



Evaluating the environmental impact of crude glycerol purification derived from biodiesel production: A comparative life cycle assessment study

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ABSTRACT

In recent decades, surplus crude glycerol has been generated in large amounts as a waste product of biodiesel production, leading to bottlenecks in the supply chain of the biodiesel industry. This waste glycerol represents an important potential renewable feedstock and platform chemical; however, its purification is often needed for further processing. Advancements towards glycerol purification are being made using sustainable purification techniques aimed at improving the biodiesel industry's environmental footprint. Many studies focussing on various techniques to purify glycerol can be found in the literature; however, very few studies to evaluate the environmental impacts of the purification processes have been reported. This paper provides a critical investigation on the cradle-to-gate life cycle assessment (LCA) of three different processes for purifying crude glycerol, namely, physicochemical treatment and membrane purification (PMP) processes, vacuum distillation purification (VDP) processes and ion exchange purification (IEP) processes having a functional unit (FU) of 1000 kg of purified glycerol. These purification processes were modelled using Aspen plus software v12.1 in combination with Super Pro Designer v13. CCaLC2 (Carbon Calculations over the Life Cycle of Industrial Activities) was used to measure the environmental impacts associated with each process. By following the ISO 14044:2006 methodology and utilising the CCaLC2 tool, seven different types of potential environmental impacts have been investigated, which include carbon footprint, water footprint, acidification, eutrophication, ozone layer depletion, photochemical smog and human toxicity. Sensitivity analysis of the LCA was carried out using the response surface method (RSM) to determine the most effective parameter within the LCA. The total carbon footprint of the PMP, VDP and IEP processes are 3466.82, 1745.72 and 2239.71 kg CO₂ eq. FU⁻¹ respectively. The LCA study determined that waste generated as a result of crude glycerol impurities from the three processes had one of the highest environmental impacts on the overall process. For the PMP and IEP processes, the raw materials used in the physicochemical treatment also contribute significantly to the carbon footprint and other environmental impacts. Lastly, aspects concerning the environmental impacts from the PMP glycerol purification process have been addressed by analysing the raw materials from different sources accompanied by altered waste disposal methods (i.e. the incineration of generated wastes as opposed to landfilling) in an attempt to reduce the overall environmental impacts. For the PMP process, which has the highest carbon footprint, usage of differently sourced raw materials and altered waste disposal treatments resulted in 39% reduction in total carbon footprint and 54% reduction in the total ozone layer depletion. Sensitivity analysis of the LCA shows that the glycerol content within the crude glycerol was the most significant parameter.

1. Introduction

Due to a substantial increase in population and booming economic development over the last few decades, the world is facing the dilemma

of global warming and, consequently, climate change. These environmental concerns mainly arise due to the excessive use of fossil fuels, leading society to shift towards more sustainable fuels such as biofuels. Biodiesel is a biofuel with huge potential to replace traditional fossil

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fuels since it is made from renewable sources such as animal fats, vegetable oil or used cooking oil. Moreover, biodiesel is biodegradable and non-toxic with reduced greenhouse gas emissions when compared to traditional fossil fuel derived diesel. As biodiesel can be used with existing diesel engines and infrastructure and numerous countries can produce it locally, global biodiesel production has increased tremendously (Brahma et al., 2022). Globally, around 56 billion liters of biodiesel was produced in 2022 alone and its production is predicted to increase around 7% over the next decade (OECD-FAO Agricultural Outlook 2022–2031, 2022). As such, the overall sustainability of biodiesel production must be thoroughly investigated.

Crude glycerol is a main by-product of biodiesel production. Indeed, approximately 10 kg of crude glycerol is generated for every 100 kg of biodiesel produced (Attarbach et al., 2023). Therefore, large increases in biodiesel production will result in the generation of substantially large amounts of waste glycerol. Due to this, there is much research interest based around the valorization of waste glycerol, which would otherwise be incinerated on site (Pagliaro, 2017). For instance, Adánuez-Rubio et al. (2021) demonstrated chemical looping reforming of glycerol to produce highly pure syngas using Al_2O_3 supported NiO oxygen carriers. Apart from traditional thermal conversion of glycerol, Abubakar et al. (2023) and Lima et al. (2022) also showed that glycerol can be converted to numerous products such as ethanol, lactic acid, acrolein, and 1,3-propanediol by biochemical, photochemical, and electrochemical routes whereas Sun et al. (2017), in their review, focused mainly on different catalytic technologies that can be utilized to convert glycerol to acrylic acid. The above studies focused on technical grade glycerol; however, Li et al. (2014) and Gama et al. (2016) used unrefined crude glycerol to produce bio-polyols for polyurethane polymer.

The composition of crude glycerol obtained as a by-product of biodiesel production is wildly inconsistent and varies widely depending on the production process and feedstock used. Of the three-biodiesel producing processes, namely; transesterification, saponification, and hydrolysis, almost all biodiesel produced globally is produced via the transesterification process (Tan et al., 2013). Even within the transesterification process, compositions of crude glycerol can vary widely depending upon the type of catalyst used, the process efficiency, impurities contained within the feedstock and the efficiency of recovery of biodiesel and solvents from the reaction mixture. For example, crude glycerol obtained from first-generation biodiesel which uses fresh cooking oil as feed has a relatively high glycerol content when compared to crude glycerol obtained from second generation biodiesel which uses waste cooking oil as the feed (Nabgan et al., 2022). In the compositional analysis study of crude glycerol by Hu et al. (2012), it was shown that the glycerol percentage in five different samples of crude glycerol varied from 23% to 63%, and the percentage of other impurities within the samples also had considerable differences in their values. Moreover, crude glycerol has a low economic value due to the presence of relatively large amounts of impurities such as methanol, water, soap, fatty acid methyl esters (FAMES), glycerides, free fatty acids (FFAs), ash and unseparated catalyst particles (Lopes et al., 2019). To avoid glycerol becoming a financial and environmental liability for the biodiesel industry, purification and valorization of glycerol is of great interest in both the academic and industrial sectors.

Currently, three promising advanced purification technologies have attracted the most interest - vacuum distillation, ion exchange treatment and membrane separation (Ardi et al., 2015). Detailed information about each of the purification technology including the advantages and disadvantages is given in the Supplementary Information (Page 2).

There are many studies in the literature employing various techniques to purify crude glycerol such as activated carbon-based adsorption (Barbosa et al., 2022), membrane separation (Chol et al., 2018), ion exchange treatment (Lopes et al., 2019), vacuum distillation (Pitt et al., 2019), but none of these studies have evaluated the crude glycerol purification processes and the environmental performance via life cycle assessment (LCA). However, Arora et al. (2015) in their feasibility study

on two crude glycerol purification processes reported that the membrane separation process was more economical and environmentally friendly than the vacuum distillation process; however, no details on functional unit were provided as the focus of the study was on the economic aspect of the process. In one of the LCA studies involving crude glycerol, crude glycerol was converted to a glycol-ethers mixture to be used as an additive in diesel fuel. The findings suggested that use of the additive resulted in lesser greenhouse gas emissions (Asdrubali et al., 2015). Similar to this work, an LCA was performed on diesel engine running on fuel having glycerol-derived-triacetin along with diesel/biodiesel blends whereby the results reported that triacetin had no effect in profoundly mitigating the total environmental impacts of mechanical shaft work produced in a diesel engine (Tabatabaei et al., 2019). In another LCA study, Quinteiro et al. (2022) showed that rigid polyurethane foams (PUF) derived using unrefined glycerol was not always better than those of rigid PUF produced from crude oil-based polyol in terms of total environmental impacts.

Given that the purpose and goal of upgrading crude glycerol into purified glycerol is to not only bring economic benefit, but to also improve the biodiesel industry's sustainable footprint, this research paper aims to highlight the environmental impacts of different crude glycerol purification processes. Also, with industries entering the chemical market by constructing glycerol refineries, it is necessary to have an LCA study on the topic ("Argent Energy", 2022). To the best of our knowledge, there has been no comprehensive analysis done on the LCA of glycerol purification on different purification processes. In this study, the environmental impacts of the three processes previously mentioned — physicochemical treatment and membrane separation, vacuum distillation and ion exchange are investigated with the aim of providing a comparison of environmental performance of different purification processes.

2. Methodology

In general, glycerol purification processes involve a combination of physicochemical treatment and one of the available advanced purification technologies to increase the glycerol purity to close to technical grade (>95% w/w) (Chol et al., 2018). The physicochemical pre-treatment is performed before using advanced purification technologies like ion-exchange or membrane separation to prevent severe damage to these techniques due to impurities. The physicochemical treatment consists of saponification, acidification, phase separation, and solvent extraction steps, which eliminate most of the impurities, thereby producing enriched glycerol with a purity close to 80%. Saponification of crude glycerol converts impurities such as free fatty acids (FFAs) and fatty acid methyl esters (FAMES) into soaps (Hájek and Skopal, 2010). In the acidification step, a strong acid is utilized to lower the pH of the crude glycerol solution (Nanda et al., 2014) which separates the crude glycerol mixture into three distinct layers: a top layer containing FFAs, a glycerol-rich middle layer and a thin bottom layer containing inorganic salts. In the phase separation step, the glycerol rich layer is isolated by decanting the top layer containing FFAs and running off the bottom layer of inorganic salts. After the acidification step, the glycerol rich layer is neutralized with a base to remove excess acid, forming salt and water. The purity of the enriched glycerol produced after the initial stage has a high dependence on the acid/base used and its pH due to the varying levels of non-glycerol organic material (MONG) and other impurities contained within the crude glycerol (Ooi et al., 2001). Lastly, solvent extraction is used to obtain the glycerol-rich product free from inorganic salts, prior to the phase separation step. After removing methanol and water through vacuum evaporation, typical purities of the glycerol solution obtained are ~85% w/w, with the methanol typically being recycled for re-use. However, there is a need to further purify the glycerol from ~85% w/w to technical grade (>95% w/w) (Dhabhai et al., 2016) for specific applications (i.e. pharmaceutical, food and beverages industries) and advanced purification technologies - vacuum

distillation, ion exchange treatment and membrane separation are incredibly useful in this regard.

In this study, the three glycerol purification processes were modelled using Aspen Plus software v12.1 in combination with Super Pro Designer v13. Mass and energy data from the simulated process flow diagrams were used as an input to the CCaLC2 (Carbon Calculations over the Life Cycle of Industrial Activities) to measure the environmental impacts associated with each process. Fig. 1 shows the stepwise flow of results of one tool to another.

