# Original Article

# Waste-derived low-grade glycerol purification and recovery from biorefineries: an experimental investigation

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Abstract: A combination of different physio-chemical treatment steps was applied to purify industrially derived crude glycerol at laboratory scale. The full process included acid–base treatments, phase separation, and adsorption, and the glycerol purity and recovery were optimized by varying the pH during saponification and acidification, the solvent-to-glycerol ratio, and type of base used in the process to enhance both. The testing campaign resulted in a final purity of up to 87% wt starting from a very low-quality 'end-of-life' waste glycerol sampled from different refineries. The net glycerol recovery at laboratory scale reached 42% of the initial glycerol in the feedstock and the maximum ash removal exceeded 90% given the low quality of the feedstock and high content of impurities and the attempt to achieve high glycerol recovery. The experiment showed that mild operations such as saponification with KOH (pH of 8), acidification with $H_3PO_4$ (pH of 6), an ideal 2-propanol to glycerol volume ratio equal to 3 and potassium hydroxide as a base for the neutralisation step were the optimum conditions despite the differences between samples. The sequence of the processes proposed was therefore considered a viable option to treat any kind of crude glycerol to make it profitable for fuel and chemical applications. © 2024 The Authors. *Biofuels, Bioproducts and Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

*Supporting information may be found in the online version of this article.*

Key words: crude glycerol; purification; biodiesel; physio-chemical treatment; response surface methodology

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# Introduction

Waste-based biofuels play a major part in the transition towards low-carbon transportation and a net zero agenda. As second-generation biofuels, they reduce the dependence on fossil fuels and the impacts associated with the use of other forms of biomass. Biodiesel production will progressively increase up to a market volume of 200 billion USD by 2030 with a compound annual growth rate (CAGR) of 8.3% from 2021 to 2030[1] and Europe aims to reach a 3.5% of prodcution of advanced biofuels by 2030.[2] Advanced biofuels are considered to be the same products as first-generation biofuels but utilize waste-based, nonedible feedstocks that are produced by second-generation biodiesel refineries.[3] This has led to the trend of using waste feedstocks such as tallow or used cooking oil instead of vegetable oils as these feedstocks have increasingly become available. Biodiesel production also involves a transesterification reaction of fats with methanol, which yields glycerol as a byproduct, containing several impurities, especially in the case of waste-based feedstocks, due to the additional pretreatments necessary to handle the waste material used as feedstock.[4] Approximately, 10% wt of crude glycerol is produced as a byproduct during the transesterification of fats with methanol.[5] Hence, the biodiesel industry has become the main supplier of the global glycerol market – often rich in impurities – which is mainly incinerated,[6] used for cattle feed,[7,8] biogas[5,6] generation or as carbon source for lipid production,[9,10] or even transferred to landfill.[11] It is assumed that by 2025 an annual quantity of 680 000 t of second-generation, waste-based crude glycerol will be produced.[12]

Glycerol ($C_3H_8O_3$), also known as propane-1,2,3-triol, is, in its pure form, useful in the personal care and pharmaceutical industries as well as for gasification.[13,14] Some of the properties of pure glycerol are listed in Table 1.

Table 2 depicts the average glycerol composition generated by the three primary reactions that yield crude glycerol. These three main reactions are hydrolysis, which uses steam to produce fatty acids and glycerol, saponification, which uses sodium hydroxide to produce soaps and glycerol, and transesterification, which uses methanol to produce fatty acid metal esters (FAMEs) and glycerol. Typical impurities in crude glycerol are water, ashes, and matter organic nonglycerols (MONGs), which usually consist of free fatty acids (FFA), FAMEs, glycerides (mono-, di- and triglycerides), alcohols such as methanol or ethanol, and soaps (saponified fatty acids, i.e. fatty acid salts),[16] and other organic compounds (e.g., aldehydes).[17]

## Table 1. Main properties of glycerol at room temperature.

| Properties | |
|---|---|
| Chemical formula | $C_3H_8O_3$ |
| Molar mass (g mol$^{-1}$) | 92.094 |
| Appearance | Colorless hygroscopic liquid |
| Odor | Odorless |
| Density (g cm$^{-3}$) | 1.261 |
| Melting point (°C) | 17.8 |
| Boiling point (°C) | 290 |
| Solubility in water | Miscible |
| Lower heating value (MJ kg$^{-1}$) | 24 |
| Refractive index ($\eta_D$) | 1.4746 |
| Viscosity (Pa·s) | 1.412 |

*Source*: Values taken from Pal et al.[15]

The lowest purity of glycerol is obtained by the transesterification reaction (in biodiesel production), which also yields the highest amount of ashes due to alkali- and acid-based catalysts, which are used during the biodiesel production and esterification of used cooking oil. This is highly problematic because the inorganic ashes act as major inhibitors in many biotechnological applications[19–21] and frequently poison the heterogeneous catalysts of downstream chemical conversion units[22] or clog up pipes in industrial processes leading to downtime and incurring costs. A very high MONG content is generated due to partially reacted glycerides, residual FAME, or alcohol, which is used in the transesterification reaction, reducing the glycerol content even further. The usual pH value of crude glycerol in the transesterification lies above 7 (close to 11) due to the use of alkali catalysts such as sodium hydroxide, potassium hydroxide, or sodium methoxide.[23] It can also be acidic if a neutralization step involving the crude glycerol has also taken place, as in the case of low-cost, waste-based feedstocks.[24] Crude glycerol purification technologies must therefore be explored to find a suitable way to purify it and make the overall biodiesel industry more economically and environmentally sustainable.

In recent decades many researchers have been working on glycerol purification.[12,25] Remarkable purity has been achieved by different means but information on glycerol recovery is not provided in their studies due to the scale of the experiments or the pressure to achieve very high purity. As a result of this, the biodiesel industry has been very reluctant to develop glycerol upgrading plants in presence of high ashes content. The processes investigated for glycerol purification

**Table 2. Average crude glycerol composition by different production processes.[18]**

| Component | Transesterification (%) | Saponification (%) | Hydrolysis (%) |
|---|---|---|---|
| Glycerol | 30–60 | 83–84 | 88–90 |
| Ash | 10–19 | 8.5–9.5 | 0.7–1.0 |
| Water | ≤10 | 6–7 | 8–9 |
| MONG | ≤40 | 3–4 | 0.7–1.0 |

involve a combination of acidification, saponification, neutralization, and selective separation (using adsorption or membranes), as reported in Table 3.

