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Electronic Supplementary Information

Environmental and economical perspectives of a glycerol biorefinery

Giacomo M. Lari,[a] Giorgio Pastore,[a] Moritz Haus,[a] Yiyu Ding,[b] Stavros Papadokonstantakis,[b,*]
Cecilia Mondelli[a,*] and Javier Pérez-Ramírez[a,*]

[a] Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland.
E-mail addresses: cecilia.mondelli@chem.ethz.ch; jpr@chem.ethz.ch

[b] Division of Energy Technology, Department of Space, Earth and Environment, Chalmers University of Technology, Hörsalsvägen 7B, 41296 Gothenburg, Sweden.
Email address: stavros.papadokonstantakis@chalmers.se

1. Process modelling

Hereon, the modelling of the processes reported in the main manuscript with respect to the various glycerol upgrading routes is described in detail. In all cases, reactors are simulated considering that the conversion of the reactant streams occur with the same performance observed in laboratory-scale experiments; for a detailed design of full-scale continuous-flow or batch reactors, which is outside the scope of the present study, detailed information about the reaction kinetics, mass and heat transfer phenomena, pressure drop, *etc.*, would be required. The purification of pure glycerol is outlined only once in the next paragraph, since it is common to all of the processes. The software Aspen Plus V8.6 was used for all simulations.

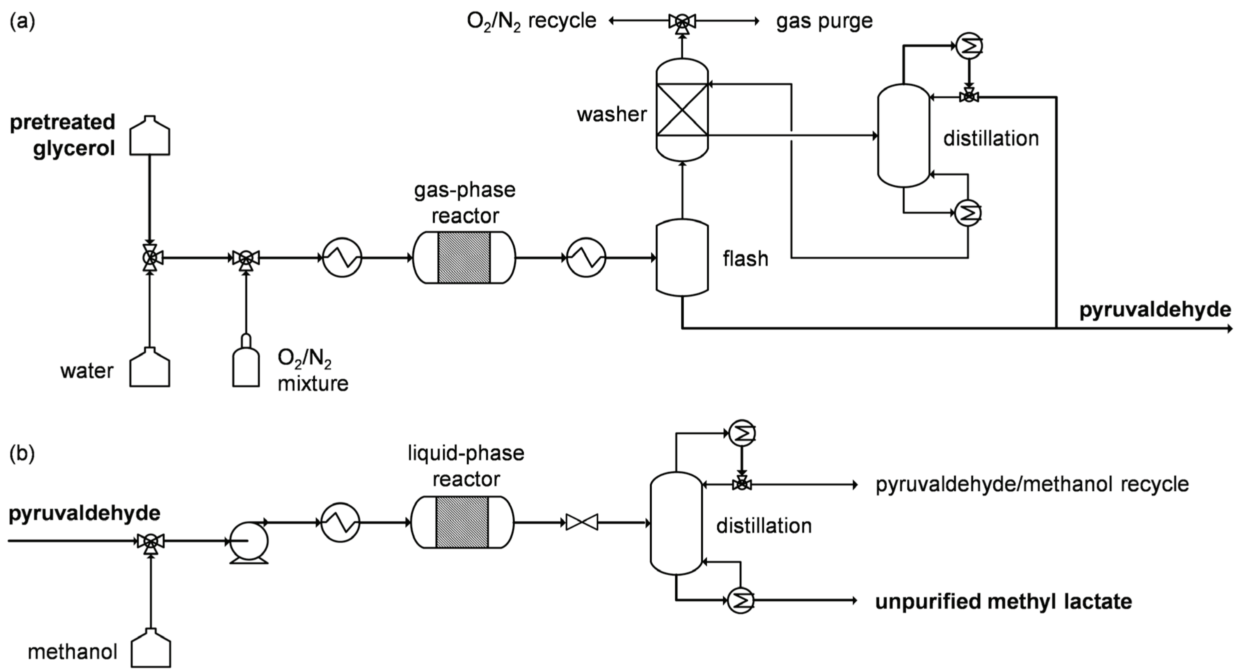
1.1. Crude glycerol purification

The crude glycerol composition and upstream processing correspond to those already reported.[1] Briefly, the ash in the feedstock is almost completely separated (99%) by conventional filtration (SSplit) and used for landfill according to the Ecoinvent model (Version 3, Landfill, ash from paper). Since in 70% of the US biodiesel production, sodium methylate represents the main constituent of the ash fraction,[1] it is assumed that the ash solely comprises this chemical species. The glycerol stream is then treated through flash evaporation (Flash2) at ambient pressure and 463 K to remove most of the methanol (92%) and the water (85%). The subsequent separation of matter organic non-glycerol (MONG) is not rigorously modelled and a separator (Sep) is simply applied assuming 100% separation of MONG and of the remaining ash due to the lack of data on the process.[1] Two scenarios are considered for the fate of the methanol and MONG waste streams, *i.e.*, both streams are treated in a conventional wastewater treatment plant or in a waste-to-energy incineration facility, modelled according to Rerat *et al.*[2] This upstream processing of crude glycerol produces an inlet stream for the reactor consisting of 98.5 wt.% glycerol, 1.2 wt.% water and 0.3 wt.% methanol.

1.2 Lactic acid

Step 1. Glycerol oxidehydration to pyruvaldehyde

Purified glycerol is mixed with water and with O_2 diluted by N_2, evaporated at ambient pressure and heated up to the reaction temperature (623 K) at the inlet of the reactor (**Scheme S1a**). The molar O_2:N_2:glycerol:water ratio is 1:80:2:94 and the flow of the substrate 0.22 kmol h^{-1}. For the process assessment of this unit, the data of the reactions taking place during the chemocatalytic gas-phase oxidehydration of glycerol are sufficient, which are summarised in **Table S1**. An isothermal continuous-flow fixed-bed reactor (RStoic) is applied in the calculations, which is loaded with 3.3 t of 5 wt.% Ag/Al_2O_3 and operated for 72 h. After this time, the catalyst requires regeneration by calcination.



Scheme S1. Flowsheet of the lactic acid production process from glycerol *via* pyruvaldehyde. (a) Preparation of pyruvaldehyde by oxidehydration over Ag/Al_2O_3 with and (b) its isomerisation over Sn-MFI in methanol. The purification and hydrolysis of methyl lactate has been reported previously.[1]

Table S1 Reactions and yields considered in the process model of the gas-phase oxidehydration of glycerol over Ag/Al_2O_3. Glycerol conversion is 77.8%.