2.1. Aspen plus

As most components in the glycerol purification process are polar, the non-random two liquid (NRTL) model was selected to accurately simulate the process combined with UNIFAC-LL to estimate the missing coefficients of the components. Oleic acid was used to represent the free fatty acid component of the crude glycerol and *n*-pentane was used to represent petroleum ether as they have comparable physical and chemical properties. Potassium oleate (the soap component of crude glycerol during the saponification process) was not available in the data bank of Aspen plus, so was user defined in the software. Missing data about this component was estimated using the Aspen property estimation system.

2.2. Super pro designer

Super Pro Designer software was mainly used for unit operations not available in Aspen such as oil separator, decanting centrifuge and ion exchange column. Results from these units of Super Pro Designer were supplied to Aspen plus using a 'separator2' unit working as a black box. Super Pro Designer v13 library contains information for the following components in this simulation: methanol, glycerol, potassium hydroxide, hydrochloric acid, water and methyl oleate. Again, potassium oleate (the soap component of crude glycerol during the saponification process) was not available in the data bank of Super Pro Designer, so it was registered, and the main properties of this chemical component were added manually.

2.3. CCaLC2

CCaLC2 is the second generation of the "Carbon Calculations over the Life Cycle of Industrial Activities (CCaLC)" carbon footprint tool, which was developed by the Sustainable Industrial Systems group based at The University of Manchester. The version of CCaLC2 used in this study was '(CCaLC2, 2023) Version: 1.700'. The methodological approach that CCaLC2 follows aligns with the internationally accepted life cycle framework as defined by ISO 14044 (2006). The CCaLC2 tool allows for the calculation of the carbon footprint and other potential environmental impacts such as the acidification, eutrophication, ozone layer depletion, photochemical (summer) smog and human toxicity, from 'cradle to gate' (business to business). The total environmental burdens for an environmental impact per functional unit are calculated using Eq. (1):

$$B_j = \sum b_{j,i} \quad (1)$$

where B_j is the total burden j per functional unit and $b_{j,i}$ is the burden j from activity i . The total burdens for each stage of the process are summed to represent the environmental burden for a specific impact within CCaLC2. Following this, the burden is translated into the environmental impact by quantification of the burden as shown in Eq. (2):

$$E_k = \sum e_{k,i} B_j \quad (2)$$

where E_k is the total environmental impact k , $e_{k,i}$ is the environmental impact coefficient and B_j is the environmental burden contributing to the impact k as calculated using Eq. (1) (Azapagic and Clift, 1999). For components that did not have an equivalent match to that within the process, the most suitable component was chosen within the Ecoinvent v3 (Wernet et al., 2016) database to represent the actual raw material/energy.

2.4. Design expert

A factorial design in response surface method (RSM) within the Design Expert software v.13.1 was utilized for carrying out the sensitivity analysis of the LCA using the design of experiments (DOE) to determine the most effective parameter. The RSM analysis is suitable for assessing the effects and interactions by altering the factors together but

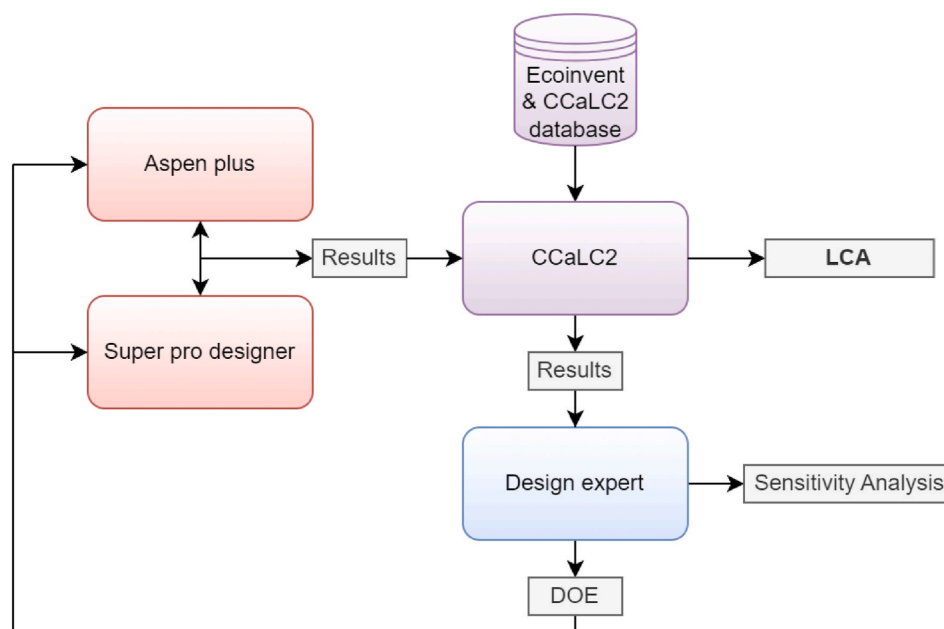


Fig. 1. Stepwise flowchart of tools used in this study.

requires a large number of test points when the number of factors are increased (Jabbari et al., 2021). In this study, as two factors with three responses were used and as the cost was just the computational time required for running simulations, the 3-level factorial design was the best choice (Van Schepdael et al., 2016).

2.5. Process description

2.5.1. Physicochemical and membrane purification (PMP) process

The PMP glycerol purification process closely follows the experimental and simulation processes proposed by Chol et al. (2018) with minor modifications. Modifications such as quantity of raw materials, temperature of flash, mainly arose because the composition of feed was changed. Fig. 2 shows the unit step operations for crude glycerol purification combined in a systematic flow sheet.

Crude glycerol was mixed with methanol in the MIXER-1 unit to improve the flow behaviour by reducing the liquid viscosity. Saponification of the crude glycerol solution was carried out in the SAPON-R unit thereby converting the impurities such as FAMES into soaps and methanol. In the acidification unit ACIDIF-R, the saponified crude glycerol was acidified using HCl, which leads to the formation of three phases-the FFA layer, the glycerol rich phase and the bottom most layer of inorganic salts. However, as the organic salt formed was KCl, it remained soluble in the liquids and a third phase did not form, as H^+ ions from the acid converted the soaps to insoluble FFA. An oil separator (LL-SEPER) which was separately modelled in Super Pro Designer was used to isolate the glycerol rich phase from the FFA layer and a solvent extraction unit (LIQ-EXTR) was used to remove inorganic salts that formed the bottom most layer. Solvents such as ethanol, propanol, pentane, hexane (used in the current study), and petroleum ether can be used to extract glycerol from the glycerol rich layer, leaving behind the inorganic salts contained within the ashes (Hunsom et al., 2013). The extracted glycerol rich solution was further neutralized with KOH base in the NEUTRA-R unit. At this stage, any remaining free fatty acids would be converted to soaps by reacting with KOH as per reaction 2 and hence, increasing the MONG content of the glycerol layer. The neutralized glycerol rich layer was then flowed to the membrane unit (MEMBRANE) for further purification, which was not possible by the physico-chemical treatments.

Traces of water and methanol solvent present in the permeate from the membrane unit were removed in the flash separator (FLASH-2). As excess methanol is used during the transesterification process to force the reaction to completion and subsequently obtain higher yields of biodiesel, substantial amounts of methanol are distributed between the FAMES and crude glycerol phase. Methanol is a toxic chemical and poses a major health and safety concern to humans, making its removal vitally important. Despite this, methanol is the most preferred alcohol in the biodiesel production as it is less expensive, it has higher reactivity, and easier separation is possible with methanol as it does not form an azeotrope with either water or glycerol. Also, methanol and other

impurities have more tendencies to accumulate in the glycerol phase as compared to biodiesel phase (Ardi et al., 2015).

Finally, the activated carbon treatment unit (AC-TREAT) was used to remove any remaining discolouration. The activated carbon treatment unit (AC-TREAT) and stream 'PURE-GLY' have been added into this simulation additionally to the PMP purification process. The LCA study only considered the section up to which the glycerol has been purified and no additional sections of the process were assessed given that this research's focus was on the purification process alone.

2.5.2. Vacuum distillation purification (VDP) process

VDP glycerol purification process loosely follows the simulation processes as proposed by Oliveira et al. (2022) and Arora et al. (2015) with slight modifications. Fig. 3 shows the unit step operations for crude glycerol purification combined in a systematic flow sheet. Crude glycerol was mixed with hydrochloric acid in MIXER-1 unit to neutralize the base (KOH) present. This neutralized crude glycerol was then heated to 130 °C using a heat exchanger (HEATER-1) before flowing it to the vacuum flash (VACFLASH) unit. The vacuum flash unit separated the more volatile part of the feed to vapour phase, which contained mostly methanol with a minute amount of water. The liquid stream from the VACFLASH unit, comprising mostly glycerol and fatty acids, was sent to the vacuum distillation column (VAC-DIST) to obtain purified glycerol from the distillate.

2.5.3. Ion exchange purification (IEP) process

The IEP glycerol purification process loosely follows the simulation processes as proposed by Isahak et al. (2016) with minor modifications. Fig. 4 shows the unit step operations for crude glycerol purification combined in a systematic flow sheet.

The feed (i.e., the crude glycerol) was first heated to 60 °C using a heat exchanger (HEATER-1) before saponifying it with KOH in the saponification reactor (SAPON-R). Saponified crude glycerol was then neutralized with the help of hydrochloric acid in the neutralization reactor (NEUTRA-R). This stream was then pumped (PUMP-1) into the decanter centrifuge (CENTRIFU), which separated oils and fats from the neutralized crude glycerol. The centrifuge block was simply modelled as a separator2 in Aspen Plus, but originally the output data of streams leaving the centrifuge (OILS and S40) was obtained from the centrifuge unit in the Super Pro Designer software. The S40 stream containing mostly the salts, methanol, water and glycerol was cooled to room temperature before flowing it through the ion exchange column (ION-EXC). This block was again modelled as a separator2 in Aspen Plus, but data was obtained from the adsorption ion-exchange unit for demineralization in Super Pro Designer.

