum (FLASH-1) to remove any non-condensable gases as a stream from the top of flash drum. However, the vapour stream (S5) exiting the flash drum consisted of some allyl alcohol vapours, hence, it was flowed through the absorber (ABSORB-1) with water to generate aqueous solution of allyl alcohol (S8). In the next unit, the bottom liquid phase stream (S6) from the flash drum and the aqueous allyl alcohol solution was mixed together and sent to the distillation column (DISTIL-1) to separate the unreacted reactants from the product. Unreacted formic acid was the bottom product of the distillation column,

**Table 4** Waste management life-cycle inventory data associated with the four processes to produce acrylic acid

| Process name | Stage | Stream name | Modelled CCaLC2 waste | Amount ($kg\ FU^{-1}$) | Database |
|---|---|---|---|---|---|
| G-AA (*via* ALY) | Stage one | Waste stream (S13) from the absorber column (ABSORBER) containing mostly water with few organic impurities (<3%) | Wastewater treatment – industrial,1 | 11 177.32 | CCaLC waste |
| | Stage two | Flue gas from the incinerator (INCINERA) | User defined based on amount of $CO_2$ present | 108 364.95 | — |
| | | Waste stream (S24) from distillation column (DISTIL-3) containing mostly water with few organic impurities (<7%) | Wastewater treatment - industrial,3 | 4041.72 | CCaLC waste |
| G-AA (*via* LAC) | Stage one | Waste stream (S5) from distillation column (DISTIL-1) containing mostly water with few organic impurities (<1%) | Wastewater treatment – industrial,1 | 17 168.37 | CCaLC waste |
| | | Waste stream (S9) from the solid filter (S-FILTER) containing mostly glyceraldehyde (>99%) | Landfill – biodegradable waste | 1794.14 | CCaLC waste |
| | Stage three | Flue gas from the incinerator (INCINERA) | User defined based on the amount of $CO_2$ present | 118 257.66 | — |
| | | Waste stream (34) from the liquid–liquid extractor (LL_EXTRC) containing mostly water with few organic impurities (<1%) | Wastewater treatment – industrial,1 | 18 307.06 | CCaLC waste |
| | | Waste stream (S44) from the distillation column (DISTIL-4) containing mostly glyceraldehyde with few organic impurities (<10%) | Disposal, organic remains, 0% water, to hazardous waste incineration | 267.40 | Ecoinvent |
| | | Waste stream (S45) from distillation column (DISTIL-5) containing mostly water with few organic impurities (<1%) | Wastewater treatment – industrial,1 | 6440.69 | CCaLC waste |
| G-AA (*via* ACR) | Stage one | Waste stream (S9) from distillation column (DISTIL-1) containing mostly water with few organic impurities (<1%) | Wastewater treatment – industrial,1 | 32 558.65 | CCaLC waste |
| | Stage two | Flue gas from the incinerator (INCINERA) | User defined based on amount of $CO_2$ present | 56 715.40 | — |
| | | Waste stream (S29) from the decanter (DECANTER) containing mostly water with few organic impurities (<10%) | Wastewater treatment – industrial,3 | 2439.89 | CCaLC waste |
| P-AA (*via* ACR) | Stage one | Flue gas from the incinerator (INCINERA) | User defined based on amount of $CO_2$ present | 168 390.83 | — |
| | Stage two | Waste stream (S17) from distillation column (DISTIL-3) containing mostly water with few organic impurities (<1%) | Wastewater treatment – industrial,1 | 24 550.62 | CCaLC waste |

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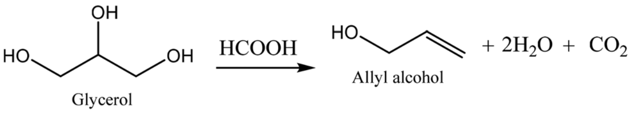
and this stream was recycled back to the mixer before the first reactor. The distillate (of column DISTIL-1) consisted of water and allyl alcohol. Given the proximity of the boiling points of these compounds (96.9 °C and 100 °C, respectively) as well as their tendency to form an azeotrope, liquid–liquid extraction has been utilized to facilitate effective separation. Hence, the liquid phase distillate was flowed into the liquid–liquid extractor (LL-EXTRC) and the DIPE organic solvent was used to extract allyl alcohol. The extract (S12) containing allyl alcohol and DIPE was sent to the second distillation column (DISTIL-2) for further purification. The top DIPE-rich distillate (S14) (of column DISTIL-2) was flashed out in a flash drum (FLASH-3) to remove non-condensable gases and the bottom liquid product of the flash was recycled back to the liquid–liquid extractor after mixing it with make up DIPE. The bottom product (ALLYL-AL) (of column DISTIL-2) containing pure allyl-alcohol was mixed with air, heated at 220 °C and sent to the oxidation reactor (REACT-2).

*Stage two: allyl alcohol to acrylic acid*

The oxidation reactor converted the allyl alcohol to acrylic acid. The product stream (S18) from the reactor was flashed out in a flash drum (FLASH-2) to remove any non-condensable gases. However, the gas stream (S19) of the flash drum also contained some acrylic acid vapours and hence, to recover these, the stream was flowed through the absorber (ABSORB-2). Water was flowed into the absorber from the top and aqueous acrylic acid solution (S20) was generated at the bottom of the absorber. The bottom liquid phase stream from the flash drum and aqueous acrylic acid solution was mixed and sent to the distillation column (DISTIL-3) for further purification to the required purity level. Waste gases (S31, S7 and S21) from the flash drum (FLASH-3) and absorber (ABSORB-1 and ABSORB-2) were sent to the incinerator to remove any toxic organic vapours and air was supplied to the incinerator for efficient combustion.



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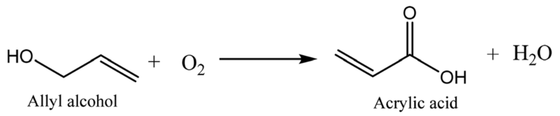

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#### 2.2.3.2. Glycerol to acrylic acid via lactic acid. Stage one: glycerol to dihydroxyacetone

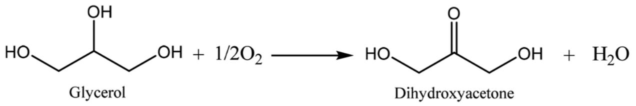
Fig. 5 provides the G-AA (*via* LAC) process flow sheet, linking together the different unit operations for each step of the overall process. The process starts by mixing glycerol with air in a batch reactor (REACT-1) to generate dihydroxyacetone (DHA). The non-condensable gases were removed from the product mixture using the flash drum (FLASH-1). The bottom liquid phase product of the flash drum was flowed through the distillation column (DISTIL-1) to separate DHA from the product mixture. In the next step, DHA was sent to the crystallizer (S-CRYSTL) to produce pure solid DHA crystals, which were then filtered in the solid filter (S-FILTER). The solid DHA crystals were washed using acetone in the washer (S-WASHER) and dried in the dryer (S-DRYER) using air operating at 50 °C to remove any residual acetone.

