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Research Paper

Environmental impacts of valorisation of crude glycerol from biodiesel production – A life cycle perspective

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ABSTRACT

Biodiesel production produces significant quantities of impure crude glycerol as a by-product. Recent increases in the global biodiesel production have led to a surplus of crude glycerol, rendering it a waste. As a result, different methods for its valorisation are currently being investigated. This paper assesses the life cycle environmental impacts of an emerging technology for purification of crude glycerol – a multi-step physico-chemical treatment – in comparison to incineration with energy recovery commonly used for its disposal. For the former, three different acids (H_3PO_4, H_2SO_4 and HCl) are considered for the acidification step in the purification process. The results suggest that the H_2SO_4-based treatment is the best option with 17 net-negative impacts out of the 18 categories considered; this is due to system credits for the production of purified glycerol, heat and potassium salts. In comparison to incineration with energy recovery, the H_2SO_4-based process has lower savings for the climate change impact (−311 versus −504 kg CO_2 eq./t crude glycerol) but it performs better in ten other categories. Sensitivity analyses suggest that that the impacts of the physico-chemical treatment are highly dependent on crude glycerol composition, allocation of burdens to crude glycerol and credits for glycerol production. For example, treating crude glycerol with lower glycerol content would increase all impacts except climate change and fossil depletion due to the higher consumption of chemicals and lower production of purified glycerol. Considering crude glycerol as a useful product rather than waste and allocating to it burdens from biodiesel production would increase most impacts significantly, including climate change (22–40 %), while fossil depletion, freshwater and marine eutrophication would become net-positive. The findings of this research will be of interest to the biodiesel industry and other industrial sectors that generate crude glycerol as a by-product.

1. Introduction

Biodiesel production generates about 10 % w/w crude glycerol as a by-product, which contains various impurities, including water, methanol, soap, free fatty acids, ashes and residual reagents (Kumar et al., 2019). The recent increase in global biodiesel production (IEA, 2022) has resulted in a surplus of crude glycerol, much of which is considered as waste (Chozhavendhan et al., 2020; Toldrá-Reig et al., 2020). To reduce waste generation and valorise crude glycerol, different methods are being considered, including energy recovery, composting, utilisation as animal feed and purification for use in different industries (Santibáñez et al., 2011; He et al., 2017). Among the last, utilising refined crude glycerol as a feedstock in the chemical, pharmaceutical or food sectors is of great interest (Chol et al., 2018). Valorising crude glycerol would not only improve the economics and the carbon footprint of the biodiesel industry (Leong et al., 2021), but would also contribute towards a transition to a circular economy.

Various technologies are used or are under development for purification of crude glycerol, including vacuum distillation, ion-exchange adsorption and physico-chemical treatment (Attarbachi et al., 2023; Kumar et al., 2019). Both vacuum distillation and ion-exchange methods are used commercially for purification of crude glycerol and are thus at the technological readiness level (TRL) 9 (Ardi et al., 2015; Jungmeier, 2014). Vacuum distillation is very effective as it produces high purity (>99 %) glycerol (Manosak et al., 2011). However, it is an energy intensive process due to the high boiling point of glycerol and due to the electricity required to operate under vacuum. Moreover, evaporators with low contact times need to be used to avoid thermal decomposition of glycerol, further decreasing the energy efficiency of distillation (Kumar et al., 2019). Although these limitations reduce the economic viability of vacuum distillation (Arora et al., 2015; K-Patents, 2015), this option is the main glycerol purification method used at commercial scale

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for applications where high-purity glycerol (>96 %) is required, particularly in the pharmaceutical and food industries (Chol et al., 2018).

Ion-exchange adsorption can also achieve glycerol purities of >95 % (Busby and Grosvenor, 1952; Asher and Simpson, 2002; Isahak et al., 2010) with the advantages of low costs, simplicity of operation and ease of scaling-up (Ardi et al., 2015). However, ion-exchange resins are sensitive to fouling in the presence of soap and fatty acids and the process generates a significant amount of wastewater, limiting the applicability of this purification method (Kumar et al., 2019). Furthermore, high salt content in crude glycerol makes the process uneconomical due to the regeneration cost (Attarbachi et al., 2023).

Chemical treatment is also used for purification of crude glycerol, which involves its acidification to convert soap into free fatty acids and precipitation of valuable by-products; the latter include phosphate and sulphate salts, depending on the acidifying agent utilised (Kumar et al., 2019). However, combining chemical with physical processes is more effective as it can produce a more refined glycerol in comparison to single-step acidification (Xiao et al., 2013) with purities >95 % (Javani et al., 2012). A physico-chemical process involves multiple steps, including saponification, acidification, filtration, solvent extraction and colour removal (Manosak et al., 2011; Ningaraju et al., 2022; Dhabhai et al., 2016). Although this purification method is still under development, it has attracted attention as it shows potential for production of technical grade glycerol (~95 % purity), typically used in the chemical sector, e.g. as an antifreeze agent, solvent, or feedstock (Chol et al., 2018). The main advantage of this emerging technology is its customisability, as different process steps, operating conditions and reagents can be used to optimise the process depending on the crude glycerol composition. Nonetheless, multiple steps increase the complexity of operation compared to other options mentioned above (e.g., ion exchange). Moreover, the larger number of reagents utilised in the process can increase waste generation and operational costs, potentially limiting the deployment of this technology. Furthermore, this treatment is only suitable if high purity (>96 %) of glycerol required for food and pharmaceutical applications is not needed and if, otherwise, crude glycerol would be incinerated.

There are no life cycle assessment studies (LCA) on the purification of crude glycerol, but a number of LCA studies have assessed the environmental impacts of valorisation of crude glycerol into various energy and chemical products in comparison with the conventional fossil-based counterparts. These products include biogas (Mahabir et al., 2021), electricity and heat (Scrucca et al., 2019); hydrogen (Galera and Gutiérrez Ortiz, 2015; Khalil, 2021); acrolein (Cespi et al., 2015), bio-adhesive (Yang and Rosentrater, 2021), dihydroxyacetone (Thanahiranya et al., 2023), lactic acid (Morales et al., 2015), propanediol (Minh Loy et al., 2023), polyhydroxybutryate (Kolonnage and Chew, 2023), propylene glycol (Gonzalez-Garay et al., 2017), rigid polyurethane foam (Quinteiro et al., 2022) and *tert*-butyl ethers fuel additives (Asdrubali et al., 2015). As the glycerol valorisation processes considered in the above studies are at an early stage of development, most of the studies have focused on identifying the optimum process conditions under which these products can achieve lower impacts than their fossil-based counterparts.

In an attempt to inform the development of the physico-chemical purification technology, this study investigates for the first time its life cycle environmental sustainability via LCA. For the purification process, three treatment alternatives using three different acids (H_3PO_4, H_2SO_4 and HCl) are considered. Moreover, the effects of the key assumptions, such as the variations in the composition of crude glycerol and the quality of the purified glycerol, are evaluated in the sensitivity analyses. The impacts are compared to those of incineration as an alternative option commonly utilised for the disposal of crude glycerol when purification is not an economically viable option (Chilakamarry et al., 2021). Comparison with vacuum distillation, the main purification methods available commercially, is not considered because the physico- chemical treatment yields low purity glycerol and is suitable in cases where this is acceptable, or to avoid incineration of crude glycerol. Since vacuum distillation produces glycerol of higher purity, it is not considered a competing technology to the physico-chemical treatment process.