The physicochemical pre-treatment was necessary to eliminate other harmful impurities, which can damage the anionic and cationic beads in the ion exchange column, significantly reducing column longevity. If the concentration of contaminant ions is significantly high, it can also

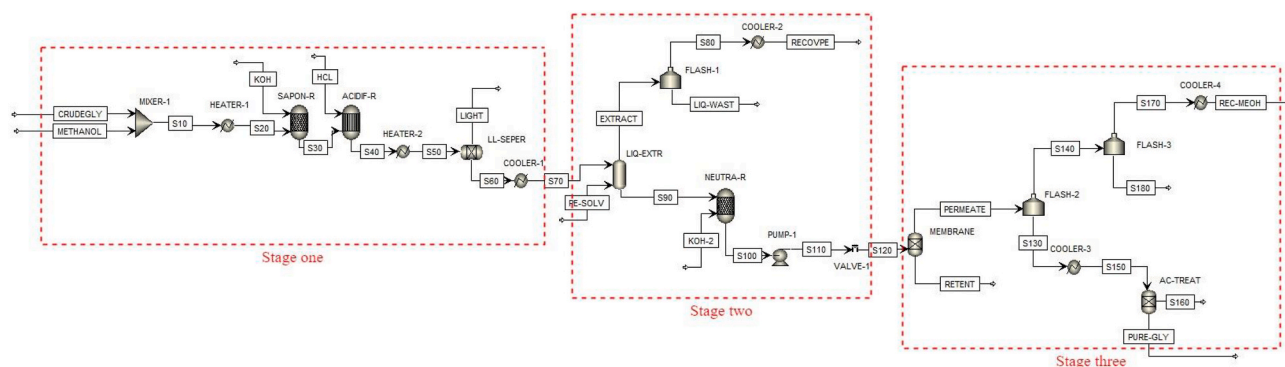


Fig. 2. Process flow diagram for PMP process.

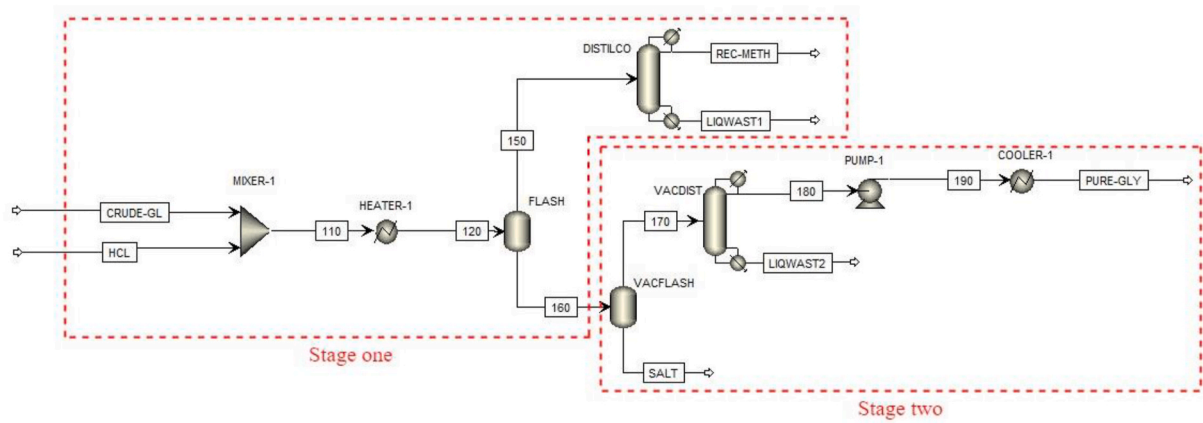


Fig. 3. Process flow diagram for VDP process.

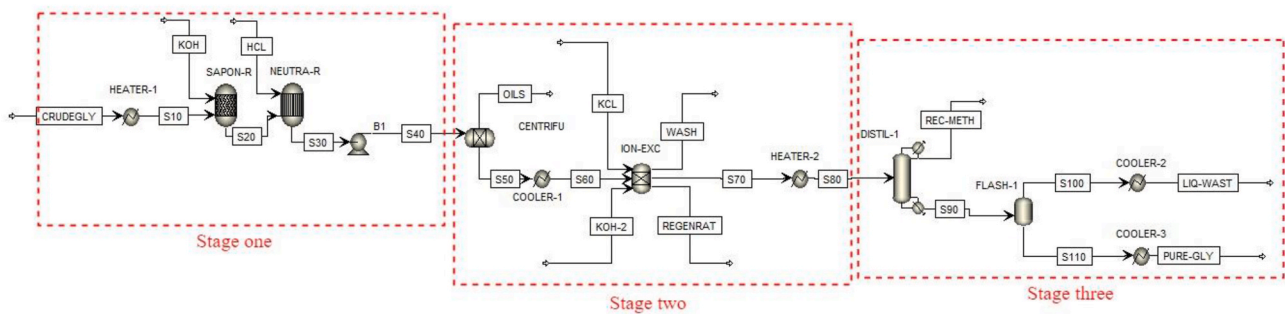


Fig. 4. Process flow diagram for IEP process.

reduce the lifespan of the ion exchange beads, as well increase the quantity of regenerants required to uneconomical levels (Rohm & Haas, 2008; Tiwari et al., 2015). The stream (S40) leaving from the ion exchange column was heated to 130 °C before flowing to the distillation column (DISTIL-1), where methanol was recovered in the distillate (REC-METH). The bottom product stream (S90) was sent to a flash drum where purified glycerol was obtained in the liquid stream (PURE-GLY).

3. LCA model development

The LCA study followed the ISO 14044, (2006) methodology for the glycerol purification process. Fig. 5 shows a general framework of an LCA study consists of four interdependent phases: goal and scope definition, inventory analysis, impact assessment and interpretation which are explored further below.

3.1. Goal and scope definition

The goal of this study is to perform the life cycle environmental impact assessment of three different purification processes of crude glycerol. The defined system boundaries for the LCA study are from ‘cradle to gate’ whereby the collection of raw materials, purification process used, and the storage and waste management were all considered. The transport of the raw materials to the purification plant and transport of wastes from the plant to the waste management sites were also considered (represented by the ‘T’ in Fig. 6). Due to the large number of transport flows and combinations between each stage, it is not practical to display all of these graphically, but rather represent them using the letter ‘T’ (Heijungs, 2014). The system boundaries for the LCA are indicated by the red box in Fig. 6. The system inputs consisted of the raw materials and energy required, whilst the system outputs included emissions, waste produced and the functional unit amount of

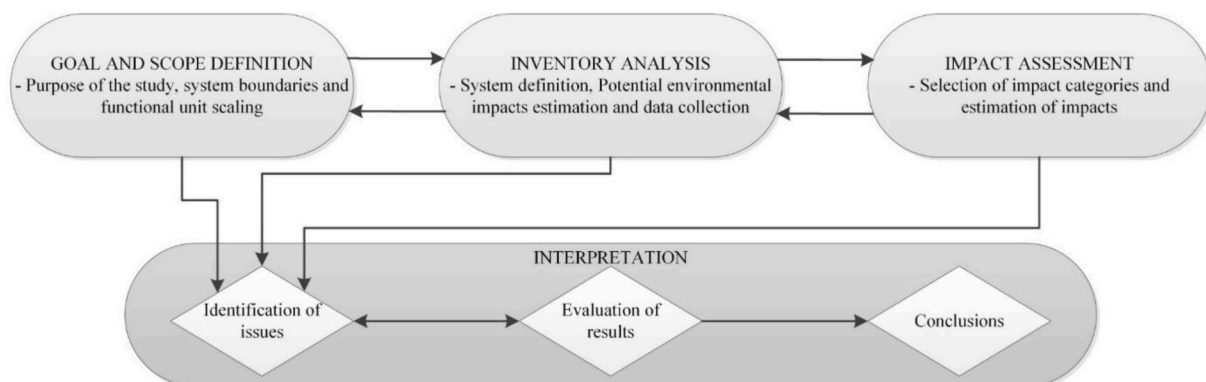


Fig. 5. LCA methodology: ISO 14044.

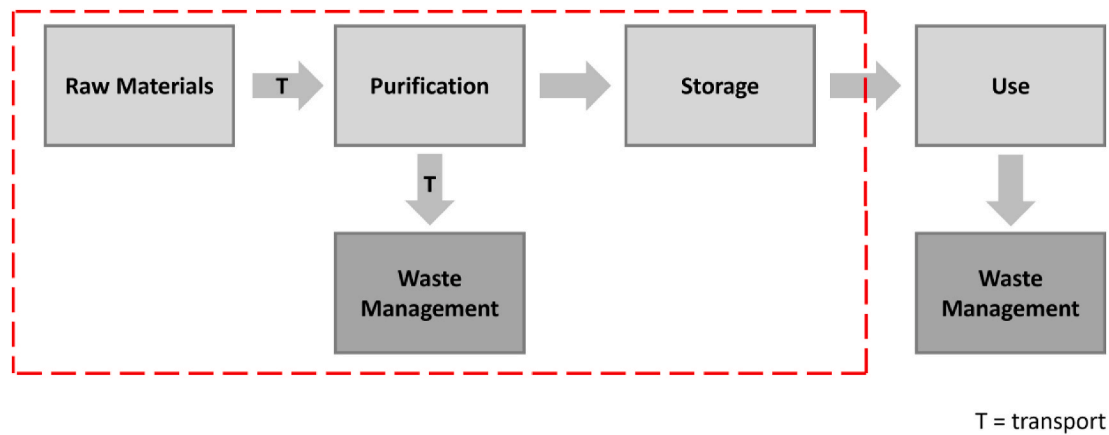


Fig. 6. System boundaries for the LCA study that uses the ‘Cradle to Gate’ approach.

product i.e., purified glycerol. Given that this study focuses on the LCA represented by the glycerol purification process the ‘use’ and ‘re-use and/or recycle’ aspects of the system boundaries have not been considered. It was decided that the transfer of material between the purification and storage stages would not be considered, as these would be negligible when compared to the magnitude of the environmental impacts posed by the transport of raw materials from the raw material sites to the purification plant.

A functional unit for the LCA was selected to define the physical processing capacity of the system, which can be used for comparisons against different systems on an equivalent basis. The functional unit of the LCA study was defined as 1000 kg (1 tonne) of crude glycerol as this value provides sensible environmental impact values per hour that would allow for the process to be compared on an industrial scale. The flow rate of the purified glycerol (i.e., purified glycerol from the purification process) was varied for each simulation, as per the flow rate and the composition of the feed crude glycerol. The normalizing factors for the glycerol purification process according to the feed flowrate is given in Table 1. Overall, three different types of glycerol purification process – PMP, VDP and IEP have been simulated in this work and details about each process can be found in Section 2.2. For the sensitivity analysis, three different types of flowrates in combination with three different

compositions of crude glycerol were used for each simulation as shown in Table 1.

3.2. Inventory analysis

3.2.1. Raw materials and energy inventory

The quantity of raw materials used as part of this LCA were defined by scaling up or down the equivalent amounts to the defined functional unit for the purification process. Raw materials with the representative modelled CCaLC2 raw materials used are shown in Table 2. The last column in this table shows the data quality and the data quality indicators have been adopted from elsewhere (Adsal et al., 2020).

To implement the LCA study efficiently, the three processes (PMP, VDP and IEP) were divided into three, two and three stages for simplification and to better understand the environmental impacts associated with each stage of the three purification processes as shown by the Aspen simulation diagram in Figs. 2–4. Each stage represents a section consisting of specific unit operations within the purification process with the associated inputs and outputs to that stage.