However, the separation sequence and results vary significantly depending on the quality of the glycerol, which varies, and types of impurities. For example, Hunsom *et al.*, Kongjao *et al.*, Javani *et al.*, and Manosak *et al.*[27,28,30,34] sourced their crude glycerol from a second-generation single feedstock biodiesel refinery – for example, used cooking oil (UCO) – whereas Chol *et al.*[18] sourced theirs from a biodiesel refinery that used canola oil as feedstock so the crude glycerol is much easier to purify. Isalmi Aziz *et al.*[36] and Ahmad Farid *et al.*[33] have used lab-based synthetic glycerol produced from the transesterification of UCO. Violeta *et al.*[29] used crude glycerol from the Mexican Cleaner Production Center of the National Polytechnic Institute. Dmitriev *et al.*[38] used crude glycerol from an industrial producer (OAO Mogilevkhimvolokno in Belarus), which is utilizing rapeseed oil as feedstock with lower ash content (3.8% wt). Nanda *et al.*[39] tested crude glycerol from an industrial biodiesel refinery with 70% wt MONG content (predominantly methanol) in comparison with15.5% wt of MONG in this work (which used only organic compounds and a negligible amount of methanol). Chen *et al.*[37] considered crude glycerol from a biodiesel refinery as well; however, the biodiesel refinery processes UCO exclusively with 2.3% wt ash content and very high methanol and moisture content (15.3% wt and 24% wt, respectively). Ningaraju *et al.*[31] purified their glycerol up to 95% wt; however, their crude glycerol was received from a biodiesel refinery that utilizes a single-waste feedstock such as UCO, making the ash content much lower (3.95% wt) than in the crude glycerol in this study (up to 11.64% wt). Some crude glycerols tested in the literature[31,37,39] present high pHs, which signal no industrial pretreatment to recover valuable compounds. Xiao *et al.*[32] have purified crude glycerol from Indiana Biodiesel, which uses the oil portion of soybeans.

There is a gap in knowledge regarding glycerol purification using feedstocks that are more difficult to purify. Despite the existing small laboratory-scale studies mentioned above, no experimental demonstrations have been achieved with such feedstocks, let alone operating plants. In particular when the bio-waste feedstock includes heterogeneous sources,

or when the operating conditions of the biodiesel plant are seasonal, or multiple glycerol streams are available within the same plant, the glycerol quality changes significantly in quality and quantity over time, posing technical challenges. No studies have been presented reporting comprehensive process optimization, especially for low-quality glycerol derived from biodiesel refineries using multiwaste feedstocks (named 'end-of-life' glycerol). 'End-of-life' glycerol differs from synthetic glycerol, pure crude glycerol from first-generation refineries or glycerol derived from second-generation biodiesel using single feedstock such as UCO. Ash content is notably higher (>11% compared to 4–5% reported in the previous studies provided in Table 3). The MONG content is more heterogeneous because part of the glycerol recovery has been carried out in post-treatment steps (acidification, separation, etc.) on an industrial level to recover FFAs and byproduct salts. Moreover, the glycerol quality derived from animal waste is considered as 'high risk', and is thus not suitable as glycerol for the market and is currently being disposed of at cost. These feedstocks are among the lowest value, impure crude glycerol available from the biodiesel supply chain. Their recovery has not been presented yet in the academic literature, nor the optimization and general methodology to treat different highly impure low-quality feedstocks.

Unlike the other studies presented, the current work is informative in terms of glycerol recovery because the process testing and optimization variables are also relevant to reduce valuable mass losses commonly ignored in literature. In this study, the influence of different physio-chemical steps is investigated to develop a systemic methodology that could apply to diverse crude glycerol feedstocks. A custom design of the experiment approach and response surface methodology (RSM) are also used to optimize glycerol purity and ash removal efficiency. The results of the process are presented in terms of mass balance to provide industrially relevant feedback on the strengths and weaknesses of the process from the perspective of the process scale up. This study is relevant for the chemical conversion of glycerol to sustainable chemicals including succinic acid,[40] dihydroxyacetone[41] or fuels (as in the collaborative European project H2020 GLAMOUR)[42] starting with different qualities of feedstock.

**Table 3. Physio-chemical purification papers with crude and purified glycerol purities.**

| Author | Year | Purification route | Crude glycerol (% wt) | Purified glycerol (% wt) | Remarks |
|---|---|---|---|---|---|
| Hajek et al.[26] | 2010 | (Saponification)/neutralization/evaporation | 51.3 | 85.1 | Type of base: KOH<br>pH–saponification: n/a<br>Type of acid: $H_3PO_4$, HCl, $H_2SO_4$, $CH_3COOH$<br>pH–acidification: 3/4 |
| Chol et al.[18] | 2018 | Saponification/acidification/anti-solvent treatment/(membrane)/(adsorption) | 40.0 | 83.5 | Type of base: KOH<br>pH–saponification: 12<br>Type of acid: HCl<br>pH–acidification: 1 |
| Manosak et al.[27] | 2011 | Acidification/neutralization/anti-solvent treatment/adsorption | 36.7 | 96.2 | Type of acid: $H_3PO_4$, $H_2SO_4$, $CH_3COOH$<br>pH–acidification: 1–6 |
| Javani et al.[28] | 2012 | Saponification/acidification/neutralization | 40.6 | 96.1 | Type of base: KOH<br>pH–saponification: >10<br>Type of acid: $H_3PO_4$<br>pH–acidification: 9.67, 4.67 |
| Violeta et al.[29] | 2020 | Neutralization/evaporation | 22.9 | 98.5 | Type of acid: $H_2SO_4$, $C_6H_8O_7$<br>pH–acidification: 6 |
| Kongjao et al.[30] | 2010 | Acidification/neutralization/anti-solvent treatment | 30.3 | 92.9 | Type of acid: $H_2SO_4$<br>pH–acidification: 1–6 |
| Ningaraju et al.[31] | 2022 | Saponification/acidification/neutralization Anti-solvent treatment/adsorption | 35–40 | 95.1 | Type of base: KOH, NaOH<br>Type of acid: $H_2SO_4$<br>pH–acidification: 8–2.5 |
| Xiao et al.[32] | 2013 | Micro-filtration/vacuum/evaporation/ saponification/acidification Vacuum evaporation/micro-filtration/ extraction/neutralization/micro-filtration/ vacuum evaporation/extraction/micro-filtration/acuum evaporation | 31.5–63.9 | 95.6 | Type of base: NaOH<br>pH–saponification: 11<br>Type of acid: HCl<br>pH–acidification: 1 |
| Ahmad Farid et al.[33] | 2021 | Saponification/acidification/anti-solvent treatment/adsorption | 40.7 | 98.2 | Type of base: KOH<br>pH–saponification: 12<br>Type of acid: HCl<br>pH–acidification: 1 |
| Hunsom et al.[34] | 2017 | Physio-chemical pretreatment (according to Manosak et al.)/adsorption | 27.2 | 93.0 | Type of acid: $H_3PO_4$<br>pH–acidification: 2.5 |
| Hunsom et al.[35] | 2013 | Physio-chemical pretreatment (according to Manosak et al.)/adsorption | 27.2 | 93.0 | Type of acid: $H_3PO_4$<br>pH–acidification: 2.5 |
| Isalmi Aziz et al.[36] | 2018 | Acidification/adsorption | 67.0 | 96.0 | Type of acid: $H_3PO_4$<br>pH–acidification: 2.5 |
| Chen et al.[37] | 2018 | Acidification | 31.8 | 55.0 | Type of acid: $H_3PO_4$<br>pH–acidification: 2.5 |
| Dmitriev et al.[38] | 2018 | Acidification | 75.6 | n/a | Type of acid: $H_2SO_4$ |
| Nanda et al.[39] | 2014 | Acidification/neutralization/evaporation/ solvent extraction/adsorption | 13.0 | 96.0 | Type of acid: $H_3PO_4$, $H_2SO_4$, HCl<br>pH–acidification: 1 |