*Stage two: dihydroxyacetone to lactic acid*

In stage two, DHA crystals were dissolved with methanol and fed to the second reactor operating at 120 °C to produce methyl lactate. The product stream (S22) from the second reactor was flowed into the distillation column (DISTIL-2) to recover the unreacted methanol and separate the methyl lactate product. Methyl lactate was then mixed with water and fed to the reactive distillation column (REACT-D) for the hydrolysis reaction. The reactive distillation column converted methyl lactate into lactic acid. Following this, the lactic acid was flowed to the third reactor with nitrogen after heating it at 360 °C.

*Stage three: lactic acid to acrylic acid*

The third reactor (REACT-3) converted lactic acid into acrylic acid. The product mixture was then cooled down in a heat exchanger (COOLER-4) and sent to the absorber (ABSORBER) to remove the non-condensable gases and generate an aqueous solution of acrylic acid. The aqueous acrylic acid solution stream (S32) was flowed into the liquid–liquid extraction unit to extract acrylic acid from the water using the DIPE solvent. The extract stream (S35), comprised primarily of acrylic acid and the DIPE solvent, was flowed into the solvent recovery column (DISTIL-3) operating at 0.3 bar. The DIPE-rich distillate was flashed out into the flash drum (FLASH-3) to eliminate non-condensable gases. The bottom liquid stream of the flash drum was flowed to the decanter (DECANTER). The water separated from the decanter was returned to the solvent recovery column as external reflux. The second liquid stream from the decanter containing residual DIPE was flashed out again in the flash drum (FLASH-4) and recycled back to the liquid–liquid extractor with makeup DIPE. The bottom liquid product from the solvent recovery column was flowed through another distillation column (DISTIL-4) for glyceraldehyde removal, followed by water removal in the final distillation column (DISTIL-5) for the required purity level of acrylic acid.



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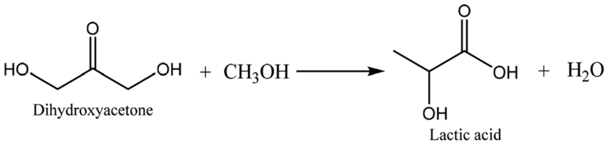

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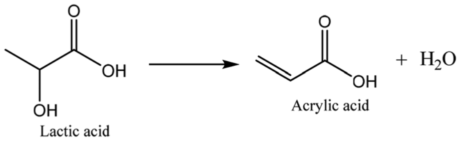

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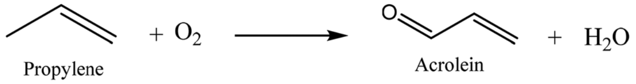
### *2.2.3.3. Glycerol to acrylic acid via acrolein. Stage one: glycerol to acrolein*

The glycerol to acrylic acid *via* acrolein process simulation was based on the process proposed by Sandid *et al.* (2023)[34] with operating conditions taken from Dimian *et al.* (2019)[35] with slight modifications in the simulations for optimizing the yield of the product. The flow sheet in Fig. 6 outlines the sequence of unit operations that are included in the process. The process started by pre-heating glycerol, steam and air to the desired temperature and flowing it through the first reactor (REACT-1) which converts glycerol to acrolein. The product stream from the first reactor was then passed through the distillation column (DISTIL-1) to remove heavy by-products such as hydroxyacetone and propionic acid. The acrolein-rich distillate stream (S8) was mixed with air, heated at 375 °C, and pressurised at 5 bar before flowing inside the second oxidation reactor (REACT-2).

#### *Stage two: acrolein to acrylic acid*

The oxidation reactor converted the acrolein into acrylic acid, however, the stream (S14) exiting the reactor was cooled immediately to prevent further by-product formation. The non-condensable gases were separated from the product stream using a flash drum (FLASH-1). However, the top stream (S16) also contained some residual vapours of acrylic acid along with the non-condensable gases. Hence, to recover the acrylic acid vapours, the top stream from the flash drum was sent to an absorber (ABSORBER) with water being flowed from the top and aqueous acrylic acid solution was recovered at the bottom of the absorber. The bottom liquid phase stream (S17) from the flash drum and aqueous acrylic acid solution (S21) were mixed and sent to the distillation column (DISTIL-2) for further purification. Azeotropic distillation was used due to the presence of water–acetic acid and water–acrylic acid azeotropes with toluene as an entrainer. The vapour distillate (S23) from the distillation column containing mostly the water and toluene was cooled and flashed out in the flash drum (FLASH-2). The bottom liquid phase product (S27) of the flash drum was flowed into the decanter (DECANTER) to separate and recycle the toluene back to the distillation column as external reflux. The bottom product (S24) of the distillation column was sent to the final distillation column (DISTIL-3) for further purification of the acrylic acid product to the required purity level. The distillate from the final distillation column consists mostly of toluene and water, therefore, it was sent to decanter for toluene-water separation. Vapour streams (S20 and S26) from the absorber and flash drum were combusted in the incinerator (INCINERA) to generate flue gas.



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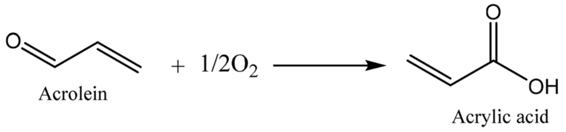

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### *2.2.3.4. Propylene to acrylic acid via acrolein. Stage one: propylene to acrylic acid*

The propylene to acrylic acid *via* acrolein process is also based on the simulation provided by Sandid *et al.* (2023)[34] with slight modifications in the operating conditions. Fig. 7 shows the unit step operations for the process. Propylene, air, and steam were mixed and heated at 366 °C before flowing it to the first fixed bed reactor (REACT-1). Propylene was oxidised to acrolein in the first reactor and the product stream was further pressurised at 6.9 bar and heated at 375 °C. The acrolein containing product stream was flowed into the second reactor (REACT-2) where acrolein was oxidised to acrylic acid. The product stream exiting the second reactor is flowed through the absorber unit (ABSORBER) where the cooling water stream reduces the temperature of the incoming vapours, produces an aqueous acrylic acid solution[36] and the non-condensable gases escape the column from the top. The top stream exiting the absorber also contains residual acrylic acid vapours along with the non-condensable gases which were then flashed out in the flash drum (FLASH-1). Finally, these streams, S10 and S12, were mixed in MIXER-2 and flowed into the extractor (LL_EXTRC).