‘Glycerine, from vegetable oil, at esterification plant’ was selected to represent the crude glycerol from the production of biodiesel since this component provided the closest match to that of the purification process within the Ecoinvent database. This component was produced (12.7 wt %) along with vegetable oil methyl esters (87.1 wt%) from waste cooking oil which aligns with the ratios obtained within the biodiesel industry, where 1 kg of biodiesel produced makes 0.1 kg of glycerol. ‘Hexane’ was selected to represent the petroleum ether (PE) solvent as part of the purification process in stage 2, as this chemical was reported in the literature when discovering a suitable solvent for industrial use (Dhabhai et al., 2023). The activated carbon as part of stage 3 was chosen to be used in a 1:10 wt ratio, that is, 100 kg of activated charcoal was required per functional unit. Within the Ecoinvent database, ‘charcoal, at plant’ was chosen to provide the environmental impacts required to represent the process due to the high quality of the dataset for this component and the limited option of other suitable materials used to represent the environmental impacts of this raw material. ‘Potassium hydroxide, at regional storage’ represented KOH, and the environmental impacts for this raw material are associated with the manufacturing process of potassium chloride brine electrolysis in electrolytical cells including all precursors, ancillary materials, and transports. Starting from the mining of potash salts, the processes of concentration of the potassium chloride, conditioning, drying and transport to the regional storage were included in the environmental impact of producing potassium chloride shown as ‘potassium chloride, as K₂O, at regional storehouse’ (Isahak et al., 2016) used Amberlite IRN-78 and Amberlite 200C to remove the free ions, since these raw materials were not present in the Ecoinvent database. ‘Anionic resin, at

Table 1

Details about the different flowrates and composition of crude glycerol used in the simulation as feed.

Total flow rate of crude glycerol (kg/h)	Component	Mass Fractions			Normalizing factor for functional unit
1000	Glycerol	0.300	0.400	0.500	1.000
	Methanol	0.350	0.300	0.250	
	Methyl Oleate	0.117	0.100	0.083	
	Oleic Acid	0.155	0.133	0.110	
	Water	0.058	0.050	0.042	
	KOH	0.020	0.018	0.015	
	1500	Glycerol	0.300	0.400	
Methanol	0.350	0.300	0.250		
Methyl Oleate	0.117	0.100	0.083		
Oleic Acid	0.155	0.133	0.110		
Water	0.058	0.050	0.042		
KOH	0.020	0.018	0.015		
2000	Glycerol	0.300	0.400	0.500	0.500
Methanol	0.350	0.300	0.250		
Methyl Oleate	0.117	0.100	0.083		
Oleic Acid	0.155	0.133	0.110		
Water	0.058	0.050	0.042		
KOH	0.020	0.018	0.015		

Table 2

Raw materials with corresponding modelled CCaLC2 equivalents for the LCA.

Simulation name	Purification stage	Raw Material	Modelled CCaLC2 raw material	Amount (kg FU ⁻¹)	Database	Data quality (see Table S10 in SI file)
Physicochemical and membrane process	Stage 1	Crude glycerol	Glycerine, from vegetable oil, at transesterification plant	1000	Ecoinvent	(1,1,3,3,2)
	Stage 1	HCl	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	6.6	Ecoinvent	(1,1,2,3,1)
	Stage 1	Methanol	Methanol, at plant	805	Ecoinvent	(1,1,2,2,1)
	Stage 1	KOH	Potassium hydroxide, at regional storage	10	Ecoinvent	(1,1,2,2,1)
	Stage 2	PE Solvent	Pentane, at plant	209	Ecoinvent	(1,1,2,2,1)
	Stage 2	KOH-2	Potassium hydroxide, at regional storage	0.2	Ecoinvent	(1,1,2,2,1)
	Stage 3	Activated charcoal	Charcoal, at plant	100	Ecoinvent	(1,1,2,2,1)
Vacuum distillation process	Stage 1	Crude glycerol	Glycerine, from vegetable oil, at transesterification plant	1000	Ecoinvent	(1,1,3,3,2)
	Stage 1	HCl	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	48	Ecoinvent	(1,1,2,3,1)
Ion-exchange process	Stage 1	Crude glycerol	Glycerine, from vegetable oil, at esterification plant	1000	Ecoinvent	(1,1,3,3,2)
	Stage 1	HCl	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	0.1	Ecoinvent	(1,1,2,3,1)
	Stage 1	KOH	Potassium hydroxide, at regional storage	1.57	Ecoinvent	(1,1,2,2,1)
	Stage 2	KCl	Potassium chloride, as K2O, at regional storehouse	200	Ecoinvent	(1,1,2,2,1)
	Stage 2	KOH-2	Potassium hydroxide, at regional storage	188	Ecoinvent	(1,1,2,2,1)

plant' and 'cationic resin, at plant' were used to represent the ion exchange resins and the amount used was 250 kg of each resin, which corresponds to 1000 kg/h feed flow rate, as the ratio of flow rate and resins weight was 0.5 in the work of (Isahak et al., 2016).

The energy inventory for the LCA with type of energy source used in each stage of the three purification processes and amount per functional

unit can be viewed in Table 3. A detailed description of the energy contributions that each stage provides to the energy inventory has been mentioned in the next section.

3.2.2. Transport and plant location

Transport for the LCA was defined between the raw materials and

Table 3

Energy inventory with corresponding modelled CCaLC2 equivalents for the LCA study.

Simulation name	Purification stage	Purpose	Energy type	Amount (MJ FU ⁻¹)	Database	Data quality (see Table S10 in SI file)		
Physicochemical and membrane process	Stage 1	Heat required for saponification reactor (SAPON-R)	Steam – light fuel oil, UK	34.769	CCaLC Energy	(1,2,3,1,1)		
		Heat required for heat exchanger (HEATER-1 and HEATER-2)	Steam – natural gas, UK	1725.827	CCaLC Energy	(1,1,3,1,1)		
	Stage 2	Electricity required for pump (PUMP-1)	Electricity (high voltage) – UK grid	0.708	CCaLC Energy	(1,1,3,1,1)		
		Heat required for flash separator (FLASH-1)	Steam – natural gas, UK	85.299	CCaLC Energy	(1,1,3,1,1)		
	Stage 3	Heat required for flash separator (FLASH-2)	Steam – natural gas, UK	1513.983	CCaLC Energy	(1,1,3,1,1)		
	Vacuum distillation process	Stage 1	Heat required for heat exchanger (HEATER-1)	Steam – natural gas, UK	186.123	CCaLC Energy	(1,1,3,1,1)	
Heat required for flash separator (FLASH-1)			Steam – natural gas, UK	698.395	CCaLC Energy	(1,1,3,1,1)		
Heat required for flash separator (VACFLASH)			Steam – natural gas, UK	442.812	CCaLC Energy	(1,1,3,1,1)		
Heat required for reboiler of the distillation column (DISTILCO)			Steam – natural gas, UK	256.864	CCaLC Energy	(1,1,3,1,1)		
Stage 2		Heat required for reboiler of the distillation column (VACDIST)	Steam – natural gas, UK	186.148	CCaLC Energy	(1,1,3,1,1)		
		Electricity required for pump (PUMP-1)	Electricity (high voltage) – UK grid	0.041	CCaLC Energy	(1,1,3,1,1)		
		Ion exchange process	Stage 1	Heat required for saponification reactor (SAPON-R)	Steam – light fuel oil, UK	34.470	CCaLC Energy	(1,2,3,1,1)
				Heat required for heat exchanger (HEATER-1)	Steam – natural gas, UK	88.738	CCaLC Energy	(1,1,3,1,1)
Electricity required for pump (PUMP-1)	Electricity (high voltage) – UK grid			0.659	CCaLC Energy	(1,1,3,1,1)		
Stage 2	Stage 3	Electricity required for decanter centrifuge (CENTRIFU)	Electricity (high voltage) – UK grid	4.185	CCaLC Energy	(1,1,3,1,1)		
		Heat required for heat exchanger (HEATER-2)	Steam – natural gas, UK	304.080	CCaLC Energy	(1,1,3,1,1)		
Stage 3	Stage 3	Heat required for reboiler of the distillation column (DISTIL-1)	Steam – natural gas, UK	459.051	CCaLC Energy	(1,1,3,1,1)		
		Heat required for flash separator (FLASH-1)	Steam – natural gas, UK	179.401	CCaLC Energy	(1,1,3,1,1)		

purification stages as well as the purification to waste management stages and was represented by the letter 'T' as shown in Fig. 6. Argent Energy's biodiesel facility (Stanlow, UK), which produces around 85,000 tonnes of biodiesel annually, was selected for the LCA study ("Argent Energy Biodiesel", 2023). The location of the glycerol purification plant was defined as less than 1 km from Argent Energy's biodiesel production facility. The location of the glycerol plant is significant for the LCA study, as the raw materials must be transported onto site and the emissions associated with the transport will be included as part of the LCA.

The raw material storage hubs and waste management facilities are assumed to be located within a 100 km radius of the biodiesel facility to simplify the LCA's environmental impact calculations. By assuming this radial maximum distance, the real environmental impacts posed by the glycerol purification process will be less than the environmental impacts calculated as part of this LCA study. Based on annual production, the biodiesel produced is approximately 250 tonnes per day, which will result in the production of 25 tonnes of crude glycerol ("Argent Energy Biodiesel", 2023). It is reasonable to justify the use of a 40-tonne truck to carry such material given the quantities of raw materials and wastes produced ("Argent Energy Biodiesel", 2023; Tan et al., 2013). Empty return trips have been included as part of the LCA study as the vehicle used to transport raw materials and wastes will have to travel from the source to the processing site with return trips. Within the CCaLC database, the 40-tonne truck used has a carbon footprint of 4.402×10^{-5} kg CO₂ eq./kg-km with an 85% utilisation ratio i.e. it is able to carry 85% of the maximum payload capacity. Information and data related to the transport of raw materials and wastes to and from the process site can be viewed in Table S4 within the Supplementary Information.