Further investigation from different authors who have used different feedstocks are available in Attarbachi *et al.*[43]

# Materials and methods

## Materials

Crude glycerol was supplied by three different biodiesel refineries of Argent Energy Ltd. These refineries are in the Stanlow, UK and Motherwell, UK and Amsterdam, the Netherlands and could potentially cluster to deliver a glycerol refinery. All of the biodiesel refineries utilized waste feedstocks such as animal fats like tallow, UCO, palm oil mill effluent (POME) and even worse feedstocks such as sewage sludge or 'fats, oils and greases' (FOGs). All feedstocks considered in this study are categorized as Cat 1 and Cat 2 animal by-products (ABPs), and are therefore not saleable.[44] The reduced quality of this glycerol is dictated by the transesterification downstream treatments that are applied to the waste streams before they are sampled at the biodiesel plant. After the transesterification, glycerol is acidified to pH 3 and then sent into a tricanter to remove the three phases of free fatty acids (FFAs) generated at the top and salt at the bottom. Then, the glycerol layer is neutralized to recover additional FFA. The residual methanol and water are separated through distillation. Finally, the treated glycerol is sent again through a tricanter to remove MONG, salts, and the glycerol phase, which is stored separately. After these steps, samples were collected with the composition reported in Table 4 and used in this study.

The glycerol type, appearance, and composition differ in each batch depending on which feedstock was used to produce the biodiesel. This leads to different colors (brownish, blackish), odors (pungent or pasture like), and viscosities (high and low). Hence, the glycerol content ranged from 30% to 65% wt. The list of other chemicals used in this study is summarized Table 5.

**Table 4. End-of-life glycerol feedstocks used for the purification process and obtained from the different processing refineries.**

| Composition $t=0$ | Stanlow | Motherwell | Amsterdam |
|---|---|---|---|
| Glycerol (% wt) | 60.74 | 45.67 | 62.59 |
| Ash (% wt) | 11.64 | 8.39 | 4.54 |
| Water (% wt) | 16.92 | 39.58 | 17.13 |
| MONG (% wt) | 10.7 | 6.36 | 15.74 |
| pH | 5.99 | – | 5.30 |
| COD | 931 | – | – |

All experiments were conducted using a hot plate equipped with a temperature controller. For the vacuum filtration, a Buechner funnel was used with filter paper (particle retention 5–13 µm,) and a diaphragm pump. A pH meter was used to conduct the experiments and subsequent analysis using a temperature probe, and pH probe, which is specifically used for experiments involving fats and oils.

## Purification of crude glycerol

The purification process of crude glycerol is summarized in Fig. 1. All experiments were conducted with 100 g of crude glycerol. Before any kind of treatment, the canister containing the crude glycerol was mixed thoroughly to homogenize the entire mixture, which could have been segregated over time by gravity into salts and MONG layers, depending on the composition.

First, a saponification step was carried out to convert residual MONGs such as glycerides and fatty acids to fatty acid salts (i.e. soaps) and glycerol. The pH was therefore varied between 8 and 14 at a temperature of 60 °C for the duration of 1 h. The temperature decreased the viscosity of the solution and made the pH measurements more accurate. For the saponification stage, three different types of bases of 12.5 mol L$^{-1}$ were used, namely sodium hydroxide, potassium hydroxide, and solid calcium hydroxide. Compared to previous study, solid calcium-hydroxide was also considered according to the Chuang-Wei,[45] to remove residual inorganic material from crude glycerol. Afterwards, the mixture was allowed to cool down to room temperature for more than 20 min. This was followed by an acidification step where the pH was varied between 1 and 6 using 85% phosphoric acid as recommended in the literature.[27] The mixture was then poured into a separation funnel and it was left to settle for up to 24 h, depending on which base was used. Afterwards, between two to three distinct phases were visible, namely a top fatty acid phase, followed by a glycerol phase and a solid phase consisting of precipitated salts. As the top fatty acid phase does not always appear as a distinct separate phase, a separation funnel was used to decant off the two latter phases. The fatty acid phase could potentially be used as feedstock for esterification in biodiesel reactors. The glycerol phase was separated by means of vacuum filtration carried out for a period of 2 to 4 h. The salt that was obtained could be used potentially as fertilizer depending on the type of base that is being used in the process. The polar glycerol phase was obtained from vacuum filtration and neutralized using the same type of base used for the saponification. After the neutralization, 2-propanol was added to the mixture at a ratio of 3–1:1 solvent-to-glycerol v/v. The addition of a