Reaction	Yield (%)	Product
$C_3H_8O_3 + 0.5O_2 \rightarrow C_3H_4O_2 + 2H_2O$	62.1	Pyruvaldehyde
$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O$	10.2	Acetol
$C_3H_8O_3 + O_2 \rightarrow C_3H_4O_3 + 2H_2O$	4.18	Pyruvic acid
$C_3H_8O_3 + 0.5O_2 \rightarrow C_2H_4O_2 + 2H_2O$	0.7	Acrylic acid
$C_3H_8O_3 + 0.5O_2 \rightarrow C_3H_6O_3 + H_2O$	0.4	Dihydroxyacetone
$C_3H_8O_3 + 0.5O_2 \rightarrow C_3H_6O_3 + H_2O$	0.1	Glyceraldehyde
$C_3H_8O_3 + 3.5O_2 \rightarrow 3CO_2 + 4H_2O$	0.2	CO_2

Step 2. Pyruvaldehyde purification

The reactor outlet contains, in addition to N_2 and unreacted O_2, 42.16 wt.% water, 2.22 wt.% pyruvaldehyde, 0.29 wt.% acetol, 0.14 wt.% pyruvic acid, 0.02 wt.% acrylic acid, 0.01 wt.% dihydroxyacetone, 0.01 wt.% glyceraldehyde and 0.02 wt.% CO_2. This hot gas stream is cooled to nearly ambient temperature (*i.e.*, 303 K, assuming cooling water available at 283 K and a 20 K minimum temperature approach in the heat exchangers) to be condensed in a flash separator. This results in a liquid stream containing 2.85 wt.% pyruvaldehyde in water. Still, due to the low boiling point of this component, 43% of the pyruvaldehyde is still present in the gas phase after separation. Thus, the top stream of the flash separator is treated in a washer (RadFrac). Aiming at generating a 40 wt.% aqueous solution of pyruvaldehyde, *i.e.*, the maximal concentration allowed to avoid decomposition of the product, the liquid phases at the outlet of the flash and of the gas washer are mixed and fed to a distillation column (DSTWU) operated at 1 bar and with a pyruvaldehyde recovery of 99% (**Scheme S1a**).

Step 3. Pyruvaldehyde conversion to methyl lactate in methanol

The 40 wt.% pyruvaldehyde stream obtained according to the units shown in **Scheme S1a** is diluted to 3 wt.% with methanol and is fed to a continuous-flow fixed-bed reactor operated at 343 K (**Scheme S1b**).

The reactor, processing 0.24 kmol h^{-1} of the substrate, is loaded with 1.2 t of a tin-containing zeolite prepared by a post-synthetic strategy[3] (Sn-MFI) and operated for 72 h before regeneration. Over this time span, average pyruvaldehyde conversion and methyl lactate selectivity of 70 and 85%, respectively, are achieved. The formation of glyceraldehyde hemiacetal is considered to exclusively account for the residual selectivity of 15%. Downstream of the reactor, a distillation column separates 99% of the dilution methanol, generating a feed containing 75 wt.% of methyl lactate. The latter is sent to a second distillation column and finally hydrolysed to lactic acid.

Heat integration

Due to the energy-intensive separations by distillation required, process heat integration was performed in order to reduce costs associated with thermal utility consumption (cooling water, steam, natural gas). High integration potential is present because of the high reaction and separation temperatures. The resulting heat exchanger network was designed according to heuristic considerations, taking into account a realistic minimum temperature approach of 10 K. As a result of this configuration, in the overall process, the total energy requirement is reduced by *ca.* 45%.

1.3. Acrylic acid

Step 1. Glycerol dehydration to acrolein

Purified glycerol is mixed with process water to achieve a concentration of 40 wt.%, thereafter N2 and recycled glycerol are added and the resulting mixture is heated to 553 K and fed to a continuous-flow fixed-bed reactor (**Scheme S2**). The inlet composition is 26.5% glycerol, 42.4% water and 31.1% N_2, on mass basis. The reactor is assumed to be heated by an external heating utility and to operate under isothermal conditions (553 K). The stoichiometric reactions considered in the modelling of the reaction over $FePO_4$ are reported in **Table S2**. The reactor is operated for 70 h before removal and replacement of the catalyst.

Step 2. Acrolein purification

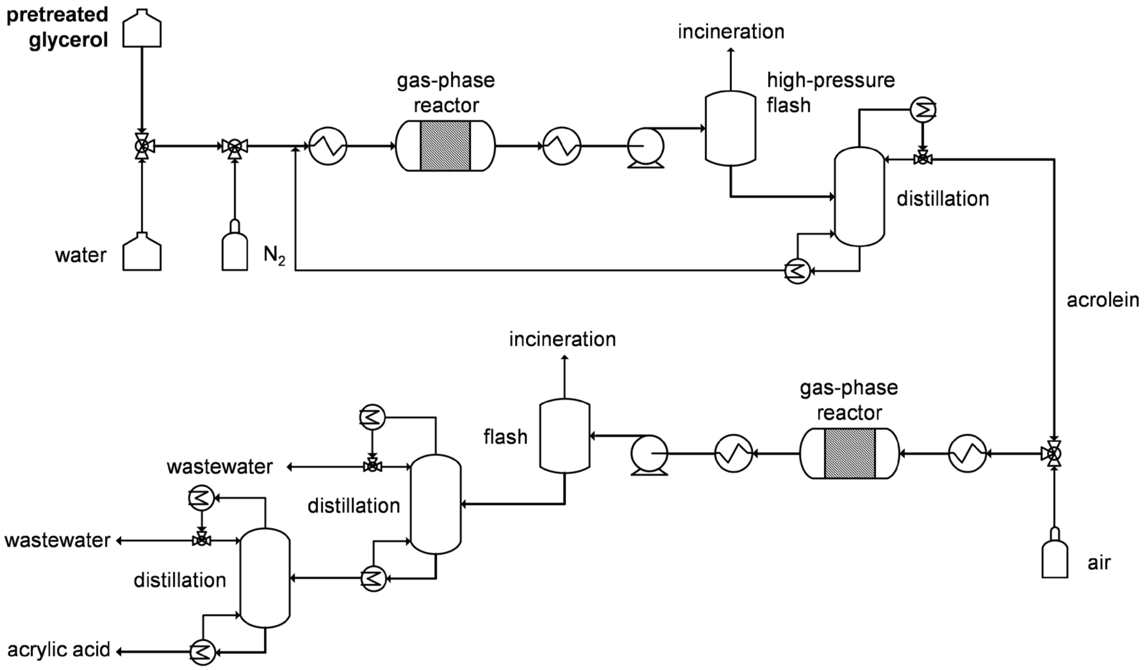
The reactor effluent contains unconverted glycerol, acrolein, N_2 and by-products. To avoid loss of the volatile product, it is compressed to 9 bar, prior to the removal of the gases by flash separation. The gaseous fraction is incinerated, while the liquid stream is treated in a distillation column that separates an aqueous solution of acrolein (25 wt.%) at the top from an aqueous solution of glycerol (20 wt.%) at the bottom.

Step 3. Acrolein oxidation

The concentrated acrolein stream from **Step 2** is mixed with air, heated to 573 K and fed to a continuous-flow fixed-bed reactor loaded with a catalyst based on V-Mo mixed oxides. Isothermal conditions (573 K) are assumed, provided by an external cooling utility to remove the reaction heat. The stoichiometric reactions considered in the simulations are compiled in **Table S3**. The reactor is operated for 70 h before regeneration of the catalyst by calcination is performed and every 700 h the catalyst is completely removed and replaced.

Step 4. Acrylic acid purification

The effluent of the reactor is cooled to 273 K and treated in a flash separator to remove permanent gases. The small amount of gaseous by-products is treated in an incineration facility. Acrylic acid is then concentrated to yield the commercial grade product (>99% purity) using two distillation columns. The heads, consisting of diluted aqueous solutions of the by-products are sent to a conventional wastewater treatment plant.



Scheme S2. Flowsheet for the acrylic acid production process from glycerol.