#### *Stage two: acrylic acid purification*

Extraction of acrylic acid from its aqueous solution was carried out using the liquid–liquid extraction process with DIPE as the solvent.[35] The extract (STREAM S14) comprising mostly acrylic acid and the DIPE solvent is then flowed into the solvent recovery column (DISTIL-1) operating at 0.3 bar to produce a distillate abundant in DIPE. The distillate was flashed out in the flash drum (FLASH-2) to remove any non-condensable gases and the bottom liquid stream is sent to the decanter (DECANTER). Water separated from the DIPE solvent in the decanter was recycled back to the solvent recovery distillation column as an external reflux. The raffinate phase from the extractor also contained some remaining DIPE solvent and hence, it was flowed into a second distillation column (DISTIL-2) for purification. The DIPE-rich liquid distillate from the distillation column was mixed with the DIPE solvent coming from the decanter and finally recycled back to the liquid–liquid extractor with makeup DIPE. The bottom liquid product from the solvent recovery column containing mostly water and acrylic acid was sent to the final vacuum distillation column (DISTIL-3) operating at 0.1 bar for reaching the required purity level. Waste streams from flash drums (S34, S29 and S35) were incinerated in the incinerator (INCINERA)

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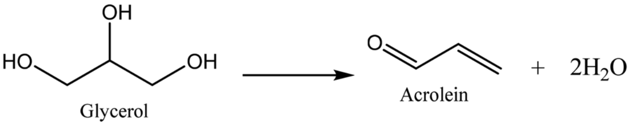
to generate flue gases and excess air stream was flowed into the incinerator to ensure complete combustion.



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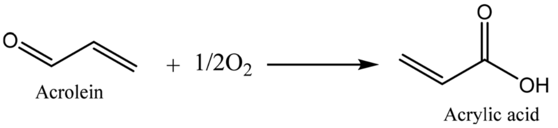

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**2.2.4. Impact assessment.** The CCaLC2 life cycle assessment (LCA) software,[37] developed at the University of Manchester (UK), was utilized to model the four acrylic acid production processes, and quantify environmental impacts based on the CML 2001 impact assessment methodology.[38] The life cycle impact assessment of this study focuses on damages to the natural environment and human health and the impacts analysed in this study include global warming (GW) measured in kg $CO_2$ eq., water footprint (WF) measured in $m^3$ $H_2O$ eq., acidification (AD) measured in kg $SO_2$ eq., eutrophication (EP) measured in kg $PO_4$ eq., ozone layer depletion (OLD) measured in kg R11 eq., photochemical smog (PCS) measured in kg $C_2H_4$ eq., and human toxicity (HT) measured in kg dichlorobenzene (DCB) eq. The description of the units of the impact categories used in this study are shown in Table 5.

## 3. Results and discussion

Different sections and stages were sequentially segregated to analyse the potential environmental impacts of the LCA for a clearer comparison across the four processes. Furthermore, a detailed examination of each stage of the LCA for all acrylic acid production processes allowed to pinpoint environmental 'hot spots' and identify areas having comparatively higher environmental impacts. Table 6 describes the potential environmental impacts of the four acrylic acid production processes.

### 3.1. Comparison of environmental impacts of glycerol-based and propylene-based acrylic acid production processes

The global warming (GW) of the LCA study for the 'cradle-to-gate' system, underlined the importance of selecting sustainable raw materials and clean energy sources for a given industrial process. Fig. 8 provides information about the specific contributions of the three sections to the four environmental impacts. The total global warming of the G-AA (*via* LAC) process was the highest followed by the G-AA (*via* ALY) and G-AA (*via* ACR) process, whereas the P-AA (*via* ACR) process has the overall lowest global warming impact. Keeping the GW value of the G-AA (*via* ACR) process as a reference, an increase of 25% and 34% in GW value is observed for the G-AA (*via* ALY) and G-AA (*via* LAC) processes. For the G-AA (*via* LAC) process, this was expected as there is an extra reaction involved in this process when converting glycerol to acrylic acid, thereby requiring an entire extra stage. Moreover, the amount

Table 5 Description of the impact categories used in this study[39–41]

| Impact category | Units | Description |
|---|---|---|
| Global warming | kg $CO_2$ eq. | Carbon dioxide equivalent ($CO_2$ eq.) is a standardized metric used for comparing global warming potentials of different greenhouse gases. It represents the carbon dioxide amount with an equivalent climate impact as a given quantity of a greenhouse gas. |
| Acidification | kg $SO_2$ eq. | Acidic gases such as sulphur dioxide ($SO_2$) react with water in the atmosphere to form "acid rain", a process known as acid deposition. When this rain falls, often there is a considerable distance from the original source of the gas, and it causes ecosystem impairment of varying degree, depending upon the nature of the landscape ecosystems. |
| Eutrophication | kg $PO_4$ eq. | Eutrophication is caused by the over-enrichment of water courses by nitrates and phosphates leading to the reduction of oxygen in water. Its occurrence can lead to the damage of ecosystems, increasing the mortality of aquatic fauna and flora and to loss of species dependent on low-nutrient environments. |
| Ozone layer depletion | kg R11 eq. | Ozone-depleting gases cause damage to stratospheric ozone or the "ozone layer". All chlorinated and brominated compounds that are stable enough to reach the stratosphere can have an effect. CFCs, halons and HCFCs are the major causes of ozone depletion. Damage to the ozone layer reduces its ability to prevent ultraviolet (UV) light entering the earth's atmosphere, increasing the amount of carcinogenic UVB light hitting the Earth's surface. |
| Photochemical Smog | kg $C_2H_4$ eq. | Ozone can be created in atmospheres containing nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the presence of sunlight. Low level ozone is implicated in impacts as diverse as crop damage and increased incidence of asthma and other respiratory issues. Damage to the ozone layer reduces its ability to prevent ultraviolet (UV) light entering the Earth's atmosphere, increasing the amount of carcinogenic UVB light hitting the Earth's surface. |
| Human toxicity | kg dichlorobenzene (DCB) eq. | The emission of some substances (such as heavy metals) can have impacts on human health. Assessments of toxicity are based on tolerable concentrations in air, water, air quality guidelines, tolerable daily intake and acceptable daily intake for human toxicity. |
| Water footprint | $m^3$ $H_2O$ eq. | Water footprint is an environmental indicator that measures the volume of fresh water used throughout the production process of a product whereas water stress is defined based on the ratio of freshwater withdrawals to renewable freshwater resources. |