The rest of the paper is structured as follows: the LCA methods and data are detailed in the next section and the results are presented in Section 3. The conclusions and recommendations are provided in Section 4.

2. Methods

The LCA methodology applied in the study follows the ISO 14040/44 standards (ISO, 2006a; ISO, 2006b). The goal and scope of the study are defined next, followed by inventory data in Section 2.2.

2.1. Goal and scope definition

The main goal of this study is to assess the environmental sustainability of the multi-step physico-chemical process for purification of crude glycerol from biodiesel production. Three alternative acids (H_3PO_4, H_2SO_4 and HCl) that can be used in the acidification step are considered in turn to identify environmentally the most sustainable option, as well as the main hotspots in the system. A further goal is to compare the physico-chemical process to incineration with energy recovery.

The functional unit is defined as the treatment of 1 tonne of crude glycerol. The reason for selecting the functional unit based on the crude glycerol input rather than on the output of pure glycerol is because crude glycerol is currently considered as waste (Chilakamarry et al., 2021), so the waste-treatment perspective is appropriate. The waste-treatment perspective also allows comparison with incineration. As crude glycerol is considered a waste, no burdens are allocated to its production. This assumption, also known as the ‘zero-burden’ approach, is commonly applied in waste management LCA studies (Ekvall et al., 2007; Pradel et al., 2016). The effect of this assumption is evaluated in a sensitivity analysis by allocating burdens of biodiesel production to crude glycerol on an economic basis.

The scope of the study for both the physico-chemical process and incineration starts with the acquisition of waste crude glycerol and ends with the recovery of valuable products (Fig. 1). In the physico-chemical process, crude glycerol is diluted by a solvent, saponified and then acidified (with either H_3PO_4, H_2SO_4 or HCl) to allow the separation of free fatty acids and the precipitation of inorganic salts, which are then removed from the solution. The residual liquid is neutralised, filtered and the solvent removed by evaporation. Finally, purified glycerol is passed over activated carbon to remove colour. In this process, in addition to glycerol, heat and salts are recovered as co-products.

For incineration, it is assumed that crude glycerol is transported to the incinerator site and incinerated with recovery of electricity and heat.

2.2. Inventory data and assumptions

The next section details the data and assumptions for the purification of glycerol, followed by those for incineration. Both systems are assumed to be based in the EU and so average EU data for materials and energy have been used wherever available. All the background life cycle inventory (LCI) data are from the Ecoinvent 3.8 database (Ecoinvent, 2022).

2.2.1. Purification of crude glycerol

As mentioned earlier, the physico-chemical process considered here is still under development so primary industrial data are not available. Instead, data for the operation of the process have been estimated based on literature data for the laboratory-scale process, scaled-up to an industrial scale following the method described in Piccinno et al. (2016). This method describes the procedures for estimating the solvents,

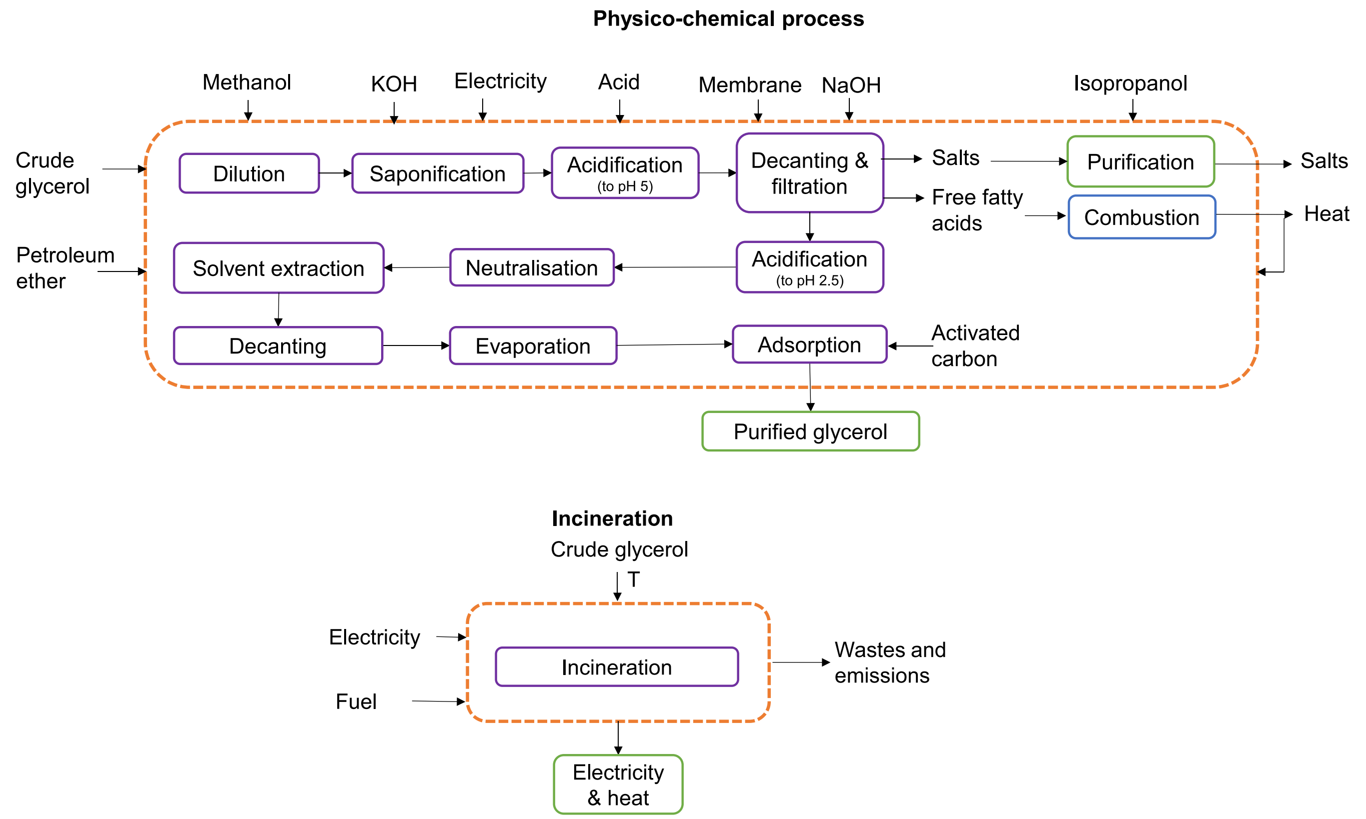

Fig. 1. System boundaries for the physico-chemical process and incineration. [The physico-chemical process has been credited for the production of purified glycerol, salts and surplus heat. Incineration has been credited for generation of electricity and heat. Transport of raw materials and wastes is considered for the physico-chemical process but not shown for simplicity. T: transport.].

reactants and energy use in large-scale chemical plants using data from laboratory-scale processes. Following this approach, the quantities of methanol and other solvents have been scaled-up using a 20 % reduction factor. Furthermore, it is assumed that 95 % of the solvents used in the industrial-scale process would be recovered and recycled (Geisler et al., 2004). The amounts of the KOH and the acids (H_3PO_4, H_2SO_4 or HCl, for the respective options) are estimated based on the optimum pH requirements for the corresponding treatment steps. The energy used for heating, mixing and pumping is estimated using Eq. S1-S3 in the Supplementary Information (SI). The material and energy consumption in the purification process depends highly on the composition of crude glycerol. As indicated in Table 1, its composition can vary widely because of the wide variety of feedstocks and separation processes used in biodiesel production. In the base case, an average crude glycerol composition shown in Table 1 is used to develop the material and energy balances of the purification process. The effect of variation in the crude glycerol composition on the impacts of the process is investigated in a sensitivity analysis. Inventory data for the base case are summarised in Table 2, while those for the lower and higher values related to crude glycerol composition can be found in Tables S1 and S2 in the SI, respectively. The data for the various steps of the purification process shown in Fig. 1 and the assumptions used in the scaling-up are summarised below.