Table S2 Reactions and yields considered in the process model of the dehydration and oxidation of glycerol to acrylic acid over $FePO_4$ and V-Mo mixed oxides, respectively.[4,5] Glycerol and acrolein conversions are 83.5 and 95.0% in the first and second step, respectively.

	Reaction	Yield (%)	Product
Dehydration	$C_3H_8O_3 \rightarrow C_3H_4O + 2H_2O$	71.4	Acrolein
	$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_2O$	0.9	Acetone
	$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O$	0.2	Acetol
	$C_3H_8O_3 \rightarrow C_2H_4O + CH_2O + H_2O$	5.7	Acetaldehyde
	$C_3H_8O_3 + H_2 + 0.5O_2 \rightarrow C_3H_6O_2 + 2H_2O$	0.1	Propanoic acid
	$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_2O$	0.2	Propanal
	$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_2O$	0.8	Allyl alcohol
	$C_3H_8O_3 \rightarrow 3C + 3H_2O + H_2$	1.2	Coke
Oxidation	$C_3H_4O + 0.5\ O_2 \rightarrow C_3H_4O_2$	95.0	Acrylic acid
	$C_2H_4O + 0.5\ O_2 \rightarrow C_2H_4O_2$	4.2	Acetic acid
	$C_3H_6O + 2O_2 \rightarrow C_2H_4O_2 + CO_2 + H_2O$	0.6	Acetic acid

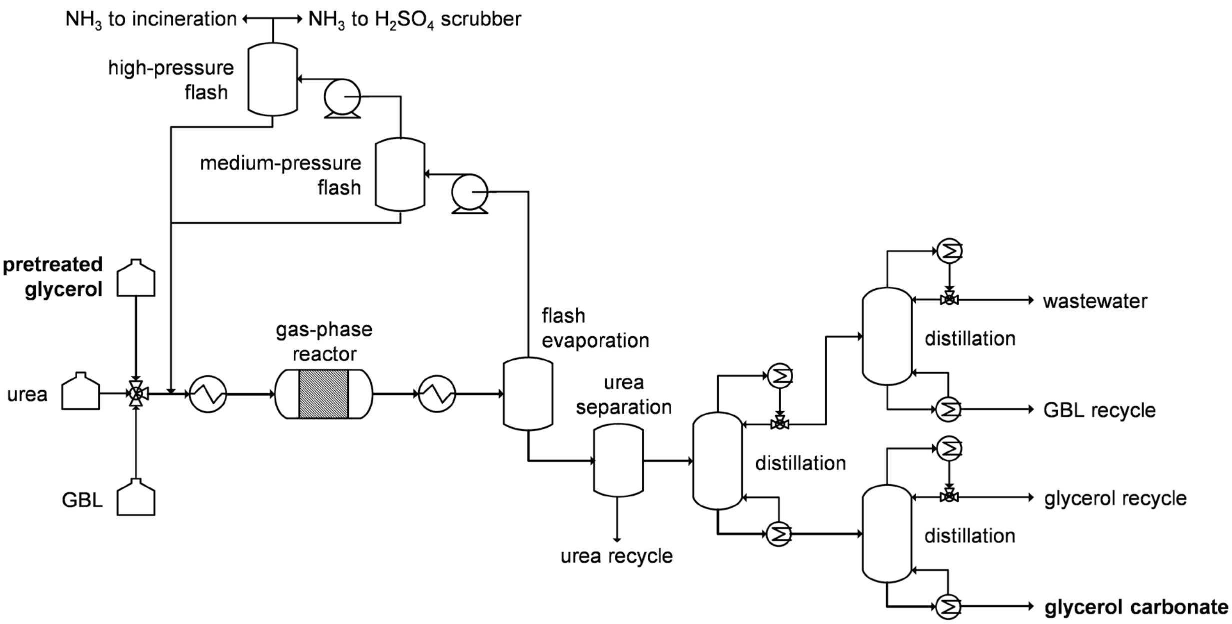
Heat integration

Due to the required energy intensive separations by distillation, process heat integration was carried out in order to reduce costs associated with the thermal utility consumption. Since the presence of low-boiling azeotropes lowers the level of available heat, the only way to reduce energy consumption is to heat the feed to the reactor using the reactor effluent. This achieves a reduction of *ca.* 78% of the energy requirement.

1.4. Glycerol carbonate

Step 1. Glycerol carbonation

Purified glycerol is mixed with urea and the with the γ-butyrolactone (GBL) solvent and sent to the reaction section, after mixing with the recycle streams containing unconverted glycerol and urea as well as



Scheme S3. Flowsheet for the glycerol carbonate production process from glycerol using urea as the carbonating agent.

the solvent (**Scheme S3**). The molar glycerol:urea:GBL ratio at the reactor inlet is 1:1:18. The continuous-flow fixed-bed reactor is loaded with a technical catalyst based on a Mg-Al mixed oxide, obtained by calcination of a hydrotalcite-like compound and forming using bentonite as the binder, and operated at 423 K and 10 mbar. Since complete selectivity to glycerol carbonate is claimed, the only reaction considered in the present work is:
$C_3H_8O_3 + CO(NH_2)_2 \rightarrow C_4H_6O_4 + 2NH_3$
The conversion of both glycerol and urea is 60%.

Step 2. Preliminary purification and recycle

The reactor effluent contains unconverted glycerol and urea, glycerol carbonate and ammonia, which are highly diluted in GBL. Separation of the light components, *i.e.* NH_3, is readily done *via* vacuum flash separation. The flash temperature is adjusted in order to achieve a glycerol carbonate molar recovery of 99.9%. This preliminary operation results in an almost total removal of NH_3 and methanol, introduced in the system as crude glycerol impurity, in the vapour phase. *Ca.* 10% of the solvent is also removed as a vapour, together with negligible amounts of glycerol and glycerol carbonate. Direct venting of the vapour phase is not desirable due to the high amount of solvent carried along. Additionally, flash separation stages operated at 0.1 and 1 bar are used to recover the solvent and the flash temperatures are adjusted to recover more than 98% GBL. The vented phase mainly contains NH_3 and residues of GBL and is sent to incineration. Alternatively, it is treated in an absorber operated with a concentrated sulphuric acid solution to yield $(NH_4)_2SO_4$.

Step 3. Glycerol carbonate purification

The liquid removed from the preliminary flash stage is composed by unreacted glycerol and urea, glycerol carbonate and residual GBL. A preliminary stage based on precipitation is adopted to separate urea, since this compound is not distillable and, in any case, prolonged residence time at temperatures near or above its melting point (403 K) might lead to crystallisation or decomposition.[6] A sequence of distillation columns is applied to separate the purified glycerol carbonate from glycerol and the solvent, which are recycled, as well as from residual light ends. The first, operated under vacuum (10 mbar), is employed to remove the solvent from the mixture of glycerol and glycerol carbonate. The second, working at atmospheric pressure, separates the desired product with the wanted purity (99%) from glycerol, which is recycled. The head fraction of the first column is treated in an additional distillation unit that accomplishes the removal of residual light ends from the solvent before its recycling.