3.2.3. Storage and waste management

Glycerol is a viscous liquid, which is chemically and microbiological stable at room temperatures and can last up to two years in a cool (<5 °C), dry, and well-ventilated area ("Glycerin Products: Storage and Shelf Life Guidelines", 2023). It is typically stored on an industrial level in large tanks or containers made of materials such as stainless steel. Glycerol is also sold to the market for usage periodically, so the storage containers used, and the volume of refrigeration units required for storing purified glycerol was calculated based on glycerol produced in three-month periods (1980 h, pro-rated based on plant running for 7920 h/year). The total mass of glycerol expected to be produced in 1980 h of process plant running time for each flowrate and composition is given in Table S7 (Supplementary Information) for different plants. The energy usage required was calculated based on each unit having a volume of 10.0 m³ at 60 % maximum capacity. As per (Evans et al., 2014), the relationship between the volume of refrigeration units and total energy use per year (kWh/year) is given by Eq. (1).

$$\text{Energy usage per year} \left(\frac{\text{kWh}}{\text{year}} \right) = 374.93 * (\text{Volume of refrigeration unit})^{0.8173} \quad (1)$$

The waste management section of the LCA includes all facilities that treat wastes discarded from the four stages of the purification process. Waste management strategies used in this LCA include 'disposal, solvents mixture, 16.5 % water, to hazardous waste incineration', 'disposal, used oil, 10% water, to hazardous waste incineration', 'disposal, salt, 0% water, to residual material landfill' and 'wastewater treatment' as can be seen in Table 5.

3.3. System description

3.3.1. Physicochemical and membrane purification process

3.3.1.1. Stage one: saponification and acidification. Stage one includes saponification and acidification steps for crude glycerol that were

carried out in reactors SAPON-R and ACIDIF-R, respectively as shown in Fig. 2. Inputs to this stage were crude glycerol, methanol (for dilution), KOH (for saponification) and HCl (for acidification). In stage one, the unit operations requiring energy were the saponification reactor (SAPON-R, 34.769 MJ FU⁻¹) and the heat exchangers (HEATER-1 and HEATER-2, 1725.827 MJ FU⁻¹). Data for this component has been sourced from the Ecoinvent database within CCaLC2 software.

3.3.1.2. Stage two: oil separation, liquid-liquid extraction, and neutralization. Stage two of the PMP process included the following operational units: oil separator (LL-SEPER), heat exchangers (COOLER-1 and COOLER-2), liquid-liquid extractor (LIQ-EXTR), flash drum (FLASH-1), and neutralization reactor (NEUTRA-R). Inputs to this stage were potassium hydroxide (KOH-2) and *n*-hexane (PE Solvent). For the heat exchangers, it was assumed that the temperature difference ΔT between the outlet and inlet cooling water stream would be 10 °C (20 °C–30 °C), to calculate the mass flow rate of cooling water required for the heat exchangers. The process water used for cooling was sent to wastewater treatment post-use and the environmental impacts of this treatment were included in the LCA study.

Outlets from stage two include light liquid (LIGHT) from the oil separator, liquid waste (LIQ-WAST) from the flash drum, and the *n*-hexane recovery (RECOVPE) stream. As the light liquid stream (294.604 kg FU⁻¹) mostly contained glycerol, K-Oleate, and M-Oleate, it was regarded as hazardous oil waste as these components are FAMES & soaps and was sent to hazardous waste incineration within the waste management stage. Liquid waste stream from the flash drum (161.24 kg FU⁻¹) consisting of methanol, water and *n*-hexane was regarded as waste and therefore sent to a hazardous waste incineration treatment facility within the CCaLC2 database. Due to the high mole fraction of *n*-hexane in the hexane recovery streams, this stream was not treated as waste as solvents from the stream can be further recovered, treated, and re-used as part of the liquid-liquid extraction process within stage one.

3.3.1.3. Stage three: membrane separation. Stage three of the purification process consists of the pump (PUMP-1), membrane separation unit (MEMBRANE), flash separator (FLASH-2 and FLASH-3), heat exchangers (COOLER-3 and COOLER-4) and activated treatment column (AC-TREAT). High voltage electricity was provided to the pump (P-100) and the amount of electricity required per functional unit was 0.708 MJ FU⁻¹ whereas the total amount of energy required for the flash separator 1515.866 MJ FU⁻¹ (Table 3).

The outputs of stage three consisted of retentate stream (RETENT) from the membrane separation unit (MEMBRANE), recovered methanol (REC-MEOH) from flash drum, purified glycerol (PURE-GLY) from activated carbon column (AC-TREAT) and liquid waste stream (LIQ-WAST2) from the flash drum (FLASH-3). Retentate stream from the membrane separation unit containing the salts was disposed by landfilling and the carbon footprint associated with the disposal were being accounted for in the LCA study as shown in Table 5. The cooling water required (36250.52 kg FU⁻¹) for the heat exchangers and cooling required for flash separator 2 was added to the process water required to be treated at the wastewater treatment facility. The recovered methanol stream was not sent to waste management as it can be further purified and then re-used as part of the purification process. For this LCA, the activated carbon treatment used was 100 kg of charcoal per functional unit, aligning with the 1:10 ratio from the literature for removing the brown colour and the final impurities in the treated glycerol (Dhabhai et al., 2016).

3.3.2. Vacuum distillation purification process

3.3.2.1. Stage one: vacuum flash separation and methanol recovery. Stage one includes the neutralization of crude glycerol that was carried out in the mixer (MIXER-1) and methanol and salt removal that was achieved

in the vacuum flash as shown in Fig. 3. Inputs to this stage were crude glycerol and HCl for neutralization. In stage one, the unit operations requiring energy were heat exchangers (HEATER-1), the vacuum flash drum (VACFLASH), the compressor (COMP-1) and the distillation column (DISTILCO). The heat required for the heat exchanger, vacuum flash drum and reboiler of the distillation column reactor was equal to 1266.243 MJ FU⁻¹ and energy required for the pump were provided using high voltage electricity of 261.210 MJ FU⁻¹. Output for this stage was stream 140 that flowed into the second stage, waste stream (SALT) from the vacuum flash and liquid waste (LIQWAST1) from the bottoms of the distillation column. Since the liquid waste stream from the distillation column contained mostly methanol and water, it was sent to a hazardous waste incineration facility within the CCaLC2 water and salt waste stream from vacuum flash was disposed by landfilling.

3.3.2.2. Stage two: vacuum distillation. Stage two of the VDP process included the following operational units: vacuum distillation column (VACDIST), heat exchangers (COOLER-1), and pump (PUMP-1). The energy required for the reboiler was provided in the form of heat sourced from 'Steam – natural gas, UK' and high voltage electricity was provided for the functioning of the pump as described in Table 3. The total process water of 18646.74 kg FU⁻¹ used for cooling was sent to wastewater treatment post-use and the environmental impacts of this treatment were included in the LCA study.

3.3.3. Ion exchange purification process

3.3.3.1. Stage one: saponification and neutralization. Stage one includes saponification and neutralization steps for crude glycerol that were carried out in the reactors SAPON-R and NEUTRA-R, respectively as shown in Fig. 4. Inputs to this stage were crude glycerol, KOH (for saponification) and HCl (for acidification). In stage one, the unit operations requiring energy were the saponification reactor (SAPON-R), heat exchanger (HEATER-1) and the pump (PUMP-1). The saponification reactor required 34.470 MJ FU⁻¹ of heat whereas the heat exchanger required 88.738 MJ FU⁻¹ of heat. Pump was operated with high voltage electricity providing energy of 0.659 MJ FU⁻¹.

3.3.3.2. Stage two: decanter centrifugation and ion exchange treatment. Stage two of the IEP process included the following operational units: the decanter centrifuge (CENTRIFU), heat exchangers (COOLER-1 and HEATER-2), and the neutralization ion exchange column (NEUTRA-R). Inputs to this stage were potassium hydroxide (KOH-2) and potassium chloride. The energy required for the heat exchanger was provided in the form of heat sourced from 'Steam – natural gas, UK' and for the decanter centrifuge, high voltage electricity was provided as described in Table 3. Water type 'process water' was chosen to be the best representative of the cooling water and was sent to wastewater treatment post-use. Only the regenerate stream (REGENRAT) from the ion-exchange unit was sent to disposal of anion exchange resin water by municipal incineration, the wash stream (WASH) contained mostly potassium chloride and could be used again after recycling.

3.3.3.3. Stage three: methanol recovery and flash separation. Stage three of the purification process consisted of the distillation column (DISTIL-1), flash separator (FLASH-1), and heat exchangers (COOLER-2 and COOLER-3). Energy in the form of heat for the reboiler of the distillation column and flash separator (638.453 MJ FU⁻¹) was provided using 'Steam – natural gas, UK' within the CCaLC2 database as it would accurately model the environmental impacts associated with the heat provided. Heat exchangers and condenser of the distillation column required 21642.94 kg FU⁻¹ of process water, which was again sent to the wastewater treatment facility.

3.4. Impact assessment

The results from the LCA were evaluated based on the environmental impacts, which include Carbon footprint (CF) measured in kg CO₂ eq., Water footprint (WF) measured in m³ H₂O eq., Acidification (AD) measured in kg SO₂ eq., Eutrophication (EP) measured in kg PO₄ eq., Ozone layer depletion (OLD) measured in kg R11 eq., Photochemical smog (PCS) measured in kg C₂H₄ eq., and Human toxicity (HT) measured in kg dichlorobenzene (DCB) eq. CF was chosen as it is a relevant impact to recognize the effects of global climate change, the other impacts were selected as these are the ones mostly affected when a chemical purification process is to be evaluated.

4. Results and discussion

Sequentially segregating and analyzing different potential environmental impacts allowed for a clearer comparison of different sections in the LCA. Moreover, each stage of the LCA for all the purification processes were analyzed and investigated using the data provided by CCaLC2 to find 'hot spots', identifying areas in which the glycerol purification can be improved on a sustainable basis. Table 5 shows potential environmental impacts for three purification processes for raw materials, production, storage and transport section.

Comparison of simulation results for PMP, VDP and IEP between the literature and this work in shown Table S9 (Supplementary Information) shows to confirm model validation. Apart from minor modifications in the simulations, the main difference arising in the composition of purified glycerol was due to the composition of the starting feed. The FFA component along with residual water were not included in the composition of crude glycerol feed in the work of Arora et al. (2015), whereas FFA was presented as palm oil in (Isahak et al. (2016) in place of oleic acid, again lacking water as an impurity in the feed.

4.1. Environmental impacts of PMP process

The carbon footprint (CF) of the LCA study for the 'cradle to gate' system, highlighted the importance of selecting sustainable raw materials and efficient disposal of the waste for a given industrial purification process. Table 5 shows the different environmental impacts associated with the PMP purification process whereas Fig. 7 provides info about the individual contributions of the four sections to different environmental impacts. Out of the four sections, the purification section where the actual purification processes were carried out had the most CF emissions. Within this section, 36% of total CF (1260 kg CO₂ eq. FU⁻¹) were emitted only in the disposal of wastes generated by the physicochemical treatment, whereas 229 kg CO₂ eq. FU⁻¹ was generated by the energy usage of the technical equipment such as the flash-drums and heat exchangers. Contributions of the three stages to the CF within the purification section can be seen in Fig. 8. Following the purification section, the raw materials used in stages one and two had the biggest impact on the PMP process accounting for 40 % of the total CF and methanol was the largest contributor to the CF of the raw materials making it a 'hot-spot'. Alternatives to this solvent should be investigated as further work to reduce the solvents environmental impact although an economic analysis will be required to determine the solvents suitability. After methanol, crude glycerol added the most to the CF with 419 kg CO₂ eq. FU⁻¹.