Table 1
Crude glycerol composition and heating values.[a]

Compound	Average (base case)	Lower glycerol & higher free fatty acids content	Higher glycerol & lower free fatty acids content
Glycerol (wt.%)	40.37	26.76	54.43
Water (wt.%)	12.04	7.98	16.23
Free fatty acids (wt.%)	42.38	61.80	22.30
Ash (wt.%)	5.21	3.45	7.02
HHV (MJ/kg)	23.5	25.4	21.6
LHV (MJ/kg)	21.3	23.0	19.6

[a] Composition based on Manosak et al. (2011), Xiao et al. (2013), Contreras-Andrade et al. (2015), Dhabhai et al. (2016), Chol et al. (2018) and Ningaraju et al. (2022). HHV (higher heating value) calculated based on Demirbaş (1997) and LHV (lower heating value) according to EPA (2007), based on the crude glycerol elemental composition detailed in Table S3.

Crude glycerol is first diluted by methanol (1:1 wt) to reduce its viscosity and ease the operation (Dhabhai et al., 2016; Chol et al., 2018). KOH is then added to the solution in a 1.6:1 mol:mol ratio relative to free fatty acids to saponify the ester content to $>$ 99 % (Ningaraju et al., 2022; Javani et al., 2012). Saponification is carried out at 60 °C over 30 min (Chol et al., 2018; Dhabhai et al., 2016). The solution is then acidified to pH 5 by mixing in slowly (30 min) H_3PO_4, H_2SO_4 or HCl to form free fatty acids and potassium salts (K_2HPO_4, K_2SO_4 or KCl). The acidified solution is left to rest for 5 h to separate. The top layer, containing free fatty acids, is decanted and combusted on site to recover heat. Some of the heat is used in the process (2.3–2.4 GJ/t crude glycerol) and the surplus (7–7.1 GJ/t crude glycerol) is assumed to be exported either to nearby industrial installations or district heating system, crediting the system for the avoided heat from natural gas. Emissions from the combustion of fatty acids are estimated via the “LCI calculation tool for regionalised waste treatment” designed by Doka (2021), based on the elemental composition of free fatty acids (Table S5); for the emissions and other inventory data related to combustion, see Table S6.

The remaining solution is filtered to separate the precipitated potassium salts from crude glycerol. Microfiltration on a ceramic membrane is considered for these purposes as it can achieve $>$ 90 % glycerol purity (Buenemann et al., 1988; Xiao et al., 2013; Saleh et al., 2011).

Table 2
Inventory data for the physico-chemical process for different acids.

Inputs/ outputs	Item	H_3PO_4	H_2SO_4	HCl	Unit (per t crude glycerol)	Scaling-up assumptions and data sources
Inputs	Crude glycerol	1.0	1.0	1.0	t	
	Methanol [a]	40.0	40.0	40.0	kg	Laboratory scale data from Chol et al. (2018). Reduced by 20 % compared to laboratory scale as suggested by Piccinno et al. (2016). Assumed to be recovered and recycled at a 95 % rate (Geisler et al., 2004).
	KOH	115	115	115	kg	The amount scaled-up linearly from the laboratory scale using data from Ningaraju et al. (2022).
	Acid [a]	127	63.4	47.1	kg	Calculated to achieve the required pH of reactions.
	Membrane	1.7×10^{-4}	1.7×10^{-4}	1.6×10^{-4}	Module	A ceramic membrane with the composition described by Ou et al. (2023) is considered. Membrane utilisation is estimated according to an average flow of 20 L/m^2 h and a membrane lifetime of five years (Ou et al., 2023).
	NaOH	649	638	616	mg	Estimated based on a membrane cleaning frequency of ten days and 0.5 L NaOH (50 % solution) used per module (Tangsubkul et al., 2006).
	Isopropanol [a]	8.7	7.2	3.8	kg	Laboratory scale using data from Ningaraju et al. (2022). Other assumptions same as for methanol.
	Petroleum ether	106	106	106	kg	Laboratory scale data from Mousavi et al. (2022). Other assumptions same as for methanol.
	Activated carbon	7.1	7.1	7.1	g	Estimated using on data from Manosak et al. (2011).
	Electricity [a]	4.4	4.3	4.2	MJ_{el}	The electricity used for stirring and pumping is estimated using Eq. (S1) and (S2). Average European grid electricity considered (see Table S4).
	Transport [a]	41.0	34.5	32.5	t·km	Includes the transport of all materials and wastes used in the purification process, with the exception of crude glycerol, which is assumed to be produced on site by the biodiesel plant.
Outputs	Purified glycerol	365	365	365	kg	Estimated according to a final purity of 94 % (Buenemann et al., 1988; Xiao et al., 2013; Saleh et al., 2011) and glycerol recovery efficiency of 87 % (Aiken, 2006).
	Potassium salt [a]	218	179	95.9	kg	Estimated based on the stoichiometric relationships.
	Heat [a]	6980	7008	7076	MJ_{th}	Surplus heat from the on-site combustion of free fatty acids after accounting for the heat used in the process, estimated using Eq. (S3).
	Wastes to landfill	52.1	52.1	52.1	kg	Filtration wastes, which includes ash, salts and membrane waste.
	Wastes for incineration [a]	155	153	150	kg	Spent activated carbon and waste solvents.

[a] The quantities of different acids (H_3PO_4, H_2SO_4 and HCl) required in the acidification step vary in the three alternatives of the physico-chemical process. As a result, the amount of potassium salts (K_2HPO_4, K_2SO_4 or KCl) produced and isopropanol used to dissolve the impurities from salts also vary. Due to these variations, the electricity, heat, waste solvents and transport quantities also differ among these alternatives.

Materials and energy required for microfiltration are estimated according to Ou et al. (2023) based on the average transmembrane pressure of 345 kPa (Saleh et al., 2011; Chol et al., 2018; Goswami and Pugazhenthi, 2021). Potassium salts are recovered from the membrane after backwashing. The water from backwashing is decanted and the recovered salts are washed with isopropanol to dissolve the impurities which are precipitated together with the salts (Ningaraju et al., 2022; Javani et al., 2012). The solution is filtered via the ceramic membrane and the recovered salts are dried to evaporate the residual solvent. Isopropanol is recovered by evaporation and reused in the process. After the filtration, the crude glycerol solution is further acidified to pH 2.5 with the same acid used in the first acidification step to complete the acidification process and then neutralised by adding KOH. Solvent extraction with petroleum ether in a 2:1 wt ratio is then utilised to separate and remove residual free fatty acids from the crude glycerol (Mousavi et al., 2022). The glycerol-rich phase is recovered by decanting and the solvent is evaporated, allowing the recovery of both methanol and petroleum ether for further use in the process. Finally, the colour is removed by adsorption on activated carbon and the purified glycerol is recovered.