Heat integration

Due to the required energy-intensive separations by distillation, process heat integration was conducted in order to reduce costs associated to thermal utility consumption. Heat integration potential is present because of the different temperature levels applied in the reaction and separation sections. However, first-principle calculations reveal a saving of only *ca.* 50% of the energy needed by the process without heat integration. This is not surprising if one considers that the separation section, which accounts for almost half of total energy, is associated with higher temperature levels with respect to the reaction section. Therefore, only minor heat recovery can be performed for the cold reactor inlet and for the feed of the first distillation column using the hot reactor effluent as the energy source. A heat exchanger network heuristically designed considering a realistic minimum temperature approach of 10 K indicates an effective reduction of *ca.* 46% of the total energy requirement.

1.5. 1,2-propanediol

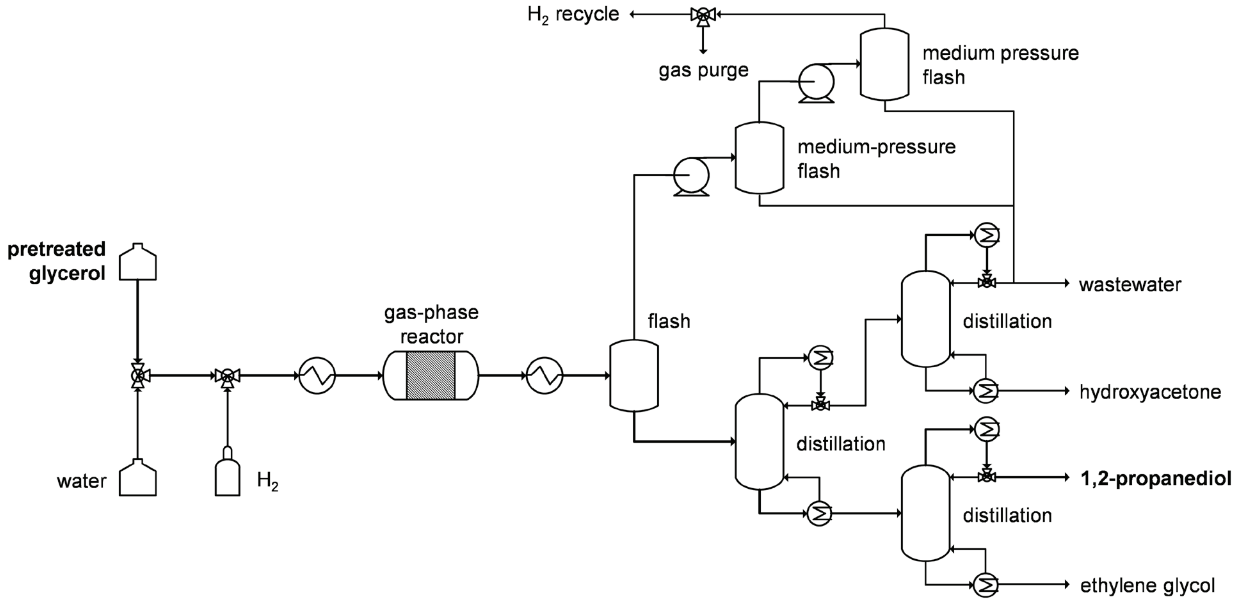
Step 1. Gas-phase dehydration/hydrogenation of glycerol to 1,2-propanediol and by-products

Purified glycerol is heated to 551 K and evaporated at ambient pressure (**Scheme S4**). A pure H_2 feed and the gaseous recycle are heated and mixed with the substrate vapour at the inlet of the reactor. The fresh H_2 flow rate is adjusted to obtain a molar H_2:glycerol ratio of 141 at the reactor inlet. Whenever necessary, a dilution water stream in the form of a vapour at 373 K and 1 bar is also added to attain the desired concentration of glycerol at the reactor inlet (30-94 wt.%, on a H_2-free basis). The hydrogenolysis reaction is performed in a continuous-flow fixed-bed reactor containing Cu/Al_2O_3 and operated at 1 bar and with a temperature difference between inlet and outlet of 70 K (473-403 K).[7] The latter helps tuning the relative importance of dehydration and hydrogenation, maximising the yield. In any case, an externally cooled reactor has to be applied: the outlet reaction temperature of 403 K permits the use of cooling water, with generation of low-pressure (2 bar) steam. The stoichiometric reactions considered in the modelling are listed in **Table S3**.

Step 2. Condensation of the reactor effluent to remove and recycle gases

In addition to 1,2-propanediol, the reactor effluent contains unconverted H_2, water and by-products. Among all by-products, only ethylene glycol and acetol could be accurately quantified from available selectivity data,[7] while the residual by-products could only be quantified from the mass balance and are assumed to consist of only 1-propanol, as this is the heaviest component between those possibly present. Firstly, the reactor effluent is cooled to 298 K to condensate and separate 1,2-propanediol from the gases. This results in the removal of *ca.* 90% of 1-propanol and methanol, *ca.* 70% of water and *ca.* 100% of unreacted H_2. Due to the large excess of H_2 used in the reaction, a gas-phase recycle with purge is introduced. The purge ratio is adjusted to avoid accumulation of products, by-products and impurities in the recycle loop, thus obtaining the desired glycerol concentration at the reactor inlet. It should be noted that all the impurities introduced in the reactor with the feed (methanol) or the recycle stream (methanol, 1-propanol) are considered inert in the catalytic reactor. In any case, their concentration is low keeping the molar glycerol:methanol ratio over 5.

Whenever a low water concentration is required at the reactor inlet (80 and 94 wt.% glycerol, on H_2-free basis), this compound is removed from the recycle stream using two additional compression stages, with intermediate cooling at 298 K and removal of the condensate. In this way, it is possible to reduce the purge ratio and, thus, the amount of fresh H_2 required. 2 bar for 80 wt.% glycerol and 5.5 bar for 94 wt.% glycerol in the medium-pressure flash stage and 5 bar for 80 wt.% glycerol and 30 bar for 94 wt.% glycerol in the high-pressure flash stages attain the desired water condensation and minimise the purge ratio. The condensate removed from the compression stages is sent to a conventional wastewater treatment



Scheme S4. Flowsheet for the 1,2-propanediol production process from glycerol.

Table S3. Reactions considered in the process model of the gas-phase oxidehydration of glycerol at various concentrations in water over Cu/Al_2O_3 at full conversion.[7]

Reaction	Yield$_{@30\%}$ (%)	Yield$_{@60\%}$ (%)	Yield$_{@80\%}$ (%)	Yield$_{@94\%}$ (%)	Product
$C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$	96.1	95.4	95.5	95.2	1,2-propanediol
$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O$	0.8	0.9	0.8	0.9	Acetol
$C_3H_8O_3 + H_2 \rightarrow C_2H_6O_2 + CH_3OH$	2.2	2.7	2.7	2.4	Ethylene glycol
$C_3H_8O_3 + 2H_2 \rightarrow C_3H_8O + 2H_2O$	0.9	1.0	1.0	1.5	1-propanol

facility or is incinerated if its net low heating value is higher than 3 MJ kg^{-1}. The H_2-rich purge flow is burnt in an incineration facility.

Step 3. Purification of 1,2-propanediol

Since no peculiar separation challenges were identified for the present system, *i.e.* non-ideal mixture behaviour, azeotropes, product thermal stability or product reactivity, a simple atmospheric distillation train is adopted. Column sequencing was determined by heuristics considerations while product recoveries in each column were set after proper sensitivity analysis to obtain reasonable sub-optimal values able to minimise the overall energy consumption of the distillation train. The number of trays was selected to obtain a column reflux ratio equal to 1.3-1.7 times the minimum reflux ratio and the feed stage is determined as that able to minimise the reflux ratio for a given number of stages. In addition, the number of trays is limited to keep the height/diameter ratio lower than 30-40, to avoid possible structural deficiencies of the column. For the sake of simplicity, the optimal values for the number of stages and design specifications found in the 30 wt.% glycerol case were used also for the other substrate concentrations.