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**Table 6** Potential environmental impacts of four acrylic acid production processes

| | Process | | | |
|---|---|---|---|---|
| Environmental impact | G-AA (*via* ALY) | G-AA (*via* LAC) | G-AA (*via* ACR) | P-AA (*via* ACR) |
| Global warming (kg $CO_2$ eq. $FU^{-1}$) | 167 393.76 | 179 631.05 | 133 981.22 | 55 181.66 |
| Acidification (kg $SO_2$ eq. $FU^{-1}$) | 406.21 | 553.87 | 411.01 | 79.60 |
| Eutrophication (kg $PO_4$ eq. $FU^{-1}$) | 188.42 | 263.00 | 198.58 | 17.03 |
| Ozone layer depletion (kg R11 eq. $FU^{-1}$) | $5.69\times10^{2}$ | $7.94\times10^{2}$ | $5.76\times10^{2}$ | $1.38\times10^{3}$ |
| Photochemical smog (kg $C_2H_4$ eq. $FU^{-1}$) | 31.82 | 30.53 | 20.84 | 9.27 |
| Human toxicity (kg DCB eq. $FU^{-1}$) | 61 263.74 | 84 973.27 | 62 996.71 | 4490.59 |
| Water footprint ($m^3$ $H_2O$ eq. $FU^{-1}$) | 283.34 | 220.23 | 121.46 | 67.91 |

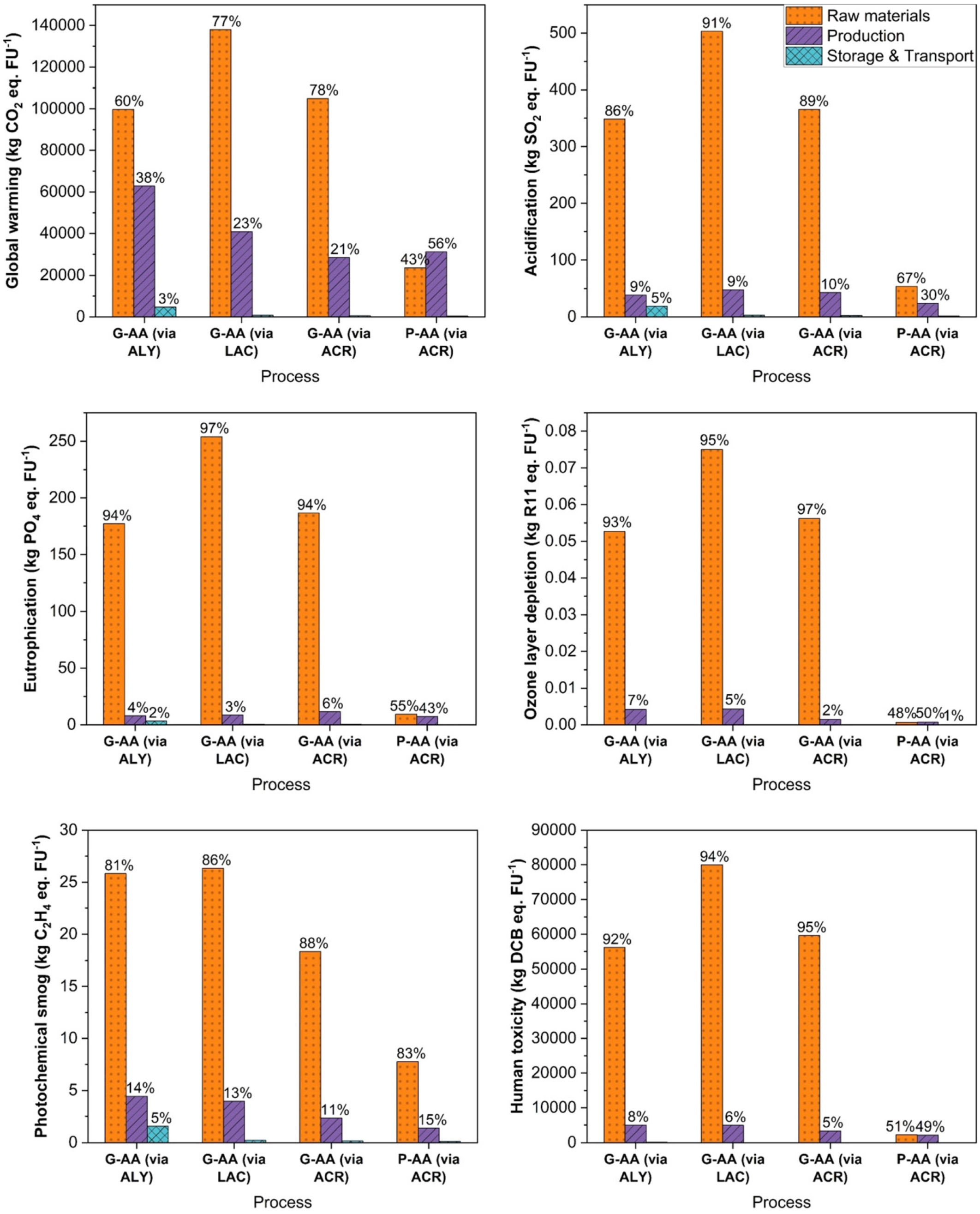

**Fig. 8** Potential environmental impacts for each process section across the four acrylic acid production.

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of glycerol used for the G-AA (*via* LAC) process was higher (55% higher compared to the G-AA (*via* ALY) process and 34% higher compared to G-AA (*via* ACR) process) as there are a total of four reactions involved in three stages of the process, namely – dehydrogenation of glycerol to dihydroxyacetone, conversion of dihydroxyacetone to methyl lactate, hydrolysis of methyl lactate to methanol and dehydration of lactic acid to acrylic acid. Hence, to obtain an equal amount of the product as the functional unit, a greater amount of initial reactant is required unless the yield is 100% for each of the four reactions involved, which is highly unlikely.

Among the three areas namely, raw materials, production and storage and transport, raw materials had the highest contributions to total environmental impacts among all the impact categories for glycerol-based processes. This was particularly due to the usage of glycerol derived from epichlorohydrin, which contributed to 51% of the total global warming for the G-AA (*via* ALY) process, whereas the contribution was 74% for G-AA (*via* LAC) and G-AA (*via* ACR) processes. Production of this glycerol involves chlorination of propylene to epichlorohydrin and glycerine dichlorohydrine at 510 °C, followed by hydrolysis of epichlorohydrin and glycerine dichlorohydrine to glycerol using caustic soda.[29] Sourcing the raw material from such an unsustainable and energy-intensive process will therefore add a high environmental impact to the process. The scenario was changed for the P-AA (*via* ACR) process where the production section contributed 56% to the overall GW compared to 43% contribution from the raw materials. As propylene was used instead of epichlorohydrin-derived glycerol, raw materials had a lower GW value for the P-AA (*via* ACR) process. This was mainly for two reasons, first the amount of propylene needed for this process was lower *i.e.* 9758.91 kg $FU^{-1}$, and second the GW of propylene for 1.50 kg $CO_2$ eq. per kg. Comparatively, the GW value of epichlorohydrin-derived glycerol was higher *i.e.* 4.93 kg $CO_2$ eq. per kg.