The amount of purified glycerol produced by the process (Table 2) is estimated according to a final purity of 94 % (Buenemann et al., 1988; Xiao et al., 2013; Saleh et al., 2011) and glycerol recovery efficiency of 87 % (Aiken, 2006). The system expansion approach is used to credit the system for the avoided production of 94 % pure glycerol and potassium salts (K_2HPO_4, K_2SO_4 or KCl) using alternative processes. For the purified glycerol, the avoided production of glycerol from propylene, one of the widely-used commercial methods for producing glycerol (Bagnato et al., 2017), is credited to the system after accounting for the difference in the quality of glycerol produced from these two routes. For this purpose, the approach described by the European Commission in the Product Environmental Footprint guide (Manfredi et al., 2012) is utilised to account for the lower purity of glycerol produced by the process considered here (94 %) compared to its production from propylene (99.7 %). A Q_s/Q_p (quality of the secondary material/quality of the primary material) ratio of 0.19 is considered for this estimation, according to the market prices of glycerol of different purities (Made-in-China, 2022; Oleoline, 2021; ChemAnalyst, 2022). The market prices of glycerol are provided in Table S7. The effect of the variations in the prices on the Q_s/Q_p factor is examined in the sensitivity analysis.

For the potassium salts, Ecoinvent data for K_2SO_4 and KCl have been used to credit the system for the avoided production of these salts. Due to a lack of LCI data for K_2HPO_4, its production has been modelled based on the process information provided in Havelange et al. (2022); the resulting inventory data can be found in Table S8.

The spent activated carbon and waste solvents are assumed to be incinerated with energy recovery and the system is credited for the heat from natural gas and average European grid electricity. The remaining salts removed by filtration after the solvent extraction step and the waste membrane are landfilled. Note that the purification process is assumed to be carried out on the site of the biodiesel plant. Accordingly, no transportation of crude glycerol is considered. A generic transportation distance of 100 km is considered for the materials utilised by the process, while distances of 50 and 25 km are assumed for the incineration and landfill sites, respectively.

2.2.2. *Incineration*

As mentioned in previous sections, purification of crude glycerol is not always an economically viable option; hence it is often disposed of via incineration with energy recovery, due to its significant energy content (16.1–22.6 MJ/kg crude, depending on the feedstock) (Bala-Litwiniak and Radomiak, 2018; Weidema, 2015). The LCI data for incineration of crude glycerol are calculated via the “LCI calculation tool for regionalised waste treatment” (Doka, 2021) using its elemental composition (Table S2) and energy content (Table 1). The detailed inventory data for the incineration process are reported in Table S9. The system is credited for the equivalent amount of European grid electricity (see Table S4 for the composition) and heat from natural gas. The latter is considered appropriate as natural gas is the major source of heat in Europe.

2.3. *Life cycle impact assessment*

GaBi 10.7 software (Sphera, 2019) has been used for the LCA modelling. The life cycle impacts are estimated using the ReCiPe 2016V1.1 impact assessment method at the mid-point level, following the hierarchist approach (Huijbregts et al., 2017). All 18 impact categories are considered, as follows: climate change (CC), fossil depletion (FD), metals and minerals depletion (MMD), water depletion (WD), human toxicity - cancer & non-cancer (HTc & HTn-c), freshwater, marine and terrestrial ecotoxicity (FET, MET and TET, respectively), freshwater and marine eutrophication (FE and ME), land use (LU), terrestrial acidification (TA), particulate matter formation (PMF), photochemical ozone formation - ecosystems & human health (POFe & POFh), ozone depletion (OD) and ionizing radiation (IR).

3. Results and discussion

The next section first presents the environmental impacts of the glycerol purification process, followed by comparison with incineration in Section 3.2 . The subsequent Section 3.3 discusses the findings of the sensitivity analyses.

3.1. *Impacts of crude glycerol purification*

The environmental impacts of the purification process and the relative contributions of different life cycle stages are summarised in Fig. 2 and Fig. 3, respectively. As can be seen in Fig. 2, the climate change (CC) impact of treating crude glycerol is net-negative for all three types of acid, with the utilisation of H_2SO_4 leading to the lowest impact (−311 kg CO_2 eq./t crude glycerol) and HCl to the highest (−171 kg CO_2 eq./t). This is due to the system credits from the avoided production of purified glycerol, potassium salts and heat being higher than the impact of the treatment processes, as shown in Fig. 3. Note that the same amounts of purified glycerol and heat are credited to each variant of the treatment process as comparable amounts of both are produced regardless of the type of acid used (Table 2). However, due to the difference in the quantities and the type of potassium salts (K_2HPO_4, K_2SO_4 and KCl) produced by the three process variants, different system credits are applied per t of crude glycerol, specifically, 245 kg CO_2 eq./t for the process with H_3PO_4, 173 kg CO_2 eq. for H_2SO_4 and 56.8 kg CO_2 eq. for HCl. The higher credits for K_2HPO_4 compared to K_2SO_4 and KCl are mainly due to the higher avoided impact from the utilisation of phosphoric acid for its production (Table S8). Nonetheless, the H_3PO_4-based process causes a higher CC impact than that with H_2SO_4 (−226 vs −311 kg CO_2 eq./t crude glycerol) due to the higher impact from the production of H_3PO_4 relative to HCl and H_2SO_4. Furthermore, H_3PO_4 behaves as a monoprotic acid, thus a larger amount of the acid is required to achieve the desired pH in the acidification step ($pH \leq 5$).

The use of KOH is the main source of the CC impact for all three process variants (37–48 % before the system credits), while the contribution of the acids varies from 1 % (H_2SO_4) to 23 % (H_3PO_4). It should be noted that > 99 % of the acids and KOH are utilised for the saponification or acidification of the fatty acids. Therefore, the impact from their utilisation could vary significantly depending on the crude glycerol composition. This is discussed further in Section 3.3.1.

Solvents and waste treatment also show significant contributions to CC for all three process variants: 19–25 % each before the credits. Of this, the treatment of waste solvents accounts for 87 % of the impact from waste treatment. Accordingly, reducing the amount of solvents used in the process or improving their recovery would help to decrease the impact from crude glycerol treatment. Other materials utilised, electricity and transport show negligible contributions to CC.