A sequence of columns is employed for the process scenarios using 60-80-94 wt.% glycerol solutions, in which the product is firstly separated, together with ethylene glycol, from a water-rich stream containing acetol. 1,2-propanediol is then purified (99%) with recovery of ethylene glycol with a purity of 95%. Acetol with a purity of 90% is obtained from the wastewater.

A sequence of columns is employed for the process scenario using a 30 wt.% glycerol solution, in which water is firstly separated from a 1,2-propanediol-rich stream containing acetol and ethylene glycol. Acetol is then isolated with the desired purity (90%) and 1,2-propanediol is concentrated to 99% by removal of ethylene glycol. When excess hydrogen is present, a partial condenser (vapor fraction of 0.0015) is considered for the RadFrac unit. The water removed from the separation section is treated in a conventional wastewater facility.

Heat integration

Due to the required energy-intensive separations by distillation, process heat integration was performed in order to reduce costs associated to thermal utility consumption. High integration potential is present because of the high reaction and separation temperatures. Indeed, first-principle calculations, performed on the case 80 wt.% glycerol by pinch analysis, reveal a saving of *ca.* 75% of the energy needed by the process without integration. The heat exchanger network was designed considering a realistic minimum temperature approach of 10 K. As a result of this configuration, the total energy requirement is reduced by *ca.* 72%. Due to the similarities between the different process cases, this result was applied to all scenarios.

1.6. 1,3-propanediol

Step 1. Liquid-phase hydrogenation of glycerol to 1,3-propanediol

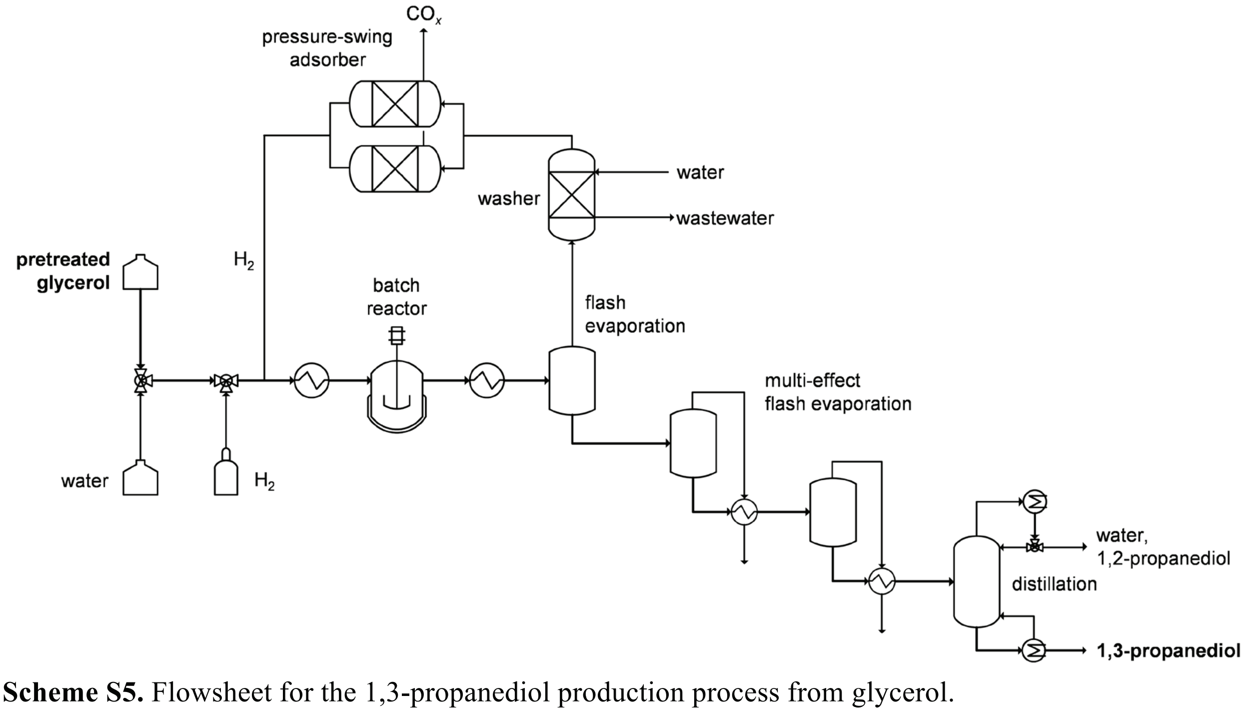
Purified glycerol is mixed with water and H_2 (50 bar, molar H_2:glycerol:water = 10:1:150), heated to 453 K and fed to a batch reactor (RStoich) (**Scheme S5**). The hydrogenolysis reaction is performed at a isothermal temperature of 453 K for 12 h using $Pt/WO_x/Al_2O_3$ as the catalyst.[8] The stoichiometric reactions considered are shown in **Table S4**.

Step 2. Gas separation and recycle

Gases are separated from the reactor outlet stream using a flash separator operated at 453 K and 50 bar. Prior to recycling them, a gas washer is applied to remove the volatile organic compounds and a purge is used to limit the accumulation of carbon monoxide and other by-products. Water from the gas purification unit is processed at a wastewater treatment plant.

Step 3. Purification of 1,3-propanediol

Taking advantage of the high-pressure conditions under which the reaction takes place and of the lighter



Scheme S5. Flowsheet for the 1,3-propanediol production process from glycerol.

Table S4. Reactions considered in the process model of the liquid-phase hydrogenolysis of glycerol over Pt/WO_x/Al_2O_3 at full conversion.[8]

Reaction	Yield (%)	Product
$C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$	66	1,3-propanediol
$C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$	2	1,2-propanediol
$C_3H_8O_3 + 2H_2 \rightarrow C_3H_8O + 2H_2O$	6	2-propanol
$C_3H_8O_3 + 2H_2 \rightarrow C_3H_8O + 2H_2O$	11	1-propanol
$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_2O$	2	Acetone
$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O$	2	Acetol
$C_3H_8O_3 \rightarrow 3CO + 4H_2$	11	CO

nature of solvent and by-products as compared to the diol of interest, a first concentration, from 3 to *ca.* 60 wt.%, is carried out by operating five flash separators at decreasing pressure (18, 10, 7, 4 and 1 bar). Thereafter, a series of two distillation columns removes the excess of water and 1,2-propanediol. The heads of all the distillation and flash separators are treated in a conventional wastewater facility.