The total water usage of the complete process amounted to 77.15 m³ water FU⁻¹ with a total water footprint (WF, stress-weighted) of 30.5 m³ water FU⁻¹ (Table S8, Supplementary information). The water stress index factor used for the calculation of the stress weighted WF was 0.395 based on the country (United Kingdom). Stage two contributed 53.6 % to the WF largely due to the process cooling required by the heat exchangers (COOLER-1 and COOLER-2) and the remaining contribution of WF was added by the water required for the heat exchangers (COOLER-3 and COOLER-4) and flash drum (FLASH-4).

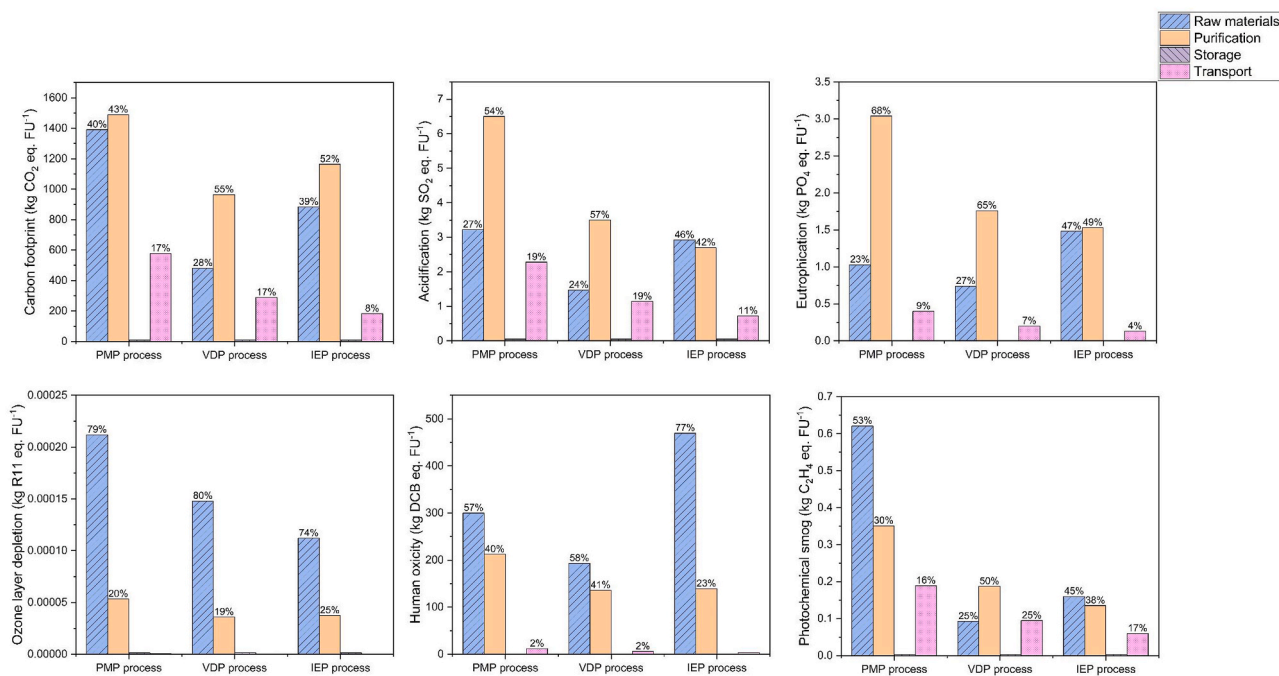


Fig. 7. Section-wise potential environmental impacts of PMP, VDP and IEP purification processes.

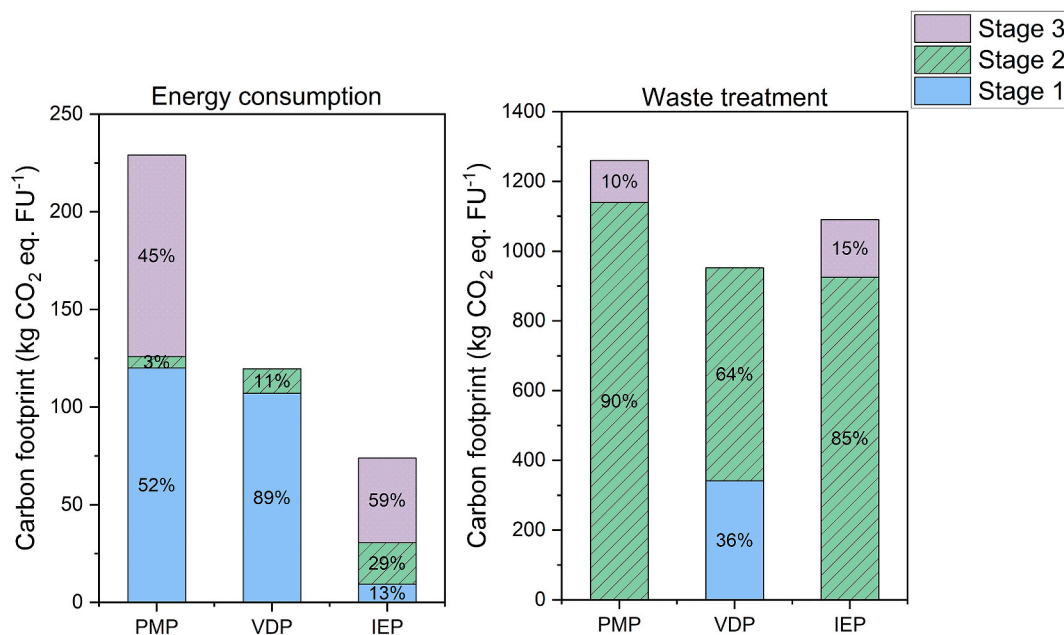


Fig. 8. Stagewise carbon footprint contribution of the purification section for PMP, VDP, and IEP processes.

In terms of the acidification and eutrophication, around 64% of the total acidification (12.06 kg SO₂ eq. FU⁻¹) and 45% of the total eutrophication (4.47 kg PO₄ eq. FU⁻¹) was contributed by the wastewater treatment needed for the heat exchangers and coolers within the purification section. Also, the transportation of materials to the production site and waste management locations contributed 2.28 kg SO₂ eq. FU⁻¹ to the AP and 0.4 kg PO₄ eq. FU⁻¹. Of these total materials, the process water made up 99 wt% of the total mass of materials transported. By installing an onsite closed-circuit wastewater treatment system, dramatic reductions could be made to the AD and EP impact through the reduction in wastewater transport. 74% of the total ozone layer depletion (OLD, 2.68 × 10⁻⁴ kg R11 eq. FU⁻¹), 49% of the total

photochemical smog (PS, 1.16 kg C₂H₄ eq. FU⁻¹), 53% of the total human toxicity (HTP, 523.64 kg DCB eq. FU⁻¹), was contributed by the raw materials such as methanol, crude glycerol and activated carbon. Improvements to the purification process that look to decrease these three impacts should focus primarily on the raw materials used, as these contributed the most. Alternatives to the use of methanol or improvements to the production supply chain should be prioritized to reduce the impact.

4.2. Environmental impacts of VDP process

The total carbon footprint of the VDP process was considerably less

than the PMP process having a value of 1745.72 kg CO₂ eq. FU⁻¹ (a decrease of 50% compared to PMP and a decrease of 22% compared to IEP). In this case, the energy usage by the equipment and waste disposal activities done in the production section had the biggest impact on the VDP process contributing around 53 % to the total CF. Vacuum distillation is an energy intensive process and hence, energy usage was considerable larger than PMP or IEP processes due to the presence of flash drums and distillation columns. Since, no physicochemical treatment was performed on the crude glycerol before feeding it to the distillation column, except for neutralization of crude glycerol with hydrochloric acid, the raw materials required in the PMP, or IEP process did not contribute to the carbon footprint of the VDP process. Along with energy usage within stage 1 and stage 2, waste disposal also contributed substantially to the total carbon footprint (48%). After the purification section, raw materials showed the second highest carbon footprint (28%, 482 kg CO₂ eq. FU⁻¹) of which most of the CF was coming from crude glycerol.

Water was required mainly for the cooling process by the condensers of the distillation columns (DISTILCO and VACDIST) and the heat exchanger (COOLER-1). Stage one and two of the purification section required 38.53 m³ water FU⁻¹ making the total water footprint (WF, stress-weighted) of 15.22 m³ water FU⁻¹. It can be noticed that the water required for the VDP process was half of the amount of water required for the PMP process. 57% of the total AD (6.17 kg SO₂ eq. FU⁻¹) and 65% of the total EP (2.70 kg PO₄ eq. FU⁻¹) is contributed by the purification section and almost all of it (>98%) is caused by the disposal of the waste generated and again, wastewater forms the majority of waste. It is worth noting that both the acidification and eutrophication potential of wastewater treatment are low (6.92E-5 kg SO₂ eq. per kg and 2.60E-5 kg PO₄ eq. per kg), however, the amount wastewater generated per functional unit (Table 4) is high which acidification and eutrophication impact high.

In the case of OLD and HT environmental impacts, 80% of the total OLD (1.85E-04 kg R11 eq. FU⁻¹) and 57% of the total HT (335.67 kg

Table 4
Waste management with corresponding modelled CCaLC2 equivalents for the LCA study.