**Table 5. Chemicals used for the experimental runs and analytical measurements.**

| Purpose | Chemical | Supplier | Product code | Grade |
|---|---|---|---|---|
| Experimental | Phosphoric acid | ACROS Organics (Geel, Belgium) | 201140010 | 85% aqueous for analysis |
| Experimental | Sodium hydroxide | Sigma-Aldrich (St. Louis, MO, USA) | 221465 | ACS reagent; >97% solid |
| Experimental | Potassium hydroxide | Honeywell FLUKA (Loughborough, UK) | 019-002-00-8 | ACS reagent; >85% solid |
| Experimental | Calcium hydroxide | Scientific Laboratory Supplies (Notthingham, UK) | CHE1490 | >95% solid |
| Experimental | Powdered activated carbon | CHEMVIRON (Feluy, Belgium) | WPS260-90 | n/a |
| Experimental | Propan-2-ol | Fisher Chemicals (Loughborough, UK) | P/7500/17 | Analytical reagent grade, >99.8% |
| Analytical | Hydranal coulomat AG | Honeywell FLUKA (Loughborough, UK) | 34836 | n/a |
| Analytical | Sodium hydroxide | Honeywell FLUKA (Loughborough, UK) | 7139500.00 | 0.1 N |
| Analytical | Sodium metaperiodate | Supelco, EMSURE (St. Louis, MO, USA) | 1.06597.1000 | ACS reagent, for analysis |
| Analytical | Sulfuric acid | Supelco, TITRIPUR (St. Louis, MO, USA) | 1.09074.1000 | Titripur, 0.1 N |
| Analytical | Ethylene glycol | Fisher Chemicals (Loughborough, UK) | BP230-1 | >99% |
| Analytical | Bromothymol blue | Sigma-Aldrich (St. Louis, MO, USA) | 114413 | ACS reagent, 95% |
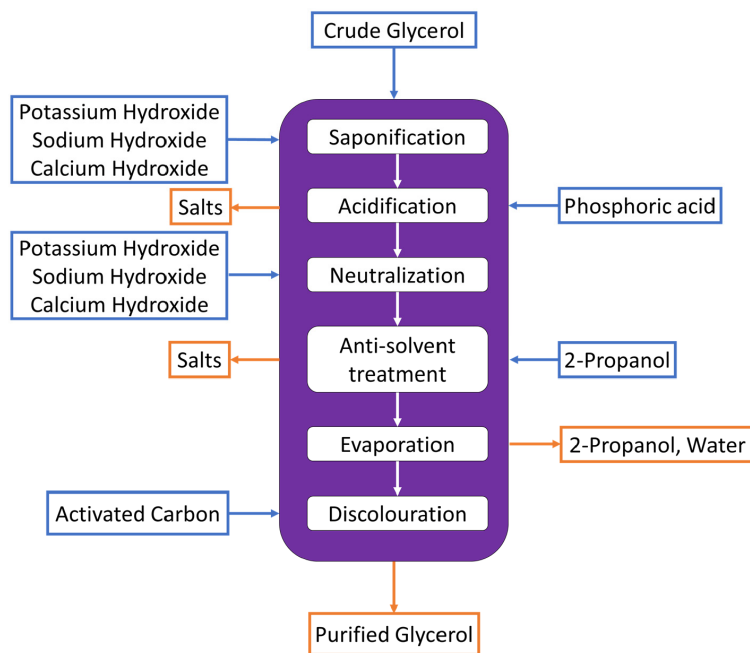


Figure 1. Crude glycerol purification process using a physiochemical route.

polar alcohol does lead to an anti-solvent treatment effect which forces the precipitation of salts due to the alteration of polarity (lower dielectric constant), which was present in the crude glycerol. These salts were removed from the mixture by means of vacuum filtration. Afterwards, the mixture was evaporated for 2 h at 115 °C to remove excess solvent and water, followed by the addition of 10% wt (based on the residual mass of the sample) of pulverized activated carbon, type WPS260-90. The adsorption stage was operated at 60 °C for 2 h. Afterwards, the mixture was vacuum filtrated to separate the pulverized, loaded, activated carbon from the glycerol mixture.

## Analytical methods

### Mass determination

The glycerol, ash, water, and MONG were analyzed according to British Standards. The glycerol analysis was conducted using BS 5711-3:1979, which is technically similar to the Ea 6–51 method of the AOCS and utilizes titration where glycerol reacts with sodium periodate ($NaIO_4$) in an aqueous acid solution, producing formaldehyde and formic acid. The formic acid is then used to quantify the glycerol content. The ash content was analyzed using BS 5711-6:1979: approximately 10 g of glycerol was placed in a crucible, heated to self-ignition to remove volatiles, and then placed into an oven (Nabertherm P300, Nabertherm, Tucson, AZ, USA) heated to 750 °C for 10 min. This was followed by cooling to room temperature over a period of 10 min and a further 15 min inside a desiccator to remove excess moisture. For the determination of the water content, the BS 5711–8:1979 was used, which utilizes a Karl Fischer titrator (Metrohm 899 Coulometer, Metrohm, Herisau, Switzerland). Finally, the MONG content was determined by Eqn (1).

$$\text{MONG } (wt\%) = 100 - \text{Glycerol } (wt\%) - \text{Water } (wt\%) - \text{Ash } (wt\%) \tag{1}$$

### High-performance liquid chromatography analysis

To validate the quantification of glycerol from titration, a high-performance liquid chromatography (HPLC) method was developed and used to quantify a more accurate value of the crude and purified glycerol. High-performance liquid chromatography equipment (Thermo Fisher Scientific Ultimate 3000, Altrincham, UK) with a refractive index detector (RID) and the column Phenomenex 00H-0138-K0 (Macclesfield, UK) was used. The mobile phase used was 1% wt formic acid solution at a flow rate of 0.6 mL/min with the temperatures of the column and RID being at 60 and 55 °C, respectively. The injection volume in the HPLC was 10 μL per sample vial as suggested in the literature.[46,47] The analysis was conducted with crude glycerol from the Stanlow biorefinery and also its purified version. The information about the standard calibration and use of the HPLC are reported in the Supplementary Information.