1.7. Epichlorohydrin

Regarding the glycerol-to-epichlorohydrin production process, the modelling only comprised the section devoted to the dehydrochlorination of dichloropropanol (**Scheme S6**). The first process step, *i.e.* the hydrochlorination of the triol, is equivalent to that of the conventional technology and has already been modelled.[9]

Step 1. Gas-phase conversion of dichloropropanol to epichlorohydrin and solid regeneration

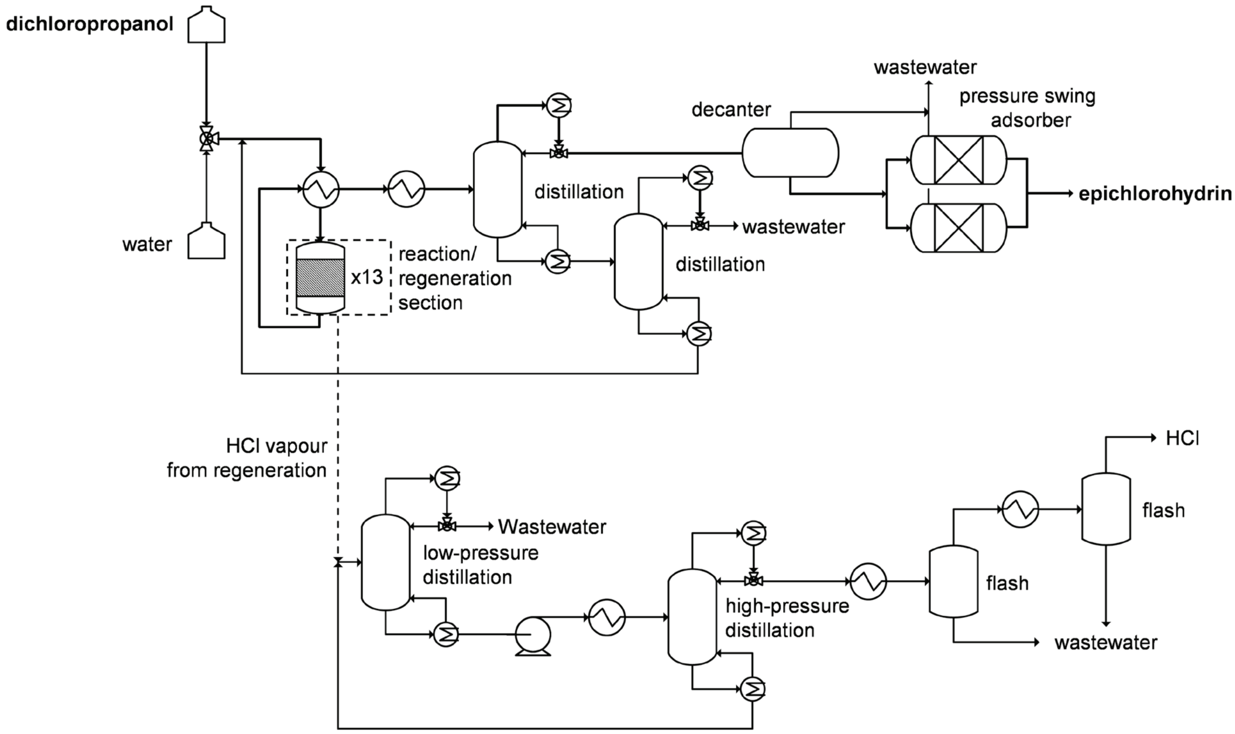
Dichloropropanol is mixed with water (10 wt.%), vaporised at 423 K and fed to a continuous-flow fixed-bed reactor loaded with a Mg-Al mixed oxide obtained by calcination of a hydrotalcite-like compound and operated isothermally at the same temperature. Two main reactions are considered (**Table S5**). Due to the rapid deactivation of the active material, a reactor configuration containing N in-parallel vessels working alternatively in reaction and regeneration mode was developed. The number of reactors depends on the times of reaction and regeneration. In the present analysis, these are equal to 0.5 and 6 h, respectively, and therefore 13 reactors are needed. Average values of catalyst activity are calculated from activity data by integration of the yield-*vs.*-time curve and the active material is assumed to the used in 100 reaction-regeneration cycles prior to its replacement.

Step 2. HCl purification

Upon calcination, the material releases a mixture of HCl and water. For the concentration of the first to 99%, the change in water-HCl azeotrope composition with pressure (20.5% at 1 bar and 17.5% at 4 bar) is exploited to break the distillation boundary present at 1 bar. Therefore, a low- and a high-pressure column are used to separate water from an HCl-rich flow. The highest boiling azeotrope is always recovered at the bottom of the column. Two flash condensation stages, in series and operated at 389 K and 348 K, are applied to recover pure gaseous HCl.

Step 3. Epichlorohydrin purification

The reactor effluent contains water, epichlorohydrin, unreacted dichloropropanol, chloroacetone and other by-products. Since the overall yield of the latter species is very low (<1%) and they have a higher boiling point than other organic components, they are considered to be removed as heavies together with water and to be treated in a conventional facility. A first distillation column performs a separation to obtain the epichlorohydrin-water azeotrope as distillate stream and, according to the mass balance, a diluted dichloropropanol-stream as bottom (0.9 mol.%). The light fraction is then condensed. In the liquid phase, two immiscible fractions separate, enabling the recovery of an epichlorohydrin-rich layer (96.4%), which



Scheme S6. Flowsheet for the epichlorohydrin production process from glycerol using a regenerable solid reactant. The section devoted to the concentration of HCl obtained upon regeneration of the active material is represented at the bottom.

Table S5. Reactions considered in the process model of the gas-phase conversion of dichloropropanol to epichlorohydrin over a Mg-Al mixed oxide at 41.0% conversion.[10]

Reaction	Yield (%)	Product
$C_3H_6OCl_2 \rightarrow C_3H_5OCl + HCl$	39.3	Epichlorohydrin
$C_3H_6OCl_2 \rightarrow C_3H_5OCl + HCl$	2.7	Chloroacetone

is further concentrated by pressure-swing adsorption over molecular sieves. The aqueous layer is treated in a wastewater facility. The bottom stream from the first distillation column is further purified by distillation attaining an almost pure water stream, which is partially used to adjust the reactant concentration in the recycle to the desired value (10 wt.%) and partially sent to a wastewater treatment facility. A safety purge, arbitrarily fixed at 5% of the recycle, is introduced in order to take into account the presence of by-products impurities, which could not be quantified experimentally.