Following the raw materials section, the production section had the highest environmental impact over all the impact categories for the glycerol-based processes. The energy required by heat exchangers, pumps, compressors, and reboilers of the distillation columns in the form of heat and electricity contributed to 26% of the overall GW for the G-AA (*via* ALY) process. This GW by energy consumption, however, was less for the G-AA (*via* LAC) and G-AA (*via* ACR) processes with contributions of 13% and 10% respectively. It is worth noting that the production section of G-AA (*via* LAC) had a lower energy requirement compared to that of the G-AA (*via* ALY) process despite having six distillation columns and two heat exchangers. For the G-AA (*via* ACR) process, the GW added by the energy consumption was the lowest among the glycerol-based processes mainly due to the lower number of unit operations requiring heat and electricity. However, the energy consumption for the P-AA (*via* ACR) process was lower than the energy consumption for the G-AA (*via* ACR) process *i.e.*, 111 250.16 MJ $h^{-1}$ compared to 140 290.41 MJ $h^{-1}$. This is because both the oxidation of propylene to acrolein and dehydration of glycerol to acrolein occur in a gas phase reaction; however, since propylene is already in the gas phase, it does not need extra energy for vaporisation required for the case of glycerol. Conversely, the contribution of GW due to disposal of the waste generated was the highest for this process predominantly because of large quantities of the flue gas generated in this process.

As mentioned earlier, the glycerol-based processes having intermediates allyl-alcohol, lactic acid and acrolein were divided into two, three and two stages, respectively, and the propylene-based processes were divided into two stages. Fig. 9 provides information about the GW impacts of each stage of the four acrylic acid production processes emitted by three areas *i.e.*, raw materials, energy consumption and waste management. The treatment of wastes generated from the absorber and distillation column added 18 851.85 kg $CO_2$ eq. $FU^{-1}$ (11% contribution) to the total GW for the G-AA (*via* ALY) process. This value was significantly lower for G-AA (*via* LAC) and G-AA (*via* ACR) processes with a contribution of 2.5% (4490.65 kg $CO_2$ eq. $FU^{-1}$) and 7% (9400.94 kg $CO_2$ eq. $FU^{-1}$). It should be noted that the GW was added because the disposal of waste generated for the G-AA (*via* LAC) process was the lowest among the four processes as can be seen in Fig. 9. This was predominantly because of lower waste generated in this process. Moreover, the GW due to the amount of flue gas generated for this process was also the lowest and had a value of 2217.22 kg $CO_2$ eq. $FU^{-1}$. For the P-AA (*via* ACR) process, unlike the energy consumption scenario, the contribution to the overall GW value because of disposal waste generated was the highest predominantly due to large quantities of flue gas generated in this process.

For all the glycerol-based and propylene-based processes, water was majorly required by the heat exchangers and condensers of the distillation columns for cooling purposes as well as by absorbers to absorb vapours of the product and generate aqueous solutions. The water needed comprises the freshwater consumed per functional unit within the process and that needed to reintegrate losses of water due to evaporation, which were assumed to be approximately 7% of the cooling water.[42] Since, the location of the plant was Stanlow within the UK, the water stress index factor used for the estimation of the stress-weighted WF was 0.395. The total water usage of the G-AA (*via* ALY) process was equal to 718.60 $m^3$ water $FU^{-1}$ making a total water footprint (WF, stress-weighted) of 283.85 $m^3$ water $FU^{-1}$ (Table S15, ESI†). Stage one (glycerol to allyl alcohol) within the G-AA (*via* ALY) process contributed to 87.7% of the WF mostly due to the water required by the absorber (ABSORB-1) and the heat exchanger (COOLER-1), whereas the remaining contribution to WF was due to the second absorber (ABSORB-2) and the heat exchanger (COOLER-2) within the stage two. The G-AA (*via* LAC) process required 557.55 $m^3$ water $FU^{-1}$ for the cooling process, whereas 27.54 $m^3$ water $FU^{-1}$ as raw materials making the total water footprint of 231.11 $m^3$ water $FU^{-1}$. For the G-AA (*via* ACR) process, the production section required 307.98 $m^3$ water $FU^{-1}$ for the cooling process making the total water footprint (WF, stress-weighted) 121.65 $m^3$ water $FU^{-1}$.

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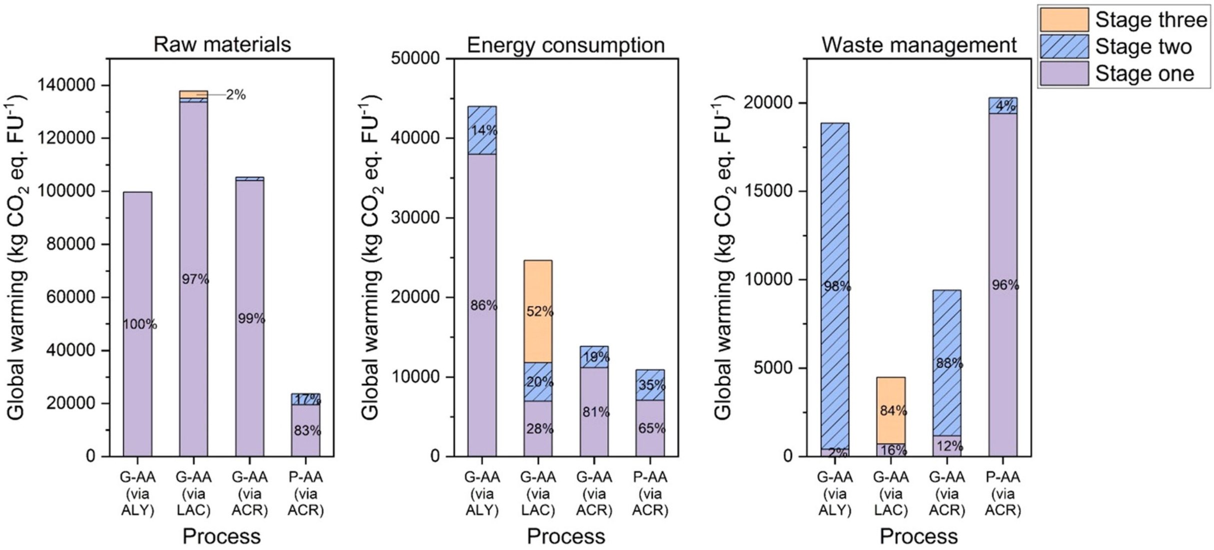

**Fig. 9** Contribution of raw materials, energy consumption and waste management to GW for the for acrylic acid production processes. For G-AA (*via* ALY) stage one and two denote glycerol to allyl alcohol and allyl alcohol to acrylic acid, respectively; for G-AA (*via* LAC) stage one, two and three denote glycerol to DHA, DHA to lactic acid, and lactic acid to acrylic acid, respectively; for G-AA (*via* ACR) stage one and two denote glycerol to acrolein and acrolein to acrylic acid, respectively; for P-AA (*via* ACR) stage one and two denotes propylene to acrolein and acrolein to acrylic acid, respectively.