### Optimization procedure

As glycerol purification performance depends on different process parameters, a 'design of experiment approach' was used to determine the best possible set of variables for the optimal purification process instead of using the one-factor-at-time (OFAT) approach. A custom design was generated with three distinct levels for each factor to assess the effect of different variables using the response surface methodology (RSM) using JMP software. Three continuous variables (=factors) and one categorical variable (=factor) have been defined while other factors were controlled or held constant. The first continuous variable to vary was the pH of saponification (8–14), followed by the pH of acidification (1–6) and the solvent-to-glycerol volume ratio (3:1–1:1 v/v). The categorical variable investigated was the type of base used during the saponification and neutralization. The reason for choosing chemicals such as NaOH or KOH reflects the synergies between the purification step and the catalysts used during the transesterification; $Ca(OH)_2$ has been chosen due to its potentially positive effect of catalyst removal in crude glycerol according to Chiu *et al.*[45] In this study, the response factors were chosen as the glycerol purity (2) and the ash content (3). In total, 24 runs were conducted, which can be seen in Table 6.

$$y_{\text{Glycerol}} = \frac{m_{\text{purified}} \bullet w_{Gly,t=\text{end}}}{m_{\text{feed},t=0} \bullet w_{Gly,t=0}} \tag{2}$$

$$y_{\text{Ash}} = 1 - \frac{m_{\text{purified}} \bullet w_{\text{Ash},t=\text{end}}}{m_{\text{feed},t=0} \bullet w_{\text{Ash},t=0}} \tag{3}$$

Other variables of the analysis were not changed therefore phosphoric acid has been used as acidification agent,[26] hydrochloric acid, 2-propanol as solvent[48] and the amount of activated carbon for the adsorption process.[27,36,49]

## Results and discussion

### Characterization of crude glycerol

As anticipated, the crude glycerol from waste-based biodiesel feedstocks varied significantly leading to different results of compositions. This has mainly to do with the various feedstocks that were used at the different locations and how the refinery was operated. Feedstocks with glycerol purities down to 30% wt were possible, especially due to the higher moisture (water) content of the feedstock, lowering the viscosity of the entire mixture, or increasing the MONG content and leading to the opposite effect. Furthermore, the glycerol batches could differ in terms of viscosity, odor, and color as can be seen in Fig. 2.

Here, Stanlow glycerol (Fig. 2, right) is a monophasic, dark orange mixture with higher viscosity. Motherwell and

Amsterdam glycerols (Fig. 2, left) are rather characterized as emulsions between the polar glycerol, water, alcohol phase and the nonpolar MONG phase. Generally, the pH of all glycerols is approximately 5 due to the pre/treatment steps of neutralization which have taken place in the biodiesel refinery prior to being sent for further treatments.

## Response surface methodology for the optimization of the purification process: model fitting and ANOVA

The custom design was used to find the optimum value for the responses glycerol purity (Y1) and ash content (Y2) based on four different varied factors, three continuous and one categorical as reported in Table 6. The results of the experiments are summarized in Table 7.

After conducting the 24 runs, the software fitted a model with the following estimated parameters for the purity of glycerol (Eqn 4) and the ash content (Eqn 5):

$$
\begin{aligned}
Y_1 = {} & 75.16 - 1.88 \bullet \left( \frac{(A-11)}{3} \right) + 2.38 \bullet \left( \frac{(B-3.5)}{2.5} \right) \\
& + 0.86 \bullet (C-2) + D + \left( \frac{(B-3.5)}{2.5} \right) \bullet \left( \left( \frac{(B-3.5)}{2.5} \right) \right) \\
& + \left( \frac{(B-3.5)}{2.5} \right) \bullet ((C-2) \bullet (-0.46)) \\
& + (C-2) \bullet ((C-2) \bullet (-1.43)) + \left( \frac{(A-11)}{3} \right) \bullet D \\
& + \left( \frac{(B-3.5)}{2.5} \right) \bullet D + (C-2) \bullet D
\end{aligned}
\tag{4}
$$

$$
\begin{aligned}
Y_2 = {} & 9.87 + 0.51 \left( \frac{(A-11)}{3} \right) - 0.59 \left( \frac{(B-3.5)}{2.5} \right) \\
& - 0.74 (C-2) + D + \left( \frac{(B-3.5)}{2.5} \right) \left( \left( \frac{(B-3.5)}{2.5} \right) \bullet 0.04 \right) \\
& + \left( \frac{(B-3.5)}{2.5} \right) ((C-2) \bullet -0.69) + (C-2)((C-2) \bullet 0.08) \\
& + \left( \frac{(A-11)}{3} \right) D + \left( \frac{(B-3.5)}{2.5} \right) D + (C-2) D
\end{aligned}
\tag{5}
$$

The variables $A$, $B$, $C$, and $D$ represent the pH of saponification, the pH of acidification, the solvent-to-glycerol ratio and the type of base used respectively. The ANOVA results are shown in Table 8.

The large $F$-ratio shows that the differences between the means of the response factor (glycerol purity and ash content) for different combinations of the four variables are significant and did not occur by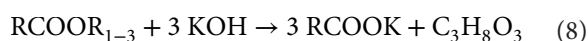 chance. This indicates that at least one of the four variables has a significant impact on the response factors. The effect test in JMP shows the variables that have the highest influence: type of base, pH of acidification, pH of saponification, and lastly solvent-to-glycerol ratio. Simultaneously, the $p$-values for both ANOVAs are below the predetermined level of significance of 0.05 which confirms that the results are significant. Furthermore, the coefficient of determination is 0.96 for the glycerol model and 0.93 for the ash model, which indicates the high suitability of the model. The adjusted coefficient of determination is lower but still in a good range of $R_{adj} = 0.89$ for the glycerol model and $R_{adj} = 0.82$ for the ash model.

By sorting the results from lowest to highest glycerol purity, it is clear that mild pH treatments with a high solvent-to-glycerol ratio and potassium as a base are mostly preferable for high glycerol content and low ash content. The reasons for this are discussed below.

## The influence of the pH of saponification and the pH of acidification on glycerol purity and ash content

The first effect investigated is the effect of the pH of saponification and the pH of acidification on the glycerol purity and the ash content. The resulting response surfaces are depicted in Fig. 3 for the glycerol purity and for the ash content respectively.

As can be seen, the glycerol purity increases by using mild pH treatment, reaching its optimal value for a pH of 8 for saponification and a pH of 6 for acidification. The aim of the saponification is to convert some of the MONG components – mainly unreacted mono-, di- and triglycerides, free fatty acids and fatty acid methyl esters – to saponified fatty acids (SFAs) (also fatty acid salts or soaps), as indicated by Eqns 6–8,[26] by adding a strong base (here KOH) to the mixture. Saponification is an endothermic reaction;[50] the temperature was increased to 60 °C according to Chol et al.,[18] to favor the reaction.

$$
RCOOCH_3 + KOH \rightarrow RCOOK + CH_3OH \tag{6}
$$

$$
RCOOH + KOH \rightarrow RCOOK + H_2O \tag{7}
$$

$$
RCOOR_{1-3} + 3\,KOH \rightarrow 3\,RCOOK + C_3H_8O_3 \tag{8}
$$

The sensitivity on the pH of saponification for the purification of crude glycerol was not investigated by other researchers.