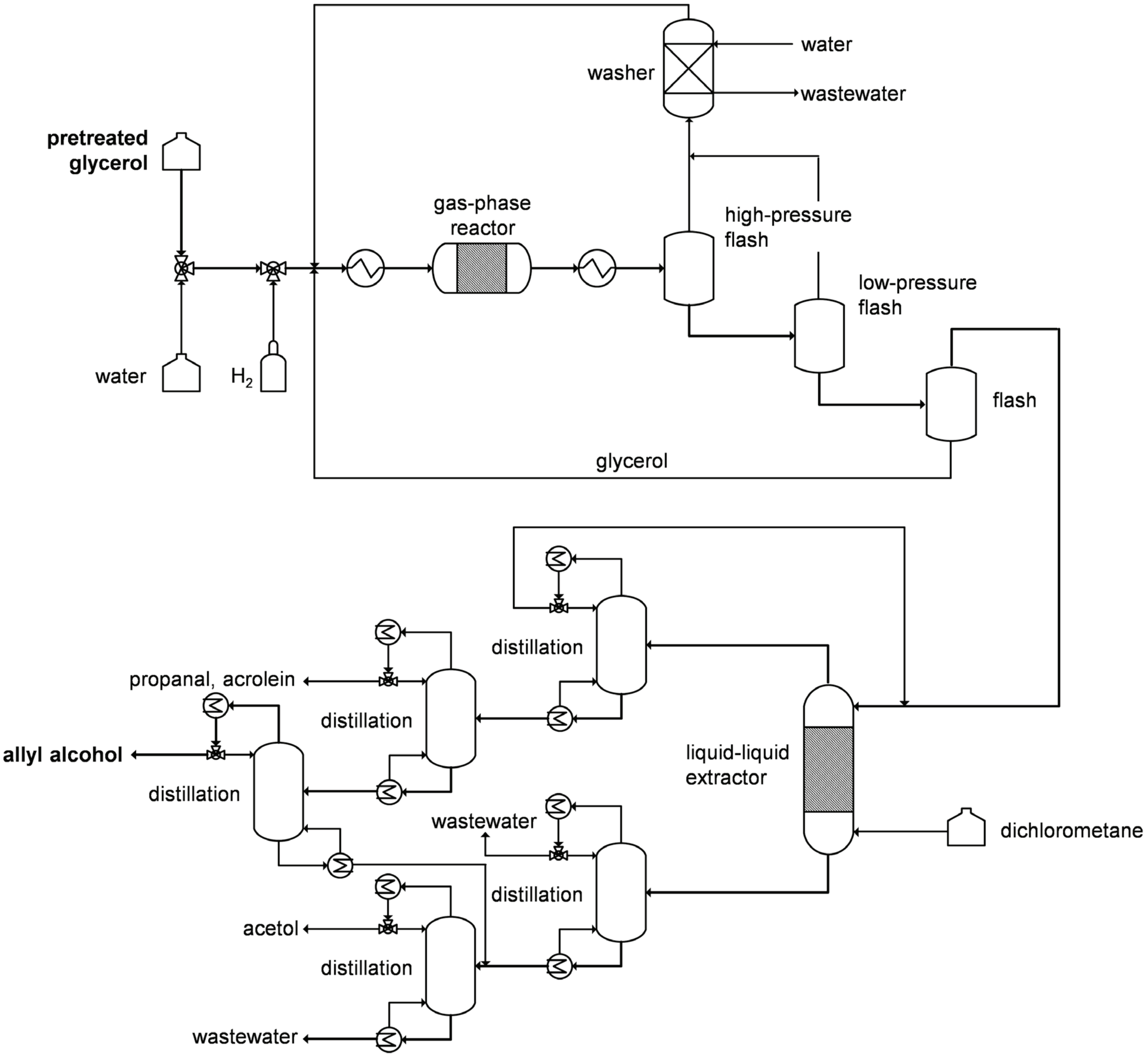
Heat integration

Due to the required energy intensive separations by distillation, process heat integration was conducted in order to reduce costs associated to the thermal utility consumption. However, the presence of low-boiling azeotropes lowers the level of available heat. The only way to reduce energy consumption is to heat the feed to the reactor using the reactor effluent, achieving a reduction of *ca.* 78% of energy requirement.

1.8 Allyl alcohol

Step 1. Catalytic gas-phase conversion of glycerol into allyl alcohol

Purified glycerol is mixed with process water, the recycle stream and H_2 and pressurised to 40 bar through a multi-stage compression system with intermediate refrigeration to 298 K, which allows reducing by *ca.*



Scheme S7. Flowsheet for the allyl alcohol production process from glycerol.

Table S6. Reactions considered in the process model of the gas-phase conversion of glycerol to allyl alcohol over Ag/ZSM-5 at 82% conversion.[10]

Reaction	Yield (%)	Product
$C_3H_8O_3 \rightarrow C_3H_4O + 2H_2O$	27	Acrolein
$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O$	25	Acetol
$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_2O$	15	Allyl alcohol
$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_2O$	15	Propanal

55% the energy consumption (**Scheme S7)**. The stream is then heated to 673 K and fed to a continuous-flow fixed-bed reactor containing a Ag/ZSM-5 catalyst. The inlet composition is 48.9% H_2, 48.7% water, 2.4% glycerol, on mass basis. Isothermal conditions (673 K at 40 bar) are assumed, provided by an external cooling utility for the removal of the heat produced upon the reaction. The stoichiometric reactions considered in the simulations are listed in **Table S6**.

Step 2. Condensation and hydrogen recycle

The reactor effluent contains large excess H_2, water, the desired product and by-products. It is cooled to 298 K to condensate and separate the organic fraction from the gas to recycle. This preliminary operation results in an aqueous stream containing > 99.5% (on molar basis) of all components heavier than allyl alcohol and a gaseous stream comprising 22 and 12% of the formed acrolein and propanol as vapours along with H_2. Hydrogen is purified prior to recycling in a simple water absorption system, which removes 99% of the residual organics. The resulting aqueous stream is treated in a wastewater facility.

Step 3. Allyl alcohol purification

The liquid effluent is a very diluted solution of the condensed organic fraction. Multiple flash separation stages are used to remove residual light ends at 1 bar at first and to separate glycerol after heating to 383 K afterwards. Considering the extremely high amount of water and the presence of several azeotropes, involving also allyl alcohol, the concentration of the organic fraction is performed by liquid-liquid extraction using dichloromethane. Thereafter, concentration of all products to commercial purity (99%) is achieved by distillation. The water removed from the separation section is sent to a conventional wastewater treatment facility, while the light ends streams are incinerated or treated in a conventional wastewater system after condensation, depending on their heating value.

Heat integration

Heat integration potential is mainly present at the reactor outlet, which can be used for pre-heating the feed and accounts alone for almost 50% of the total recovered heat. Other integration opportunities are present due to the very different temperature levels between the reaction and the downstream section, and within the separation section itself due to the complex set of distillations. A heat exchanger network, designed considering a realistic minimum temperature approach of 10 K, reduces the energy requirement by 62%.

2. Background data for the environmental and economical assessment

Table S8. Background data for the environmental and economical assessment of allyl alcohol production processes.

Substance	CED (MJ_{eq} kg^{-1})	GWP ($kg_{CO2\text{-}eq}$ kg^{-1})	Price (USD t^{-1})
Process water	$2.8\ 10^{-4}$	$2.4\ 10^{-5}$	1
Quartz sand	0.33	0.02	39.6
CuO	31.0	1.95	3188
Al_2O_3	19.1	1.24	356
Pure glycerol	23.9	1.99	270
Crude glycerol – wastewater treatment	9.97	0.92	111
Heat[a]	1.57	0.10	20
Electricity[b]	9.87	0.49	0.10
Cooling water from river	0.00	0.00	0.15
V−Mo oxide	118	7.67	79375
SiC	160	7.18	870
N_2	8.73	0.43	78.1
H_2	69.7	1.67	3404
Natural gas[b]	1.24	0.012	0.01
Media	18.6	1.04	1000
CO_2	10.5	0.82	140
Acetol	56.4	1.91	5000
Ethylene glycol	51.2	1.57	815
Phosphoric acid	20.0	1.42	1100
Glucose from sugar beet	6.49	0.51	390
Zeolites	73.7	4.20	400
Ash disposal	0.28	0.009	-
Catalyst disposal	0.32	0.01	-
1,2-propandiol	99.9	4.07	1420
Urea	30.2	1.53	267
Gamma-butyrolactone	70.0	3.29	22900
Glycerol carbonate	128	5.70	2400
Acrolein	69.6	2.49	1220
Propionaldehyde	92.9	3.31	1460
Allyl alcohol	84.2	2.78	3250
Benzene	67.5	1.79	780
Methylene chloride	40.2	3.39	1245
MgO	2.7	1.06	280
Ag	1360	100	226000
1,3-dichloro-2-propanol	80.4	6.70	5600
Epichlorohydrin	71.8	3.37	1320
HCl	60.3	2.06	160
NaOH	21.4	1.10	243

[a] Heat and electricity are measured in kWh.