Analysing the acidification and eutrophication for the G-AA (*via* ALY) process, it was observed that raw materials contributed to approximately 86% of the total acidification and 45% of the total eutrophication, mostly due to the usage of formic acid and glycerol required to produce allyl alcohol. In addition, raw materials, *i.e.*, diisopropyl ether, formic acid and glycerol, contributed to 93% of the total ozone layer depletion, 81% of the total photochemical smog, and 92% of the total human toxicity. For this process, human toxicity has a high value particularly due to the usage of formic acid as well as the usage of chlorine needed for glycerol production. For the G-AA (*via* LAC) process, 91% of the total AD and 97% of the total EP is contributed by the raw materials section, and most of it (>85%) is caused by the usage of glycerol derived from epichlorohydrin. In the case of OLD and HT environmental impacts, 95% of the total OLD and 94% of the total HT is contributed by the raw materials due to the usage of methanol and glycerol.

### 3.2. Comparison of environmental impacts for biodiesel-derived glycerol and epichlorohydrin-derived glycerol

A systematic examination of all unit operations, raw materials, energy consumption, and waste management methods enabled the identification of key processes substantially contributing to the environmental footprint. By pinpointing these environmental 'hot spots' and quantifying their impacts, targeted substitutions and process modifications could be evaluated to discern lower-impact alternatives. Glycerol derived from epichlorohydrin, being one of such hotspots, contributed to a large proportion of the environmental impacts for the glycerol-based processes as detailed above. Based on this, it can be deduced that sourcing sustainable bio-derived glycerol is important to reduce the overall environmental impacts. Since the biodiesel industry generates very large amounts of crude glycerol, it can used in glycerol-based processes to produce acrylic acid. It is known that crude glycerol contains significant amounts of impurities which can affect the performance of the reactors and the catalytic activities of catalysts used in the glycerol-based process making the purification process of the crude glycerol important. Among various purification processes, crude glycerol can be purified on a large scale by three processes—physicochemical treatment and membrane separation process (PMP), vacuum distillation process (VDP), and ion exchange process (IEP). LCA of glycerol purification processes has been recently reported, considering 1000 kg of purified glycerol as the functional unit.[21] Detailed data on the environmental impacts of purified glycerol by the three processes can be found in Table S16 (ESI†). The environmental impacts of this study have been used in the current work for estimating the overall environmental impacts of glycerol-based processes to obtain a complete overview. Fig. 10 shows a comparison of different environmental impacts after changing the source of glycerol from epichlorohydrin-derived to biodiesel-derived. It can be observed that large reductions can be made in all the impact categories, except for photochemical smog, when the source of glycerol is changed. Specifically, the overall GW reductions observed by the G-AA (*via* ALY) process by PMP, VDP, and IEP process are 15%, 33%, and 27%, respectively, whereas for G-AA (*via* LAC) and G-AA (*via* ACR) processes, the reductions were 22%, 48%, 40%, respectively. It is worth noting that G-AA (*via* LAC) and G-AA (*via* ACR) processes have more significant reductions for the VDP and IEP purification

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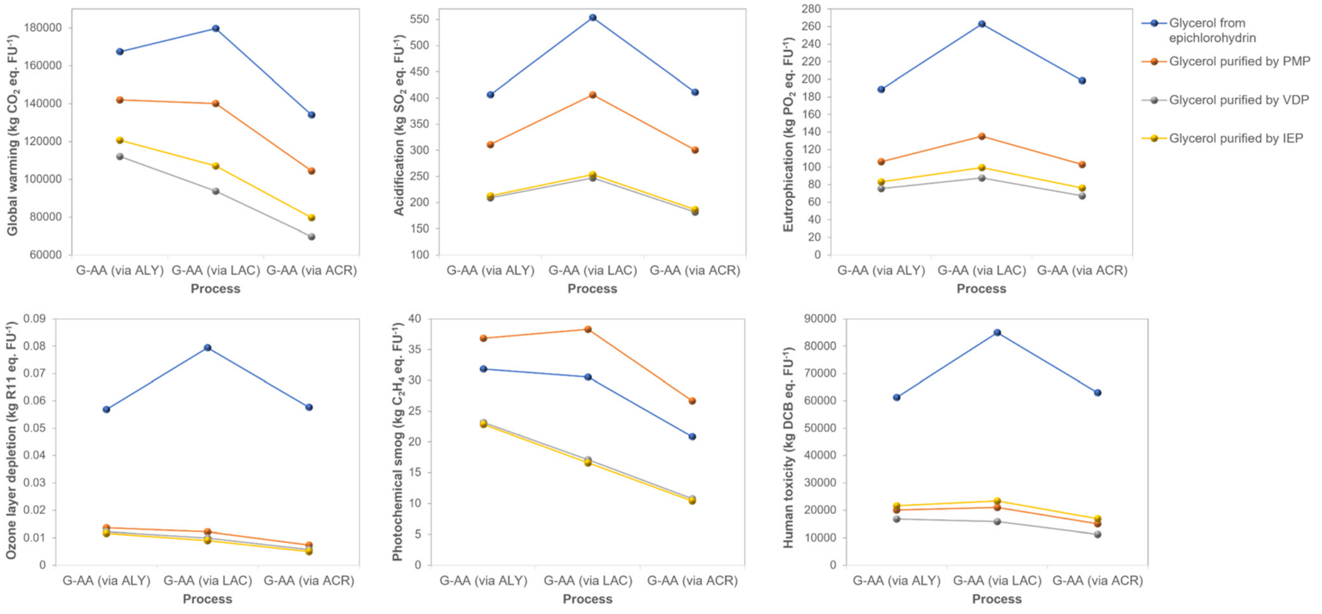

**Fig. 10** Comparison of environmental impacts between biodiesel derived glycerol and epichlorohydrin derived glycerol for the glycerol-based acrylic acid production processes.

processes compared to the G-AA (*via* ALY) process as the GW contribution due to the usage of glycerol to the total GW was higher as the amount of glycerol used in the former two processes was higher. Since crude glycerol purified by VDP and IEP has a significantly lower GW than the one purified by PMP, dramatic reductions were observed for these two cases.