The H_2SO_4-based process also has lower environmental impacts than the process using the other two acids in the remaining 17 categories. All its impacts are net-negative, except for ionising radiation, while the HCl

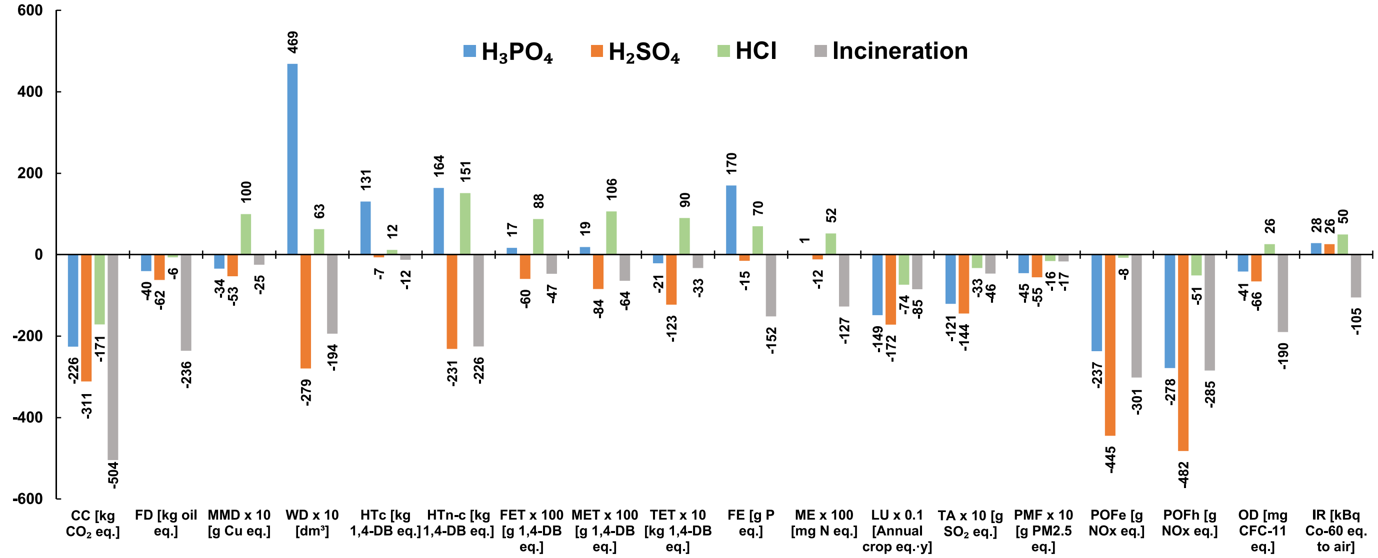

Fig. 2. Environmental impacts of the three variants of the physico-chemical process for crude glycerol treatment in comparison with incineration. [All impacts are expressed per tonne of crude glycerol. The three acids (H_3PO_4, H_2SO_4 and HCl) in the legend refer to the variants of the physico-chemical process utilising different acids in the acidification step. Waste treatment comprises incineration of liquid wastes and landfill of solid wastes. Some impacts have been scaled to fit. To obtain the original values, multiply with the factor on the x-axis, where relevant. CC: climate change; FD: fossil depletion; WD: water depletion; MMD: metals and minerals depletion; HTc: human toxicity cancer; HTn-c: human toxicity non-cancer; FET: freshwater ecotoxicity; MET: marine ecotoxicity; TET: terrestrial ecotoxicity; FE: freshwater eutrophication; ME: marine eutrophication; LU: land use; POFe: photochemical ozone formation - ecosystems; POFh: photochemical ozone formation - human health; OD: ozone depletion; PMF: particulate matter formation; TA: terrestrial acidification; IR: ionizing radiation. DB: dichlorobenzene].

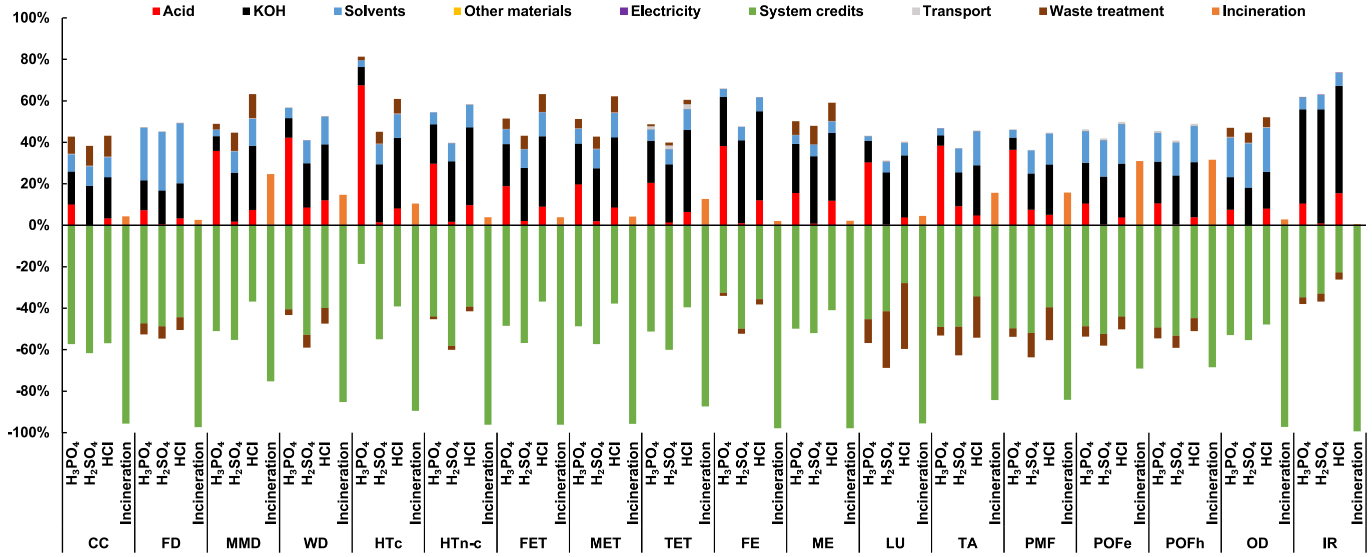

Fig. 3. Contribution analysis for the three variants of the physico-chemical process for crude glycerol treatment and incineration. [See Fig. 2 for the abbreviations].

and H_3PO_4-based systems have net-negative impacts in seven and ten categories, respectively. Like CC, the savings in the impacts are due to the credits for the purified glycerol and the co-products. All three systems have net-positive ionising radiation (25.7–49.5 kBq Co-60 eq./t crude glycerol) mainly due to the high electricity requirement for KOH production. KOH is also the main contributor to 16 impacts for the H_2SO_4 and HCl-based process (44–87 % and 46–74 %, respectively). It is also the main cause of six impacts from the H_3PO_4-based process: freshwater (39 %) and marine ecotoxicity (38 %), marine eutrophication (47 %), ionising radiation (73 %), photochemical oxidant formation ecosystem (43 %) and human health (44 %). The use of solvents is the hotspot for fossil (54–62 %) and ozone depletion (40–48 %) in all three systems. If, however, methanol is used instead of the other two solvents, the impacts in all three systems would decrease significantly (10–28 %) for most categories, with the highest reductions in fossil and ozone depletion.

The net-positive toxicity and eutrophication impacts from the H_3PO_4-based process are mainly due to the impacts from H_3PO_4 production, which contributes for 31–85 % (before credits) to these categories. Overall, H_3PO_4 is the hotspot for nine impacts, contributing 43–83 %. By comparison, H_2SO_4 contributes significantly (21–25 %) only to three impacts and HCl to 13 (7–23 %). Other materials, transport and waste treatment are minor contributors to the impacts in all three systems. However, waste treatment generates credits in ten impacts (Fig. 3) due to the avoided burdens from the heat and electricity generated by solvent incineration.