Simulation name	Purification stage	Type of waste	Modelled CCaLC2 waste	Amount of waste (kg FU ⁻¹)	Database	Data quality (see Table S10 in SI file)
Physicochemical and membrane process	Stage 2	Waste stream (LIGHT) from oil separator (LL-SEPER) containing K-oleate, oleic acid and M-oleate	Disposal, hazardous waste, 25% water, to hazardous waste incineration	294.37	Ecoinvent Waste	(3,2,3,3,3)
		Process water used for cooling in heat exchanger (COOLER-1 and COOLER-2)	Wastewater treatment	40943.68	CCaLC Waste	(1,2,3,1,3)
	Stage 3	Waste stream (LIQ-WAST) from Flash drum (FLASH-1) containing mostly methanol, n-hexane and water	Disposal, solvents mixture, 16.5 % water, to hazardous waste incineration	164.16	Ecoinvent Waste	(3,2,3,3,3)
		Waste stream (LIQWAST2) from flash drum (FLASH-3) containing mostly methanol, glycerol and water	Disposal, solvents mixture, 16.5 % water, to hazardous waste incineration	16.78	Ecoinvent Waste	(3,2,3,3,3)
		Waste stream (RETENT) from membrane separator (MEMBRANE) containing salts	Disposal, salt, 0% water, to residual material landfill	5.33	Ecoinvent Waste	(1,2,3,3,3)
		Process water used for cooling in heat exchanger (COOLER-3 and COOLER-4)	Wastewater treatment	33431.40	CCaLC Waste	(1,2,3,1,3)
Vacuum distillation process	Stage 1	Process water used for cooling in heat exchanger (FLASH-4)	Wastewater treatment	2774.07	CCaLC Waste	(1,2,3,1,3)
		Waste stream (SALT) from flash separator (VACFLASH) containing salts	Disposal, salt, 0% water, to residual material landfill	23.25	CCaLC Waste	(1,2,3,3,3)
	Stage 2	Process water used for cooling in condenser of distillation column (DISTILCO)	Wastewater treatment	20521.15	Ecoinvent Waste	(1,2,3,1,3)
		Waste stream (LIQWAST1) from distillation column (DISTILCO) containing mostly methanol and water	Disposal, solvents mixture, 16.5 % water, to hazardous waste incineration	93.08	Ecoinvent Waste	(3,2,3,3,3)
		Process water used for cooling in heat exchanger (COOLER-1)	Wastewater treatment	479.38	CCaLC Waste	(1,2,3,1,3)
		Process water used for cooling in condenser of distillation column (VACDIST)	Wastewater treatment	17533.58	CCaLC Waste	(1,2,3,1,3)
Ion-exchange process	Stage 2	Waste stream (LIQWAST2) from distillation column (VACDIST) containing mostly oleic acid and m-oleate	Disposal, hazardous waste, 25% water, to hazardous waste incineration	233.75	Ecoinvent Waste	(1,2,3,3,3)
		Waste stream (OILS) from decanter centrifuge (CENTRIFU) containing K-oleate, oleic acid and M-oleate	Disposal, hazardous waste, 25% water, to hazardous waste incineration	279.86	Ecoinvent Waste	(1,2,3,3,3)
	Stage 3	Waste stream (REGENRAT) ion exchange column (ION-EXC) containing salts	Disposal, anion exchange resin water, 50% water, to municipal incineration	189.28	Ecoinvent Waste	(3,3,2,3,3)
		Process water used for cooling in heat exchanger (COOLER-1)	Wastewater treatment	1652.93	CCaLC Waste	(1,2,3,3,3)
		Process water used for cooling in condenser of distillation column (VACDIST)	Wastewater treatment	14526.39	CCaLC Waste	(1,2,3,3,3)
		Process water used for cooling in heat exchanger (COOLER-2)	Wastewater treatment	3074.93	CCaLC Waste	(1,2,3,3,3)
Stage 3	Process water used for cooling in heat exchanger (COOLER-3)	Wastewater treatment	4041.62	CCaLC Waste	(1,2,3,3,3)	
	Waste stream (LIQ-WASTE) from flash drum (FLASH-1) containing glycerol, methanol and water	Disposal, solvents mixture, 16.5 % water, to hazardous waste incineration	56.95	Ecoinvent Waste	(3,2,3,3,3)	

Table 5
Potential environmental impacts of PMP, VDP and IEP purification processes.

Potential environmental impacts	Simulation name	Total
Carbon footprint (kg CO ₂ eq. FU ⁻¹)	PMP process	3466.82
	VDP process	1745.72
	IEP process	2239.71
Acidification (kg SO ₂ eq. FU ⁻¹)	PMP process	12.05
	VDP process	6.16
	IEP process	6.39
Eutrophication (kg PO ₄ eq. FU ⁻¹)	PMP process	4.47
	VDP process	2.70
	IEP process	3.14
Ozone layer depletion (kg R11 eq. FU ⁻¹)	PMP process	2.67E-04
	VDP process	1.86E-04
	IEP process	1.51E-04
Photochemical smog (kg C ₂ H ₄ eq. FU ⁻¹)	PMP process	1.16
	VDP process	0.38
	IEP process	0.36
Human toxicity (kg DCB eq. FU ⁻¹)	PMP process	524.63
	VDP process	335.68
	IEP process	613.33
Water footprint (stress weighted) (m ³ eq. FU ⁻¹)	PMP process	30492.62
	VDP process	13979.86
	IEP process	13081.87

DCB eq. FU⁻¹) is contributed by the raw materials used because of the usage of crude glycerol and hydrochloric acid. The purification section also contributes significantly to the HT (41%, 88.2 kg DCB eq. FU⁻¹) which is caused by the disposal, or the treatment of the waste discharged in huge amounts.

4.3. Environmental impacts of IEP process

The total carbon footprint of the IEP process increased to the value of 2239.71 kg CO₂ eq. FU⁻¹ due to high amounts of raw materials used in the process. In this case, the extra raw materials were needed for the physicochemical treatment, unlike the VDP process and similar to the PMP process, so that the crude glycerol that was fed to the ion exchange unit had a reduced fraction of the impurities. This was necessary to enhance the separation effectiveness of this method as well as to increase the number of cycles and longevity of the ion exchange beads (Rohm & Haas, 2008). In this case, the purification section contributed 52% to the total carbon footprint compared to the raw materials, which contributed 39% to the CF. Similar to the VDP and PMP process, waste disposal and wastewater treatment activities formed the majority of the CF released by the purification section. Particularly, stage 2 within the purification section had the highest wastes generated adding 946.30 kg CO₂ eq. FU⁻¹ (42.3%) to the total CF which was mainly due to the waste oil stream that was sent to a hazardous waste incineration facility. Presence of the ion exchange column unit in stage 2 also secreted huge amounts of waste streams while washing and regenerating the column. Raw materials such as crude glycerol, potassium hydroxide and potassium chloride used in the ion exchange column for washing and regeneration were responsible for a higher AD and EP. Overall, the raw materials and purification sections added substantially with combined contributions of 88% to the total AD (6.40 kg SO₂ eq. FU⁻¹) and 96% to the total EP (3.14 kg PO₄ eq. FU⁻¹). In the purification section, the waste streams that were excreted by the ion exchange column also contributed to the AD and EP.

The scenario was altered for OLDP and HTP where most of the contributions to the emissions were made solely by the raw materials. Raw materials—crude glycerol, potassium hydroxide and potassium chloride provide 74% of the total OLD (1.51E-04 kg R11 eq. FU⁻¹) and 77% of the total HT (613.33 kg DCB eq. FU⁻¹). In general, ion-exchange process is seen as an exceptionally environmentally friendly technique as it does not require a high amount of external energy, however, on an industrial scale when the amount of raw materials required is considered along with the disposal of waste generated, the technique becomes less

attractive. Also, it is already known that the technique cannot be applied if the concentration of the impurities reaches a certain threshold (>10 g/L) (Rohm & Haas, 2008).

4.4. Use case based on hotspots of PMP purification process

With methanol contributing to a large proportion of the environmental impacts as detailed above, sourcing of sustainable bio-methanol presents a possible solution to reduce this problem for the PMP process. Novel methods of producing methanol from wood begins with the pre-treatment of pinewood with impregnation fluid (Na₂CO₃) allowing for high carbon conversion in the gasification process that follows. Post gasification, the syngas is cleaned using zeolite membranes to remove carbon dioxide before methanol synthesis (Yadav et al., 2020). This can be modelled within CCalC2 by simulating the methanol used as 'methanol, from biomass'. Also, in the previous LCA of PMP process, hydrochloric acid was sourced from an industry which reacted hydrogen with chlorine to obtain the acid. If that source of raw material is changed to the one where propene and chlorine and reacted to get the HCl, a significant decline in CF and OLD of the raw materials is observed as shown in Fig. 9. Earlier, the waste disposal streams from the oil separator (LL-SEPER) and flash drums (FLASH-1 and FLASH-3) were incinerated in the hazardous waste facility. However, if the incineration treatment is replaced with an underground hazardous waste disposal method, substantial reductions seen in the total CF and total OLD are 39% and 54%, when compared to the previously discussed PMP purification process. In this way, several main hot spots causing the highest environmental impacts can be identified and substituted with those having comparatively lower environmental impacts.

4.5. Sensitivity analysis

Despite the prediction of productivity and CO₂ footprint, the Aspen-CCalC2 model is unable to do the sensitivity analysis and select the best operating conditions in a straightforward way. This could be achieved by combining the Aspen-CCalC2 model with RSM analysis, which avoids expensive and time-consuming experiments. The RSM can generate large amounts of information from a small number of simulation runs and it is able to assess the interaction effects between the independent variables on the response factor (CO₂ footprint) along with determining the optimal operating conditions.

The waste generated while removing impurities from the crude glycerol and raw materials required for the physicochemical treatment were identified as the most significant contributors (or 'hotspots') to environmental impacts. The composition and feed flowrate of crude glycerol dictates the amount of waste generated and the raw materials and energy required for the purification process in order to keep the final purity of the glycerol constant. Therefore, the feed flowrate and composition needed to produce 1000 kg of purified glycerol (the functional unit as defined earlier) were selected as factors to be assessed in the sensitivity analysis. As mentioned earlier, the composition of crude glycerol can vary greatly, and therefore three different conservative compositions of crude glycerol with a glycerol content of 30%, 40%, and 50% were selected as factors to be assessed for this analysis. The feed flowrate of crude glycerol was increased to 1.5 and 2 times with respect to the functional unit in order to capture the increasing production of biodiesel and therefore, the increasing production of crude glycerol over the next decade (OECD-FAO Agricultural Outlook 2022–2031, 2022). Details about the different flowrates and composition of crude glycerol used in the simulations can be found in Table 1. Within a specific purification process, the higher feed flowrates would generate a higher amount of purified glycerol and hence, for an appropriate comparison, all the values in association with the environmental impacts were multiplied by the normalizing factor as shown in Table 1.