These results differ from previous work by Ahmad Farid et al.[33] where a pH of 12 was used during saponification. They

**Table 6. Customized design used to assess the influence of factors on response.**

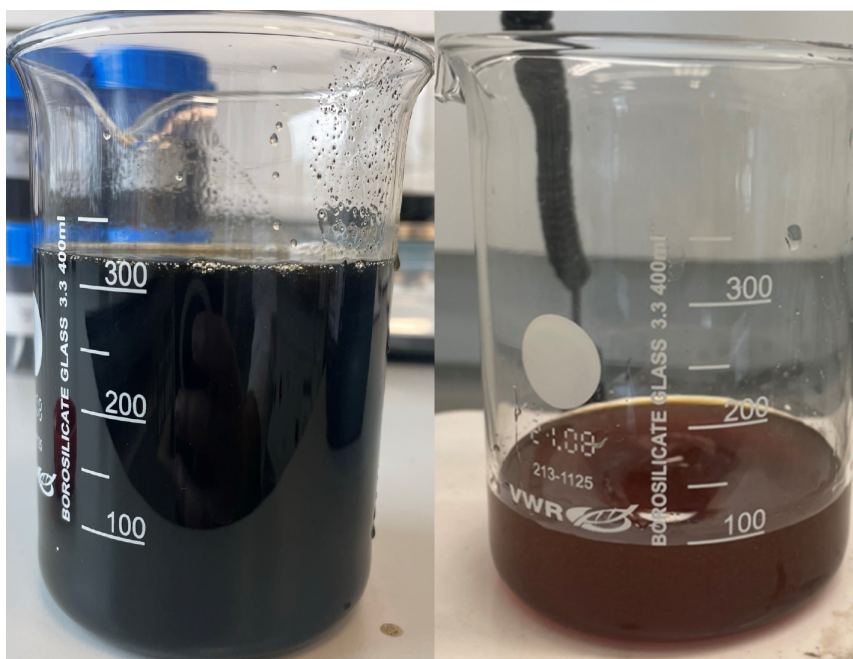| Run | pH – saponification | pH – acidification | Solvent:glycerol ratio | Type of base |
|-----|---------------------|--------------------|------------------------|--------------|
| 1 | 8 | 1 | 3 | KOH |
| 2 | 14 | 1 | 1 | KOH |
| 3 | 11 | 3.5 | 2 | KOH |
| 4 | 14 | 1 | 1 | NaOH |
| 5 | 14 | 6 | 3 | NaOH |
| 6 | 8 | 6 | 2.65 | NaOH |
| 7 | 11 | 6 | 1 | NaOH |
| 8 | 8 | 3.5 | 1 | KOH |
| 9 | 8 | 1 | 2 | $Ca(OH)_2$ |
| 10 | 14 | 6 | 1 | KOH |
| 11 | 14 | 3.5 | 1 | $Ca(OH)_2$ |
| 12 | 11 | 1 | 1 | $Ca(OH)_2$ |
| 13 | 11 | 1 | 3 | NaOH |
| 14 | 14 | 6 | 2 | $Ca(OH)_2$ |
| 15 | 11 | 3.5 | 2 | KOH |
| 16 | 14 | 1 | 3 | $Ca(OH)_2$ |
| 17 | 8 | 6 | 3 | KOH |
| 18 | 11 | 3.5 | 2 | NaOH |
| 19 | 8 | 1 | 1 | NaOH |
| 20 | 8 | 3.5 | 3 | $Ca(OH)_2$ |
| 21 | 11 | 6 | 3 | $Ca(OH)_2$ |
| 22 | 8 | 6 | 1 | $Ca(OH)_2$ |
| 23 | 11 | 3.5 | 2 | NaOH |
| 24 | 14 | 3.5 | 3 | KOH |



Figure 2. (left) Crude glycerol from Motherwell and Amsterdam plants; (right) crude glycerol from the Stanlow plant.

**Table 7. Summary of all 24 runs conducted, with the results for the glycerol purity (% wt), ash content (% wt), and glycerol recovery (%). High purity, low ashes content and high glycerol recovery are shown in green while the opposite results are reported in red.**

| Run | pH – saponification | pH – acidification | Solvent:Glycerol ratio | Type of base | Glycerol purity (% wt) | Ash content (% wt) | Glycerol recovery (%) |
|---|---|---|---|---|---|---|---|
| 4 | 14 | 1 | 1 | Sodium | 65.31 | 12.33 | 24.82 |
| 13 | 11 | 1 | 3 | Sodium | 66.95 | 12.29 | 35.08 |
| 18 | 11 | 3.5 | 2 | Sodium | 68.86 | 10.35 | 49.34 |
| 19 | 8 | 1 | 1 | Sodium | 69.53 | 11.3 | 31.96 |
| 5 | 14 | 6 | 3 | Sodium | 70.39 | 10.41 | 43.65 |
| 2 | 14 | 1 | 1 | Potassium | 71.72 | 9.46 | 24.47 |
| 16 | 14 | 1 | 3 | Calcium | 72.12 | 12.22 | 20.71 |
| 12 | 11 | 1 | 1 | Calcium | 72.59 | 10.02 | 18.82 |
| 23 | 11 | 3.5 | 2 | Sodium | 73.3 | 11.37 | 42.14 |
| 11 | 14 | 3.5 | 1 | Calcium | 73.41 | 10.98 | 15.36 |
| 8 | 8 | 3.5 | 1 | Potassium | 74.51 | 10.4 | 44.95 |
| 7 | 11 | 6 | 1 | Sodium | 75.21 | 11.8 | 42.38 |
| 10 | 14 | 6 | 1 | Potassium | 75.29 | 11.9 | 28.13 |
| 9 | 8 | 1 | 2 | Calcium | 75.53 | 11.63 | 21.00 |
| 20 | 8 | 3.5 | 3 | Calcium | 76.12 | 8.39 | 18.48 |
| 14 | 14 | 6 | 2 | Calcium | 77.47 | 8.04 | 28.10 |
| 15 | 11 | 3.5 | 2 | Potassium | 77.69 | 9.59 | 46.16 |
| 24 | 14 | 3.5 | 3 | Potassium | 78.12 | 7.69 | 41.71 |
| 21 | 11 | 6 | 3 | Calcium | 78.14 | 8.12 | 27.84 |
| 3 | 11 | 3.5 | 2 | Potassium | 79.25 | 8.51 | 47.10 |
| 6 | 8 | 6 | 2.65 | Sodium | 79.71 | 8.34 | 61.19 |
| 22 | 8 | 6 | 1 | Calcium | 79.96 | 8.56 | 34.11 |
| 17 | 8 | 6 | 3 | Potassium | 81.19 | 6.94 | 41.10 |
| 1 | 8 | 1 | 3 | Potassium | 81.84 | 7.17 | 40.42 |