As observed for climate change, the H_3PO_4-based process receives higher credits for the avoided production of K_2HPO_4 compared to the potassium salts produced when using the other two acids. However, in case the recovery of potassium salts was not feasible, the environmental impacts from the H_3PO_4 process would be much higher compared to those discussed above, leading to net-positive values in all categories, instead of the currently ten categories. Similarly, the impacts of the H_2SO_4-based process would be net-positive for 12 categories. Therefore, the environmental performance of H_3PO_4 and H_2SO_4-based processes highly depends on the recovery of potassium salts.

3.2. Comparison with incineration

As shown in Fig. 2, the climate change impact of crude glycerol incineration is also net-negative (-504 kg CO_2 eq./t crude glycerol) due to credits for the avoided heat and electricity production. This shows that incineration of a tonne of crude glycerol would achieve 193–333 kg CO_2 eq. greater saving in CC than the physico-chemical process. However, it should be noted that credits for incineration are strongly dependent on the energy mix assumed to be displaced and would vary significantly with the geographical location (Ekvall et al., 2021). Moreover, EU decarbonisation strategies are expected to decrease the climate change impact of energy, and especially that of electricity, in the future (EC, 2018). Thus, it is expected that credits from energy generation will decrease in future years. For example, if Europe achieves carbon–neutral electricity by 2050, the credits for electricity from incineration would decrease by 48 %, leading to a climate change impact of −249 kg CO_2 eq./t crude glycerol, which would then favour H_2SO_4-based treatment with −311 kg CO_2 eq./t. In addition, the climate change impact from the electricity used in the physico-chemical process and the associated supply chains would also reduce and all three process variants could surpass incineration (note that this analysis is beyond the scope of the paper). Furthermore, if the biogenic CO_2 emissions (1.7 t CO_2/t crude glycerol) from incineration of crude glycerol were accounted for (not included in this analysis as per the usual LCA practice), avoiding incineration and instead using the physico-chemical treatment such as the one considered here would avoid these emissions, while at the same time recovering valuable products. This would also be congruent with the circular economy approach.

Similar to climate change, incineration has net-negative impacts in all other categories considered due to credits for the production of heat and electricity. However, compared to incineration, the H_2SO_4-based process performs better with higher net-savings in ten categories, including human toxicity, ecotoxicity, acidification, photochemical ozone formation, metal and water depletion. On the contrary, the HCl process has higher impacts than incineration in all the categories considered, emerging as the least sustainable option for the treatment of crude glycerol. Finally, in comparison to incineration, the H_3PO_4 system is better in only four out of 18 categories, i.e., metal depletion, land use, terrestrial acidification and particulate matter formation.

Overall, this analysis highlights the potential trade-offs related to the adoption of a strategy based on the principle of the circular economy for the treatment of crude glycerol in comparison to its disposal as a waste. However, the environmental performance of the physico-chemical process might improve with the improvement in the quality of purified glycerol, which will result in higher credits from the recovery of purified glycerol. This potential improvement option is discussed in Section 3.3.3. Furthermore, the production of goods will need to adapt to a circular economy model as part of the European Green Deal (EC, 2019). Accordingly, increasing the amount of crude glycerol valorised will allow the biodiesel industry to adhere to environmental regulations by establishing a circular economy system aimed at reducing the amount of wastes produced.

3.3. Sensitivity analysis

The sensitivity analysis explores the influence of the following three parameters which could affect the impacts of the physico-chemical treatment process: i) crude glycerol composition; ii) allocation of burdens to crude glycerol as a valuable product from the production of biodiesel; and iii) credits for the production of purified glycerol assuming its different purity.

3.3.1. Effect of crude glycerol composition

As shown in Table 1, crude glycerol composition can vary significantly which affects material and energy requirements, as well as the amount of the outputs from the treatment process (Tables S1 and S2). As mentioned in Section 2.2, this is because the acid and KOH are required for the acidification and saponification of the free fatty acids in the 1:1 and 1.6:1 wt ratios, respectively. Moreover, the energy requirements of the process are also affected by the free fatty acids content as heat is recovered from their combustion. To test these effects on the results, two different compositions of crude glycerol are considered compared with the base case: i) lower glycerol (26.76 %) and higher free fatty acids (61.8 %) content; and ii) higher glycerol (54.43 %) and lower free fatty acids (22.3 %) content (see Tables S1 and S2). This compares with 40.37 % of glycerol and 42.38 % of fatty acids in the base case (Table 1).

As can be inferred from Table 3, the lower glycerol content in crude glycerol would reduce the climate change impact respectively by 31 %, 25 % and 19 % (by 96, 56 and 32 kg CO_2 eq./t crude glycerol) for the H_2SO_4, H_3PO_4 and HCl-based process relative to the base case. This is due to the additional credits for the production of potassium salts and heat, which offset the impacts from the additional acid and KOH consumption and lower credits for the purified glycerol. More specifically, the higher amount of KOH and acid required would increase the production of potassium salts by 46 % for all three acids compared to the base case. Similarly, the combustion of a higher amount of fatty acids would allow exporting 62 % more heat produced by the system, while the amount of glycerol produced would decrease by 34 % compared to the base case. On the other hand, treating crude glycerol with the higher glycerol content would have the opposite effect, increasing the climate change impact by 33–99 kg CO_2 eq./t crude glycerol (19–32 %) across the three acids compared to the base case. A similar effect is also observed for fossil depletion, which would reduce by 72–305 % for the lower glycerol content and increase by 74–314 % for the higher content. However, for all other impacts, the effect of the change in the crude glycerol composition is opposite. This is because, in the case of the lower glycerol content, the additional credits from heat and potassium salts would not counterbalance the loss of credits from glycerol production and the additional impacts of acid and KOH consumption. By contrast,

Table 3
The effect of crude glycerol composition on the impacts of the physico-chemical process.