3D surface plots with response as the normalized carbon footprint were generated using the two parameters, that is, the feed flowrate and

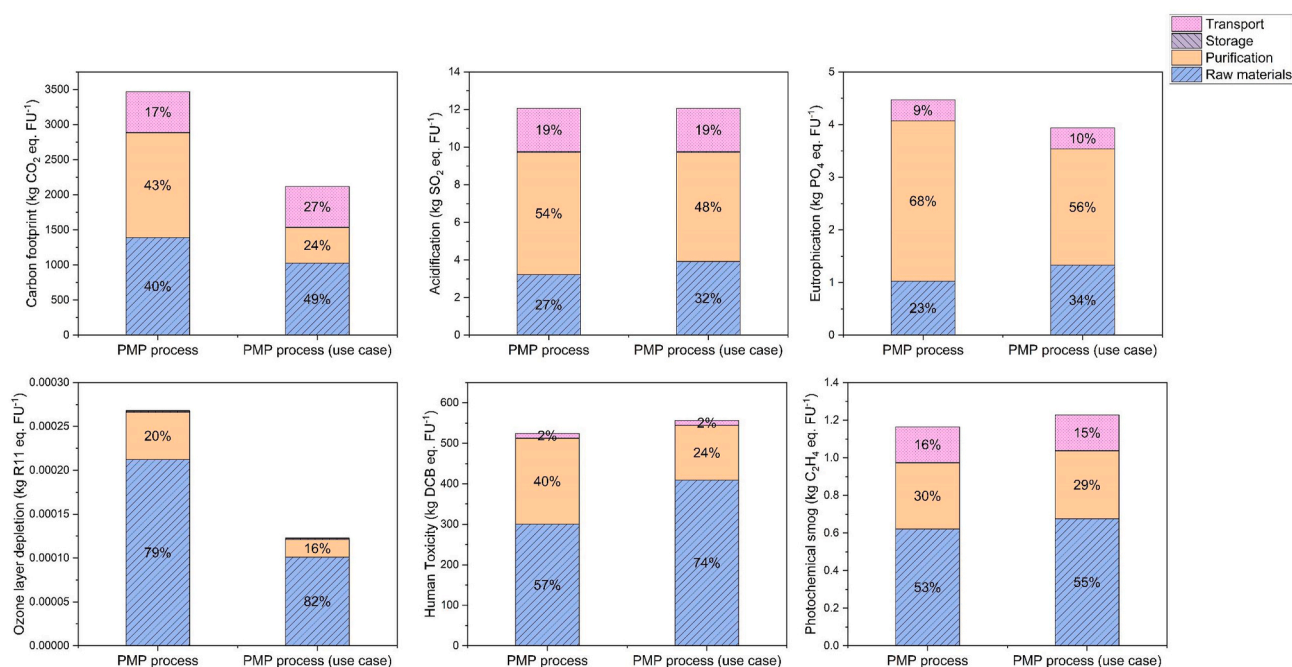


Fig. 9. Comparison of potential environmental impacts for PMP after changing the source of raw materials and altering waste disposal method.

composition of the crude glycerol, in order to discover a possible relation between the three factors. The carbon footprint results of the sensitivity analysis scenarios are illustrated in Fig. 10. The results are also given in Table S6 within the Supplementary Information.

The relationship between the glycerol content of the crude glycerol and the carbon footprint was inverse, that is, crude glycerol having a lower glycerol content had a relatively higher carbon footprint as waste is generated in a higher degree due to additional impurities. The raw materials used for crude glycerol purification with lower glycerol content were required in greater amounts to keep the final yield of purified glycerol consistent. However, the normalized carbon footprint emitted for different feed flowrates of crude glycerol for the same composition remains almost the same for all three processes. The surface response plot for the VDP process follows almost a flat linear trend between carbon footprint and glycerol content. However, this contour is steeper in the middle for the IEP process, as the raw materials required for the ion exchange unit to wash and regenerate the column decreases greatly when the impurities (i.e., salt ions) reduce. This reduced usage of raw materials in turn contributes to a lower overall carbon footprint. As the two factors—feed flowrate and composition of crude glycerol generated two other responses along with the carbon footprint – the glycerol flowrate and purity, the full factorial method also provided the optimized conditions for higher flowrate, higher purity, and lower carbon footprint (Table S7, Supplementary information).

5. Limitations of the study

Environmental impacts vary greatly with the preparation method of raw materials used as well as the supplier of the material. Data collection improvements could be made for these raw materials by undertaking an LCA on the actual raw material producing process to be used and then quantifying the emissions associated with the main raw material. Given that the raw materials are used in large quantities in the case of PMP and IEP processes, this would improve the accuracy of the environmental impact results for the crude glycerol purification process. Environmental impacts associated with the waste disposal methods can also vary greatly depending on the exact composition of the waste stream as well as the techniques used to treat the waste. For the purification processes, the quantity of energy required in the form of heat and electricity was

obtained from the simulations but, those quantities can also change with other factors such as ambient temperature at the location of the plant causing a corresponding greater or lesser heat loss. For the current three purification processes, the transport distance of raw materials from warehouse to the purification refinery and waste materials from refinery to waste management facility was assumed to be 100 kms which also would be different in practice.

6. Conclusions and prospects

This study compares the environmental impacts of crude glycerol purification processes for three different types of purification techniques namely-physicochemical treatment and membrane separation, vacuum distillation, and ion exchange, within one cradle-to-gate LCA. The aim of the study was to explore the choice of purification technology as an opportunity for minimizing the environmental impact of producing purified glycerol. Seven different types of environmental impacts – the carbon footprint, water footprint, acidification, eutrophication, ozone layer depletion, photochemical smog and human toxicity were analyzed. Based on the functional unit, the most significant environmental impacts for all purification processes were the overall carbon footprint, water footprint, acidification and human toxicity. For the three impacts (CF, AD and EP) out of the seven impacts that were covered, production stage was found to be the main contributor, followed by the raw materials section whereas the storage section had the minimum contribution for all seven impacts.

Another key conclusion of this LCA study was that the raw materials and waste disposal had the largest influence over the environmental impacts for the PMP and IEP processes. This is because both the membrane and ion exchange separation technologies require that crude glycerol feed is pre-treated to reduce its impurities in order to increase the effectiveness of the final separation, as well to increase the durability of the membrane and the ion-exchange beads. Comparatively, the VDP process requires that only inorganic impurities from the crude glycerol are removed before flowing it through the vacuum distillation unit and hence, requiring less raw materials but a greater external energy. Generally, membrane and ion exchange separation processes are seen as more environmentally friendly methods when compared to the vacuum distillation processes as, in the latter, enormous amounts of energy are

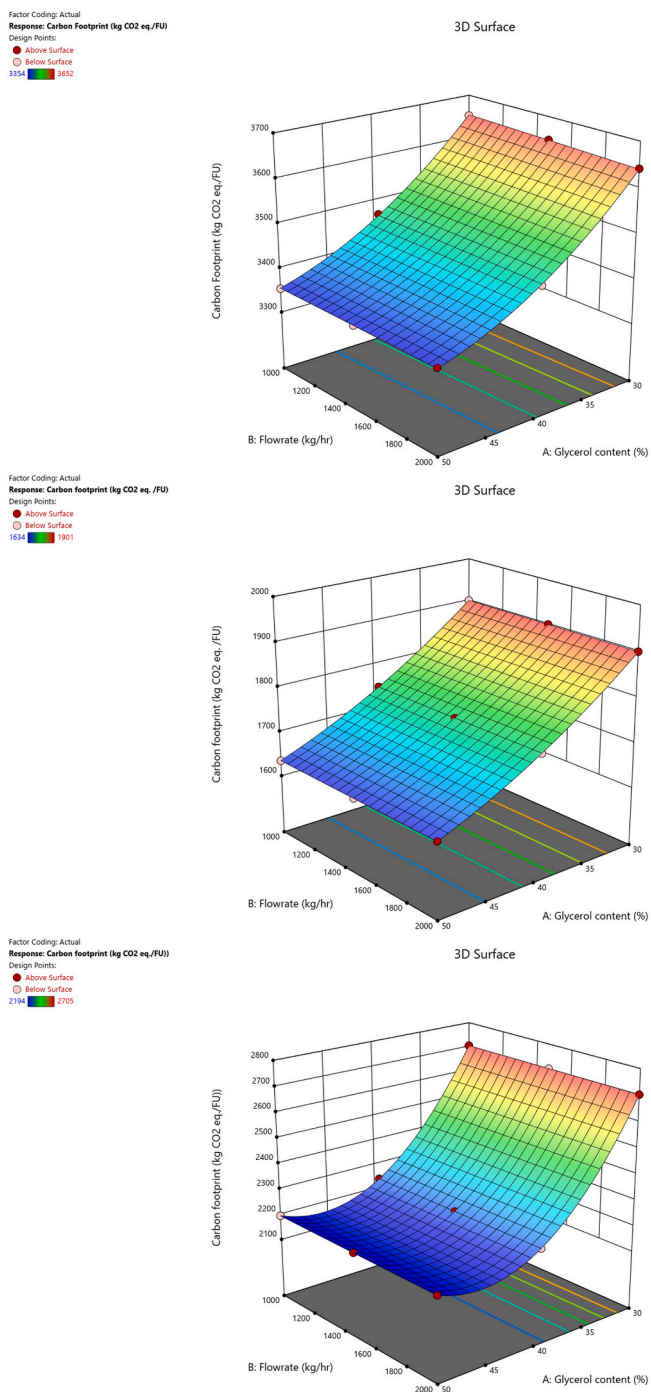


Fig. 10. Response surface plots showing the sensitivity analysis of two parameters (feed flowrate and glycerol content) on carbon footprint for PMP (top), VDP (middle) and IEP (bottom) purification processes.

used compared to the former two methods. However, in this study, it is obvious that the PMP and IEP have a higher environmental impact because of emissions due to

- 1) the use of raw materials required for physicochemical treatments
- 2) the disposal of huge amounts of waste generated, due to impurities of the crude glycerol and raw materials used.

From the use case based on hotspots of the PMP process, it can be observed that the usage of methanol from biomass as opposed to natural gas steam reformed methanol, differently sourced hydrochloric acid

along with altered waste disposal methods lead to significant reductions to the carbon footprint, ozone layer depletion potential, and the human toxicity potential. Since, the raw materials used in PMP and IEP process are in substantial quantities, an LCA study of the exact raw materials producing process could be done to increase the accuracy of this LCA study. Likewise, an LCA investigation of actual waste disposal methods and source of energy would also increase correctness the current LCA study to a higher degree.

Moreover, selecting a purification process solely based on environmental impacts is inappropriate since, economic factors also play a vital role. From this study, it might seem that vacuum distillation is a more sustainable process, however, the huge amounts of energy needed cannot be overlooked. The best approach would be to perform process intensification thereby using combination of various techniques in a hybrid purification process to achieve the desired level of purity. Overall, this study has provided a highlight on the environmental impacts of different crude glycerol purification processes.

CRedit authorship contribution statement

Yash Bansod: Conceptualization, Data curation, Formal analysis, Writing – original draft. **Benjamin Crabbe:** Conceptualization, Data curation, Formal analysis. **Luke Forster:** Formal analysis, Writing – review & editing. **Kamran Ghasemzadeh:** Formal analysis, Writing – review & editing. **Carmin D'Agostino:** Funding acquisition, Investigation, Supervision, Writing – review & editing.

Declaration of competing 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2023.140485>.

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