Moreover, the reductions observed for the environmental impact categories such as OLD and HT subsequent to the change in the glycerol source were very significant. As can be seen from Fig. 10, more than 85% of the total OLD had been reduced for G-AA (*via* LAC) and G-AA (*via* ACR) processes whereas this value was more than 75% for the G-AA (*via* ALY) process. While comparing the HT, for G-AA (*via* LAC) and G-AA (*via* ACR) processes, more than 75% of the total HT has been reduced whereas there was a reduction of more than 65% for the G-AA (*via* ALY) process.

To contextualize the findings of this study, a thorough review of published global warming potential values for acrylic acid production from various sources was conducted as shown in Table 7. The values range from 1.2 kg $CO_2$ eq. per kg of acrylic acid for lignocellulose-based production[43] to 5.6 kg $CO_2$ eq. for sugar beet-based production.[44] Notably, the Ecoinvent database reports a value of 2.3 kg $CO_2$ eq. for conventional acrylic acid production. The variations observed across these studies can be attributed to differences in feedstock, production processes, and assessment methodologies. Our approach, utilizing Aspen simulation and specific catalyst kinetics for every reactor, provides a more detailed, process-oriented assessment compared to some broader database values. This comparison underscores the importance of considering feedstock choice and process optimizations in sustainable acrylic acid production.

### 3.3. Sensitivity analysis

The source of glycerol used in each of the glycerol-based processes was identified as the most significant contributor (or 'hotspot') to all the environmental impacts analysed in this study. Comparing various sources of glycerol revealed that

**Table 7** Comparative global warming potential of acrylic acid production using various sources and processes from the literature

| Source | Global warming potential (kg $CO_2$ per kg of acrylic acid) | Ref. |
|---|---|---|
| Acrylic acid from corn | 2.0 | 43 |
| Acrylic acid from lignocellulose | 1.2 | 43 |
| Acrylic acid from sugar beet | 5.6 | 44 |
| Acrylic acid, at plant | 2.3 | 45 |
| Acrylic acid from sugarcane A-molasses *via* lactic acid | 4.4 | 14 |
| Acrylic acid from sugarcane A-molasses *via* 3-hydroxypropionic acid | 4.8 | 14 |
| Acrylic acid from sugarcane A-molasses *via* glycerol | 5.3 | 14 |
| Acrylic acid from propylene using different fuels for steam generation | 1.1–5.5 | 15 |
| Acrylic acid from glycerol using integrated biorefinery | 4.8 | 16 |
| Acrylic acid from glycerol *via* different intermediates | 6.76–14.5 | This work |

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different sources can lead to a large difference in the overall GW. Additionally, it also revealed that crude glycerol purified by different types of purification processes can lead to different GW values within a given glycerol-based process as can be seen in Fig. 10. Moreover, the initial composition of crude glycerol can vary greatly depending on the feedstock used in the biodiesel industry as well as the process type. Therefore, the purification process and the initial crude glycerol compositions with 30%, 40%, and 50% glycerol content were selected as factors to be assessed for this sensitivity analysis. Details about the different purification processes and the initial composition of crude glycerol used in the simulations can be found in Table S17 (ESI†).

The factorial method, namely the 2FI model, has been used in this sensitivity analysis, whereby this type of experimental design approach for sensitivity analysis involves systematically varying input factors across multiple levels to examine their influence on output variables. By manipulating factors at different levels, it can be identified which factors have the greatest impact on the outcomes of interest. This method allows to investigate the influence of input factors and helps prioritize such factors for further study or optimization. Through factorial experiments, sensitivity analysis provides valuable insights into the relative importance of different factors and their combined effects on the system performance, aiding decision-making and process improvement in various fields such as engineering, economics, and environmental science.

To find a potential relationship between the three variables *i.e.*, the crude glycerol composition, purification process type, and global warming, 2D plots with response as GW were created using the two parameters, *i.e.*, the crude glycerol composition and the purification process. Fig. 11 shows the sensitivity analysis of GW based on different crude glycerol purification processes and the composition of crude glycerol for the three glycerol-based processes. The results of the sensitivity analysis are also given in Table S18 within the ESI.† It can be seen that the VDP purification process had the lowest GW over all three glycerol-based processes. Moreover, the GW value increased when the percentage of glycerol in crude glycerol decreased *i.e.*, crude glycerol having 50% glycerol content had the lowest GW. It can also be observed from Fig. 11 that for G-AA (*via* LAC) and G-AA (*via* ACR) processes, there is a large reduction in global warming when the crude glycerol purification process shifts from PMP to IEP and IEP to VDP. This trend is not seen in G-AA (*via* ALY) mostly because the amount of glycerol used in the former too process was considerably larger than the latter process. Moving across the glycerol content from 50% to 30% for the three purification processes, there is a linear increase in global warming for PMP and VDP. However, a spike is observed in the IEP process while moving from 50% to 30% suggesting that this process requires comparatively more energy and raw materials while treating crude glycerol with a lower glycerol content. The 2FI model factorial method also provided the optimized conditions for the lowest global warming which came out to be 50% glycerol with the VDP purification method for all the glycerol-based processes. The extra details about desirability and prediction values for obtaining the optimal conditions are given in Fig. S1 (ESI†).

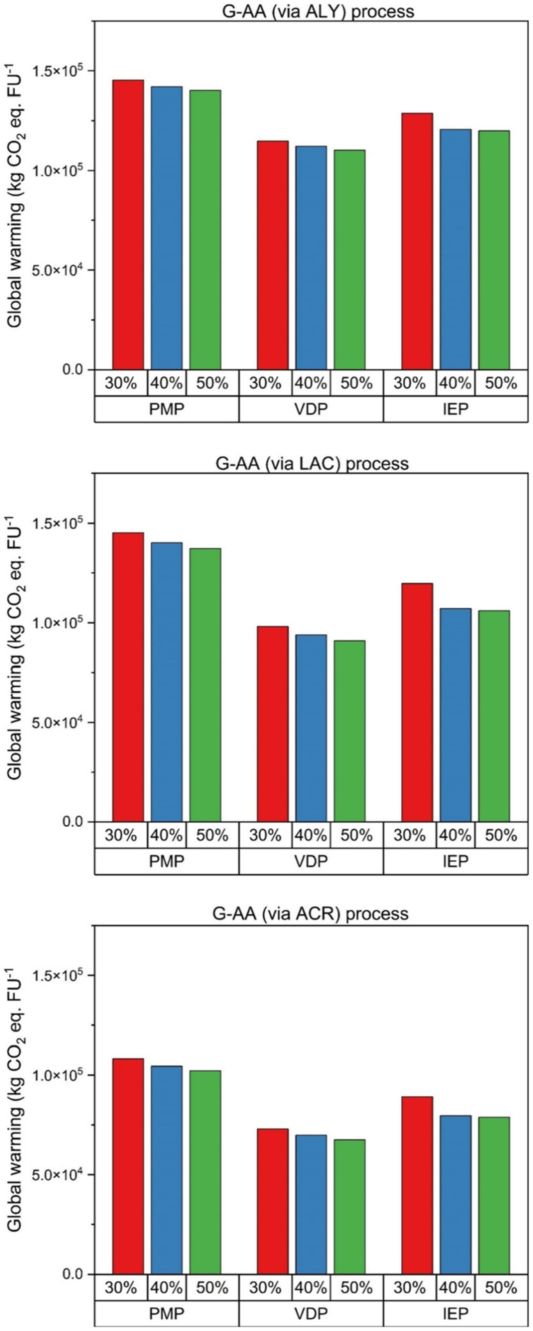

**Fig. 11** Sensitivity analysis of two parameters (purification processes and glycerol content) on global warming for G-AA (*via* ALY) (top), G-AA (*via* LAC) (middle) and G-AA (*via* ACR) (bottom) processes.