Impacts (per t crude glycerol) [a]	H_3PO_4			H_2SO_4			HCl		
	Base case[b]	*Lower crude glycerol and higher fatty acid content*[c]	*Higher crude glycerol and lower fatty acid content*[d]	*Base case*[b]	*Lower crude glycerol and higher fatty acid content*[c]	*Higher crude glycerol and lower fatty acid content*[d]	*Base case*[b]	*Lower crude glycerol and higher fatty acid content*[c]	*Higher crude glycerol and lower fatty acid content*[d]
CC [kg CO_2 eq.]	−226	−282	−167	−311	−407	−212	−171	−203	−138
FD [kg oil eq.]	−40.1	−74.1	−4.0	−62.3	−107	−16.0	−6.3	−25.5	13.5
MMD x 10 [g Cu eq.]	−34.0	−9.9	−58.2	−52.8	−36.6	−69.6	100	186	10.8
WD x 100 [dm^3]	469	964	−21.8	−279	−139	−424	62.6	359	−244
HTc x 100 [g 1,4-DB eq.]	131	200	59.5	−6.5	−0.1	−13.1	11.9	26.7	−3.4
HTn-c [kg 1,4-DB eq.]	164	443	−118	−231	−137	−329	151	421	−128
FET x 100 [g 1,4-DB eq.]	16.7	78.4	−40.3	−59.5	−37.4	−82.4	87.6	177	−5.0
MET x 100 [g 1,4-DB eq.]	19.1	95.0	−51.3	−84.3	−61.2	−108	106	217	−7.8
TET x 10 [kg 1,4-DB eq.]	−21.2	32.9	−75.8	−123	−116	−130	90.4	195	−17.8
FE [g P eq.]	170	321	19.8	−14.8	47.6	−79.3	69.8	171	−34.7
ME x 10 [g N eq.]	1.1	62.7	−67.0	−11.7	47.3	−72.7	52.0	140	−39.2
LU x 10 [Annual crop eq.·y]	−149	−111	−188	−172	−143	−201	−73.8	−0.6	−149
TA x 10 [g SO2 eq.]	−121	−96.3	−144	−144	−131	−158	−32.7	31.9	−99.6
PMF x 10 [g PM2.5 eq.]	−45.5	−31.0	−59.5	−55.3	−45.6	−65.4	−15.7	12.2	−44.5
POFe x 10 [g NO_x eq.]	−237	−12.2	−463	−445	−319	−574	−7.6	318	−344
POFh x 10 [g NO_x eq.]	−278	−49.2	−509	−482	−351	−618	−51.0	278	−391
OD x 10 [mg CFC-11 eq.]	−41.4	−33.4	−49.0	−65.7	−69.2	−62.1	26.2	64.7	−13.6
IR [kBq Co-60 eq. to air]	28.5	58.1	−0.6	25.7	53.0	−2.5	49.5	87.7	10.1

[a] The negative values represent net savings in the relevant impacts. See Fig. 2 for the abbreviations.

[b] Base case: glycerol content = 40.37 %; fatty acid content = 42.38 %.

[c] Lower glycerol content = 26.76 %; higher fatty acid content = 61.8 %.

[d] Higher glycerol content = 54.43 %; lower fatty acid content = 22.3 %.

the higher glycerol content would result in net-negative impacts for the H_2SO_4-based process in all the categories considered due to the decreased impacts from the acid and KOH utilisation. Following a similar trend, the number of net-negative impacts for the H_3PO_4 and HCl-based process would increase from ten in the base case to 16 and from seven to 15, respectively. The above analysis shows that changes in the crude glycerol composition would have a significant effect on the environmental sustainability of crude glycerol treatment.

3.3.2. Effect of allocating burdens to crude glycerol

In the base case, crude glycerol has been assumed to be a waste from biodiesel production and hence it has been considered burden-free. Here in the sensitivity analysis, it is considered as a valuable by-product and would therefore carry some of the burdens associated with the biodiesel production process. For this purpose, inventory data for the biodiesel production have been sourced from literature (Dufour and Iribarren, 2012) and are provided in Table S10. The burdens between biodiesel and crude glycerol have been allocated using economic allocation, based on the average biodiesel and crude glycerol prices in the period 2017–2021 (Table S11). As can be seen in Table S11, due to the variations in the prices of biodiesel and crude glycerol in the period, the burdens allocated to crude glycerol vary between 2.8 % and 5.2 % of the total burdens from the biodiesel production process. Therefore, this allocation range is considered here, rounded off to 3 % and 5 %. The sensitivity analysis focusses on the H_2SO_4-based process as the most environmentally sustainable option among the three process variants.

As indicated in Fig. 4, allocating burdens to crude glycerol would increase the climate change impact by 22 % and 40 % for the 3 % and 5 % burden allocation, respectively, relative to the base case. All other impacts would also increase due to the additional burdens from crude glycerol. The most noticeable increases are observed for the 5 % allocation whereby fossil depletion, freshwater and marine eutrophication become net-positive as opposed to being net-negative in the base case. Therefore, allocating the burdens to crude glycerol would have a significant effect on some impacts, including climate change, photochemical oxidants and ozone depletion – although these remain net-negative, their increase relative to the base case is significant (Fig. 4).

3.3.3. Effect of credits for the production of glycerol

In the base case, a conservative Q_s/Q_p factor of 0.19 has been assumed based on the lower price of 94 % purified glycerol to estimate the credits for its production. However, as shown in Table S7, the prices for different grades of glycerol fluctuate significantly. Therefore, the effect of using different credits on the impacts of the physico-chemical process is investigated for the Q_s/Q_p factors of 0.25, 0.46 and 1.00. The first two are estimated by considering the variation in the prices from different sources (Made-in-China, 2022; Oleoline, 2021; ChemAnalyst, 2022; Argus, 2022), as shown in Table S7. For the Q_s/Q_p factor of 1, it is assumed that the quality of purified glycerol might increase with the maturity of the process. Accordingly, no difference in the price of the glycerol produced from crude glycerol and that currently found on the market has been assumed for this scenario. The analysis here also focusses on the H_2SO_4-based process, for illustrative purposes.

As shown in Fig. 5, higher Q_s/Q_p factors would reduce further the climate change impact of the physico-chemical process by 30 % for the 0.25 factor to 390 % for the factor of 1, relative to the base case due to the higher credits for the avoided production of purified glycerol. A similar trend can also be observed for the other impacts. Furthermore, the H_2SO_4-based process would perform better than incineration in 11, 15 and 17 categories for the Q_s/Q_p factors of 0.25, 0.46 and 1, respectively, instead of the ten categories in the base case.

4. Study limitations

The main limitation of the study is that the inventory data for the physico-chemical purification process are derived from the data from laboratory experiments. Since this process is at an early stage of development, it is likely to improve during further development. Furthermore, various assumptions have been made during the scaling up to the industrial scale. Although efforts have been made to quantify the data at the industrial-scale based on the recommended frameworks in the literature, the estimated data still have a degree of uncertainty. Moreover, the material and energy used in the process are highly dependent on the crude glycerol composition, which varies significantly. This limitation has been addressed through the sensitivity analysis.