**Table 8. ANOVA results for the glycerol and ash model.**

| | Source | df | Sum of squares | Mean square | F ratio |
|---|---|---|---|---|---|
| | | | Analysis of variance | | |
| Glycerol | Model | 14 | 442.1122 | 31.5794 | 14.8604 |
| | Error | 9 | 19.1256 | 2.1251 | Prob>F |
| | C. Total | 23 | 461.2379 | | 0.0002 |
| Ash | Model | 14 | 65.0712 | 4.6480 | 8.3643 |
| | Error | 9 | 5.0012 | 0.5557 | Prob>F |
| | C. Total | 23 | 70.0725 | | 0.0015 |

because saponification is carried out at a pH of 8 without compromising the final purity obtained in other studies. The main reasons may be due to the slightly acidic properties of the crude glycerol, as can be seen in Table 4, and due to the type of base that was used and the type of MONG phase (short-chain and long-chain acids, FAME) and other components such as aldehydes or phenolic components, which are unsaponifiable.

In the process of acidification, soaps are converted into free fatty acids and separated from salts according to Eqns (9) and (10):

$$RCOOK + H_3PO_4 \leftrightharpoons RCOOH + KH_2PO_4 \downarrow \qquad (9)$$

$$3\,KOH + H_3PO_4 \leftrightharpoons K_3PO_4 \downarrow + 3\,H_2O \qquad (10)$$
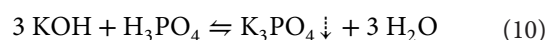
The optimal pH obtained in this study is equal to 6, which substantially agrees with the results obtained by Violeta

also differ from the work of Xiao et al.[32] who used NaOH to operate at pH of 11, or Chol et al.[18] who used crude glycerol from industrial canola-based biodiesel production and reached a final purity up to 75.4% wt. A first relevant outcome of this optimization study on pH during saponification is therefore the substantial reduction in required chemicals
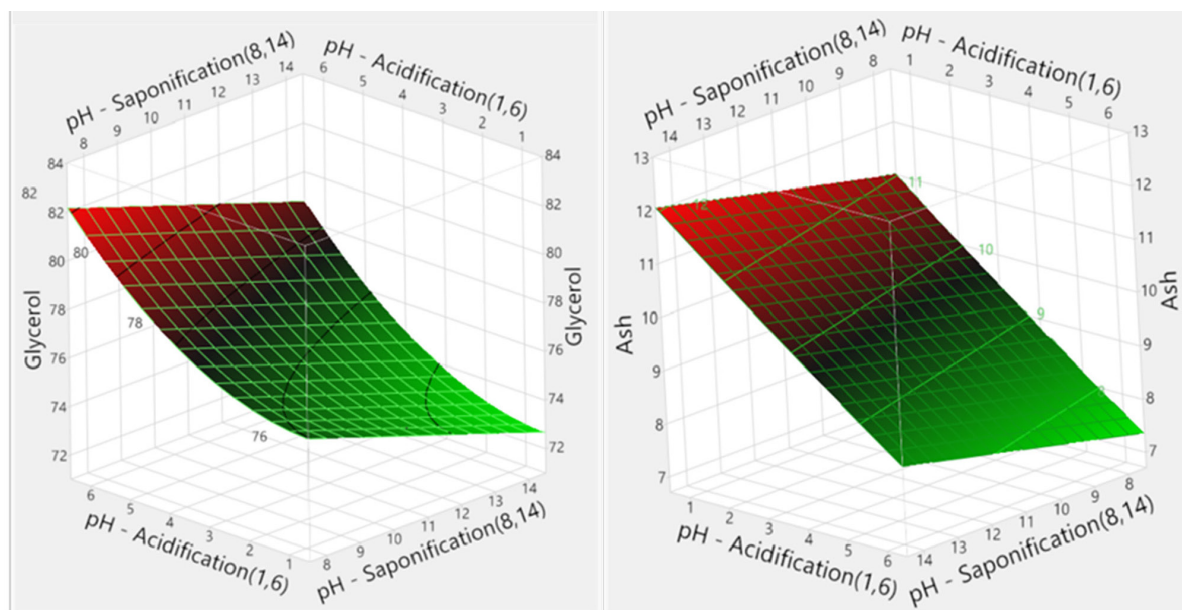
Figure 3. Response surface for the glycerol purity (left) and ash content (right), varying the pH of acidification and pH of saponification.

et al.[29] This result conflicts with the work of Kongjao et al.[30] who found that a low pH during acidification increased the UCO-derived glycerol purity at the expense of glycerol recovery, and Dhabhai et al.[51] who achieved maximum purity at a pH for acidification of 3.5. These differences can be explained by the different crude glycerol feedstocks' properties (primarily MONG content, initial pH, and moisture), and the source of the crude glycerol. In particular, acylglycerols may be more likely to form when using industrially derived crude glycerol (as in this study) due to the existence of various different short-chain and long-chain fatty acids, which might react with glycerol. This means that acidifying to a very low pH could lead to a decreased purity and yield. Low pH during acidification also increases the safety hazard and costs of purification given the increased quantity of chemicals required and corrosiveness.