## 4. Limitations of the study

Environmental impacts vary significantly with the source of raw materials, particularly glycerol in this case. Data collection

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could be improved by conducting an LCA on the actual biodiesel production process from which the glycerol is derived. Given the substantial amount of glycerol used in all glycerol-based processes, this would enhance the accuracy of environmental impact results for the acrylic acid production process. Environmental impacts associated with waste disposal methods can also vary considerably depending on the exact composition of the waste stream and the techniques used for treatment. For all the acrylic acid production processes, the quantity of energy required in the form of heat and electricity was obtained from simulations. However, these quantities can fluctuate due to factors such as ambient temperature at the plant location, causing corresponding variations in heat loss. In the current study of four acrylic acid production processes, the transport distance of raw materials from the warehouse to the purification refinery and waste materials from the refinery to the waste management facility was assumed to be 100 km, which may differ in practice. Furthermore, this study involves eight different types of catalysts, presenting a challenge in terms of comprehensive data availability for their environmental impacts. An LCA of these catalysts could be undertaken to provide a more complete environmental assessment of the entire process.

## 5. Conclusions and prospects

The LCA study reported in this work compares the environmental impacts of four different routes to acrylic acids, namely glycerol to acrylic acid *via* allyl alcohol, glycerol to acrylic acid *via* lactic acid, glycerol to acrylic acid *via* acrolein, and propylene to acrylic acid *via* acrolein, within a cradle-to-gate scope. The aim of the study was to assess different routes to quantify the environmental impact of producing acrylic acid. Seven different types of environmental impacts, global warming, water footprint, acidification, eutrophication, ozone layer depletion, photochemical smog, and human toxicity, were analysed. Based on the functional unit and individual values, the most significant environmental impacts for all purification processes were overall global warming, acidification, human toxicity, and water footprint. For all the seven impacts that were reported, the raw materials were found to be the main contributor, followed by the production section whereas the storage and transport section had the minimum contribution for all seven impacts.

Global warming values for glycerol sourced from epichlorohydrin were in the following order: P-AA (*via* ACR) (55 181.66 kg $CO_2$ eq. $FU^{-1}$) < G-AA (*via* ACR) process (133 981.22 kg $CO_2$ eq. $FU^{-1}$) < G-AA (*via* ALY) process (167 393.76 kg $CO_2$ eq. $FU^{-1}$) < G-AA (*via* LAC) process (179 631.05 kg $CO_2$ eq. $FU^{-1}$). The most important conclusion for this LCA study is that the raw materials have the largest influence over the environmental impacts of the glycerol-based processes. Generally, fossil-fuel based pathways are considered to be unsustainable processes but for this study the propylene-based process has an overall lower GW value compared to glycerol-based processes. However, the glycerol used in these processes was derived from epichlorohydrin, which is produced through an unsustainable and energy-intensive process as it requires crude oil-based propylene and high-temperature reactions.[29] Moreover, the number of catalysts used by the glycerol-based processes having intermediates allyl-alcohol, lactic acid and acrolein were one, four, and two, respectively, while two catalysts were used for the propylene-based process. Quantifying the environmental impact of catalysts was out of the scope of this study. However, the different production methods for acrylic acid use varying types and amounts of catalysts. If the information about the environmental effects of these catalysts and the regenerative processes of these catalysts were included in this study for each process, it would give a clearer picture. This additional data could help choose the most environmentally sustainable process to produce acrylic acid.

After changing the source of glycerol from epichlorohydrin to purified glycerol from the biodiesel industry, remarkable reductions can be seen in the values of all environmental impacts for all the glycerol-based processes. It was also observed that the VDP process used to purify crude glycerol resulted in the highest reduction of global warming followed by IEP and PMP. A sensitivity analysis was done for the glycerol-based processes by assessing two key factors, *i.e.* the purification method used to purify glycerol and the % glycerol content in the crude glycerol. It was obvious that as the % glycerol content increased for a purification process, global warming decreased. This is because crude glycerol having higher glycerol content would require less raw materials, lower energy requirements as well as would generate less waste.

Finally, deciding on an acrylic acid production process merely on environmental impacts is inappropriate as economic factors also play a vital role. The intermediates generated during the process such as dihydroxyacetone, allyl alcohol, lactic acid, and glyceraldehyde also have a large demand in the market. The best approach would be to perform process intensification thereby using a combination of various processes within the same refinery to produce several products to satisfy the market demand. Overall, this study provides important insights into the environmental burdens of different acrylic acid producing processes, which can help design and select greener acrylic acid production processes with reduced waste, less energy consumption, and lower carbon emissions.

## Abbreviations

| | |
|---|---|
| CCaLC | Carbon calculations over the life cycle of industrial activities |
| CAGR | Compound annual growth rate |
| UNIQUAC | Universal quasi-chemical model |
| NRTL-HOC | Non-random two liquid – Hayden-O'Connell model |
| ACR | Acrolein |
| AA | Acrylic acid |

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| | |
|---|---|
| LAC | Lactic acid |
| DIPE | Diisopropyl ether |
| DHA | Dihydroxyacetone |
| GW | Global warming |
| AD | Acidification |
| EP | Eutrophication |
| OLD | Ozone layer depletion |
| PCS | Photochemical smog |
| HT | Human toxicity |
| WF | Water footprint |
| PMP | Physicochemical and membrane purification |
| IEP | Ion exchange purification |
| VD | Vacuum distillation purification |

## Author contributions

Yash Bansod: conceptualization, data curation, formal analysis, and writing – original draft. Prashant Pawanipagar: formal analysis and writing – review & editing. Kamran Ghasemzadeh: formal analysis and writing – review & editing. Carmine D'Agostino: funding acquisition, investigation, supervision, and writing – review & editing.

## Data availability

The data that support the findings of this study are available within the article and the ESI.†

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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