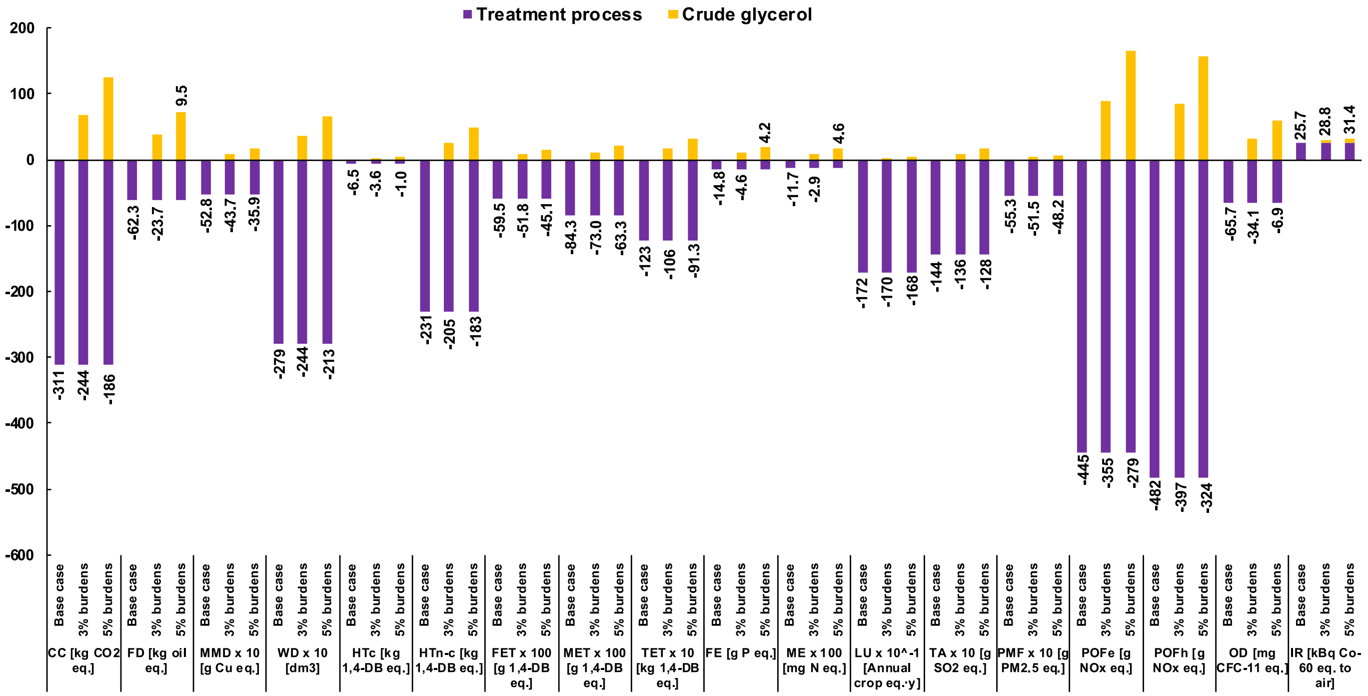

Fig. 4. The effect on the impacts of the H_2SO_4-based process of different percentage of burden allocation to crude glycerol. [All impacts are expressed per tonne of crude glycerol. Base case: burden-free crude glycerol. See Fig. 2 for the abbreviations].

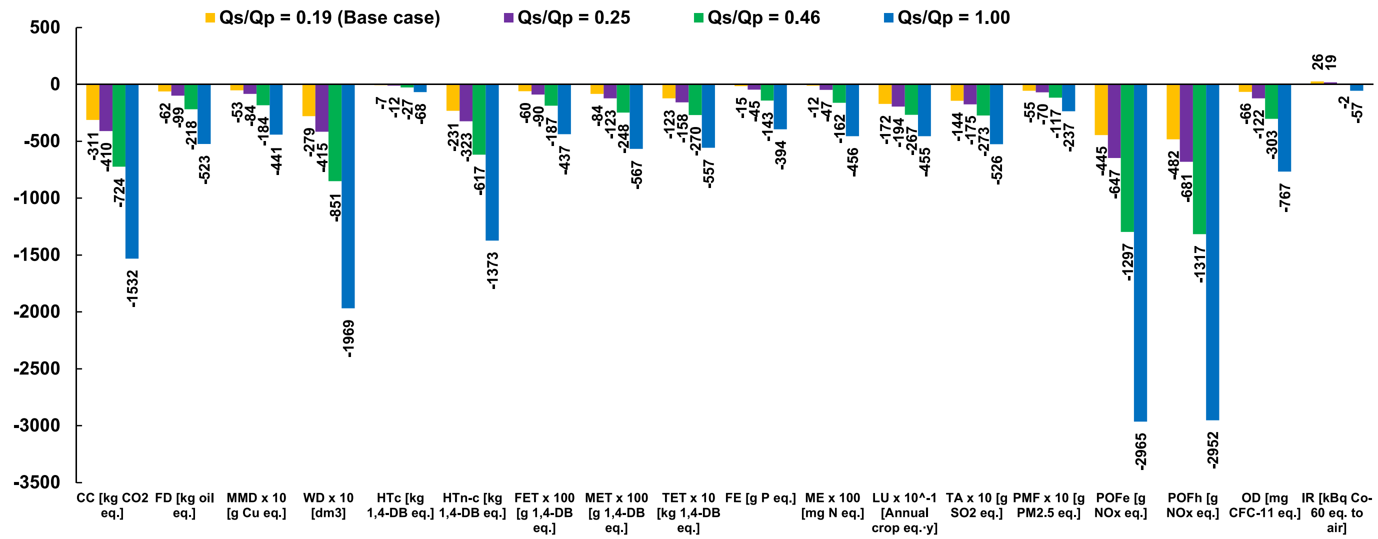

Fig. 5. The effect on the impacts of the H_2SO_4-based process of different credits for production of glycerol. [All impacts are expressed per tonne of crude glycerol. Qs/Qp represents the ratio of prices of glycerol produced from crude glycerol and that found on the market, reflecting their different purity – see Table S7 for further details. See Fig. 2 for the abbreviations].

5. Conclusions

This study has assessed the environmental sustainability of a multi-step physico-chemical treatment for the purification of crude glycerol in comparison to incineration for energy recovery. The results for the former show that using H_2SO_4 in the acidification step instead of H_3PO_4 or HCl is the best option with net-negative impacts in 17 out of 18 categories. By comparison, the H_3PO_4 and HCl- based process have net-negative impacts in ten and seven categories, respectively. The difference in the impacts between the three process variants is mainly due to the different acids utilised and the credits for the recovery of potassium salts. KOH is the main contributor to climate change (37–48 %) and also shows significant contributions (11–87 %) to all other impacts. In the H_3PO_4-based treatment, the acid is the main hotspot (42–83 %) for nine impacts, while the contribution of H_2SO_4 and HCl in their respective processes is $<$ 25 %.

In comparison to incineration, the physico-chemical process has notably lower savings in the climate change impact (38-66 %). However, compared to incineration, the H_2SO_4-based process performs better in ten out of 18 categories. On the contrary, the process with H_3PO_4 and HCl has higher impacts than incineration for most of the categories.

The sensitivity analyses suggest that the impacts of the physico-chemical treatment are highly dependent on crude glycerol composition, allocation of burdens to crude glycerol and credits for glycerol production. For example, lower glycerol content in crude glycerol would lead to lower climate change and fossil depletion due to the higher credits from the increased production of the by-products (heat and potassium salts) but all other impacts would increase due to the higher consumption of chemicals in the treatment process and lower production for purified glycerol. The opposite trend is observed in the case of treating crude glycerol with higher glycerol content.

Overall, these results show the potential of the physico-chemical process for the treatment of crude glycerol in comparison to incineration. In this context, this purification process would help to improve the sustainability of the biodiesel industry by establishing a circular economy system aimed at reducing the amount of wastes produced and increasing the economic value of the process through the production of valuable products. Future studies of this technology should investigate its potential benefits on a global scale based on its potential market penetration. Moreover, future studies should also consider socio-economic aspects of crude glycerol purification in the context of biofuels production.

CRediT authorship contribution statement

Marco Tomatis: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Harish Kumar Jeswani:** Writing – original draft, Visualization, Methodology, Formal analysis, Conceptualization. **Adisa Azapagic:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

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

All data are included in the paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2024.03.005.

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