[b] The values for natural gas are measured in MJ and they refer to heat-production purposes.

3. Integrated biorefinery

Table S9. Glycerol refinery data for the individual products considered in integration scenarios.[a]

	Lactic acid (*via* DHA)	Lactic acid (*via* PAl)	Acrylic acid	Allyl alcohol	1,2-PDO	1,3-PDO	Glycerol carbonate
Glycerol (kg/kg$_{product}$)	1.56	2.40	2.00	8.69	1.28	1.97	0.79
Operating cost (\$/kg$_{product}$)	0.66	1.7	1.4	-2.9	0.8	5.1	1.5
	(0.62)	(1.4)	(1.2)	(-5.7)	(0.6)	(2.8)	(1.2)
Price (\$/kg$_{product}$)	1.8	1.8	1.5	3.3	1.4	4.5	2.4
CED (MJ$_{eq}$/kg$_{product}$)	21.5	120	68.3	364	-4	185	69
	(15.6)	(80)	(41.8)	(-91)	(-36)	(46)	(25)
	109	*109*	*64*	*84*	*100*	*88*	*128*
GWP (kg$_{CO2,eq}$/kg$_{product}$)	1.3	6.1	4.8	28	-0.73	11.6	4.2
	(0.93)	(3.6)	(3.1)	(-0.6)	(-2.7)	(3.84)	(1.4)
	7.6	*7.6*	*2.3*	*2.78*	*4.1*	*3.2*	*5.7*
EI99 (points/kg$_{product}$)	0.14	0.66	0.37	3.5	0.13	1.13	0.50
	(0.10)	(0.41)	(0.22)	(0.57)	(-0.06)	(0.32)	(0.22)
	0.53	*0.53*	*0.23*	*0.29*	*0.33*	*0.26*	*0.26*

[a] The values of glycerol refer to pretreated glycerol, those in parenthesis to heat integration performed at the individual product level, and those in italics to fossil based production (except from the case of lactic acid where the metrics refer to the industrially applied production based on sugar beet). DHA = dihydroxyacetone, PAl = pyruvaldehyde, PDO = propanediol.

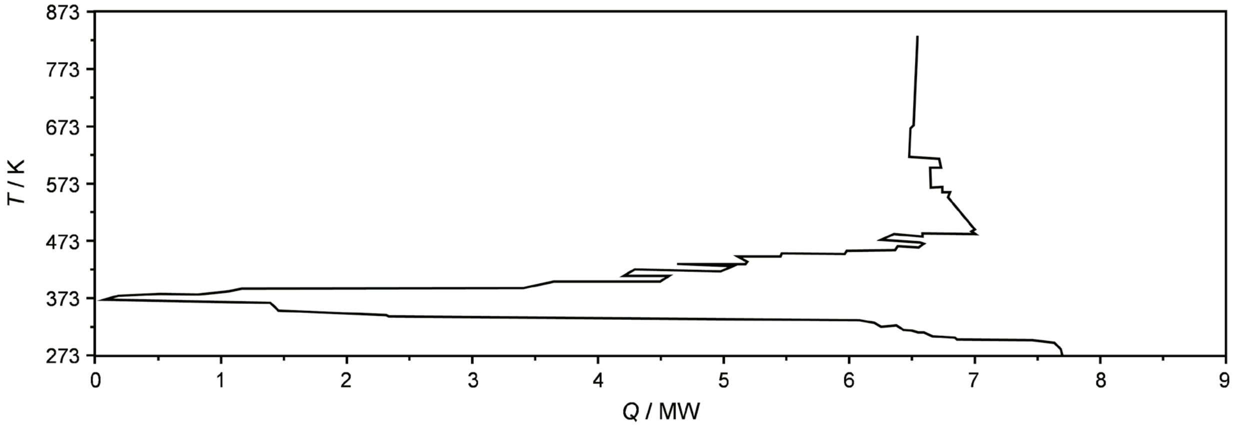


Fig. S1. Grand composite curve for the glycerol refinery, where a glycerol feed of 1 ton/hr is equally divided among all production processes.

Table S10. Glycerol refinery performance for the production mix between 1,2-propanediol and glycerol carbonate. The optimal GWP at the refinery level is achieved at 80% production of P5.

1,2-propanediol (%)	Profit (integration at refinery level)	Profit (integration at product level)	GWP (integration at refinery level)	GWP (integration at product level)
0	1.52	1.52	5.43	5.43
0.1	1.45	1.43	5.53	5.42
0.2	1.37	1.34	5.63	5.41
0.3	1.30	1.25	5.73	5.39
0.4	1.22	1.16	5.74	5.38
0.5	1.14	1.07	5.75	5.36
0.6	1.06	0.98	5.75	5.35
0.7	0.98	0.89	5.76	5.34
0.8	0.89	0.80	5.76	5.32
0.9	0.79	0.71	5.54	5.31
1	0.62	0.62	5.29	5.29

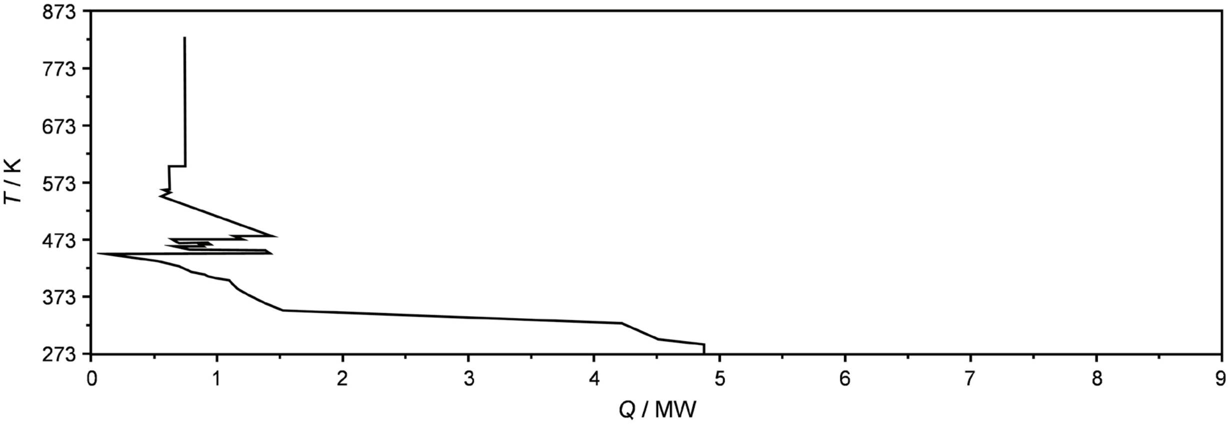


Fig. S2. Grand composite curve for the glycerol refinery, where a glycerol feed of 1 ton/hr is optimally utilised in terms of GWP 100a to produce 1,2-propanediol (80%) and glycerol carbonate (20%).

4. References

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