Figure 3 shows a clear linear curve for the ash content, which is comparable with the glycerol purity. One reason for this is the fact that more severe pH levels during the saponification and acidification add additional salts to the mixture, which may not precipitate due to their solubility in the glycerol or in the remaining water content. The other reason is the extreme pHs, especially during acidification, which may facilitate acid-catalyzed esterification despite the low temperature, as reported in the literature,[52] due to high FFA, glycerol (acting as alcohol) and excess acid, as confirmed by Violeta et al.[29] and Kongjao et al.[30]

## The influence of the pH of saponification and solvent-to-glycerol volume ratio on glycerol purity and ash content

Looking at the glycerol purity and ash content and their dependency on the pH of saponification (Fig. 4) and the solvent-to-glycerol volume ratio an optimum value can be found. At an increased solvent-to-glycerol volume ratio, the amount of precipitated salts increases (lower ash content), the final glycerol purity peaks at a solvent-to-glycerol volume ratio of 2 and decreases slightly because the solubility of salts decreases significantly when adding excess amounts of solvent. This was also confirmed by Velez et al.,[48] who studied the antisolvent treatment effect using isopropyl alcohol (2-propanol) as antisolvent. The effect becomes less significant for NaCl and $Na_2SO_4$ when adding excess amounts of solvent. However, the glycerol purity (as well as the recovery) decreases following the same trend when solvent-to-glycerol ratio increases above 2.5 due to the fact that during the evaporation more glycerol compounds are removed and also due to the higher amount of dilution with solvent.

In both cases, the influence of pH of saponification is stronger than the influence of the solvent-to-glycerol volume ratio.

## The influence of the pH of acidification and solvent-to-glycerol ratio on glycerol purity and ash content

The influence of the pH of acidification and solvent-to-glycerol volume ratio on the glycerol purity and ash content can be seen
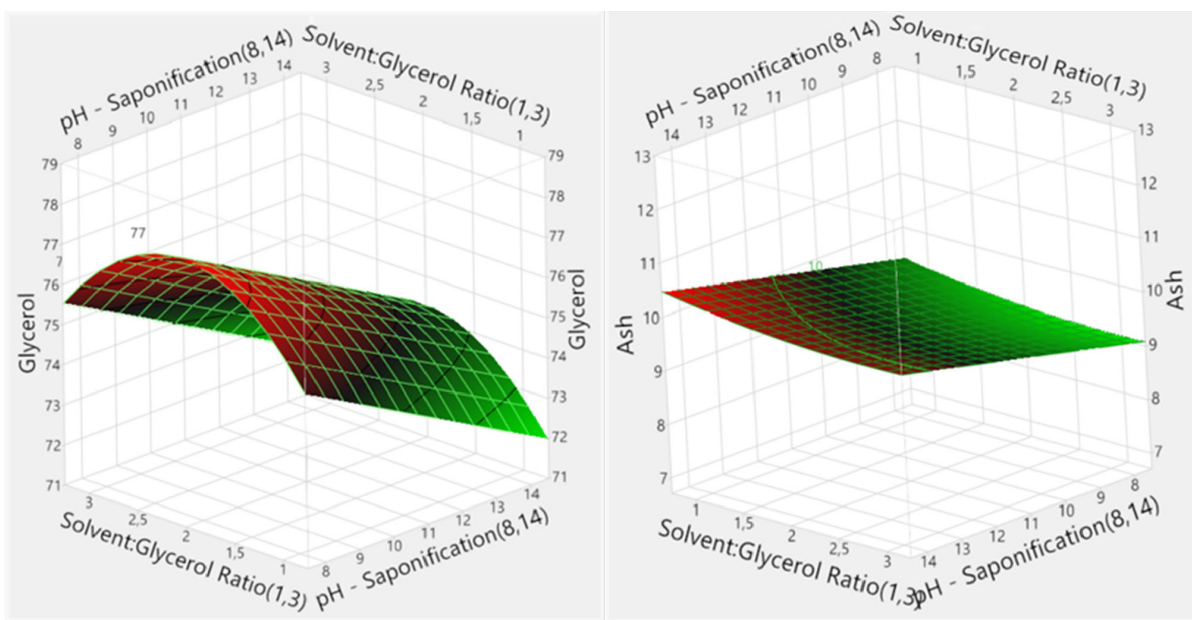
Figure 4. Response surface for the glycerol purity (left) and ash content (right), varying the solvent-to-glycerol volume ratio and pH of saponification.

in Fig. 5. A similar trend can be observed as in the previous section. A lower pH during the acidification leads, in general, to lower glycerol purity and a much higher ash fraction in the final glycerol because of the esterification of glycerols to glycerides takes place. This is confirmed in the literature.[29] As with the pH of saponification, the glycerol purity increases mostly by using a solvent-to-glycerol volume ratio of 1.5–2:1 whereas a high solvent-to-glycerol ratio of 3:1 is the best choice for the reduction of ash content in the glycerol.

## Influence of type of base

According to the experimental results provided by the JMP, the type of base used in the process for the saponification and neutralization has the highest impact of all of the factors that were investigated (Fig. 6). The best results have been achieved, in general, with the use of KOH followed by $Ca(OH)_2$ and, finally, NaOH. The selection of the type of base depends on the catalyst used in the transesterification reaction to produce biodiesel since similar elements could have the common-ion effect and the solubility of the salts in water and glycerol which is generated during the acidification and neutralization stage. The latter is also relevant for material handling within an industrial setting where synergies between reactants can reduce complexity and costs.

The biodiesel process generally applies either potassium or sodium hydroxide to catalyze the transesterification reaction from oils and fats and methanol to FAMEs and glycerol.

Hence, ionic compounds such as dissolved potassium or dissolved sodium are present in the crude glycerol phase as spent catalysts. To be able to achieve the removal of these compounds, the common-ion effect is relevant. This influences the solubility equilibrium in a mixture due to Le Chatelier and Braun's principle. The effect leads to a decrease in solubility (or increase in ionic association of a certain species) due to the addition of another soluble compound containing an ion in common with the species. The glycerol samples are derived from biodiesel refineries, which utilize mostly potassium hydroxide and sulfuric acid as catalysts for their operations. The crude glycerol contains mostly dissociated ionic compounds of potassium and sulfur. The use of potassium hydroxide is therefore more favorable to form and precipitate salts during glycerol purification.[48]

Furthermore, the solubility of the generated salts has a significant influence on the ash content as different salts have different solubilities in water as well as glycerol. Potassium-based salts have a higher solubility than calcium- or sodium-based salts in water due to their high polarity. The addition of a polar solvent such as isopropyl alcohol forces the precipitation of a large amount of salts due to the antisolvent effect, making the salts insoluble in the solvent. It also removes many of the potassium-based salts, which were generated in the prior acidification stage. The main factor is the dielectric constant of the solvent in this regard, which is a measure of its polarity.[53] The ideal solvent has a low dielectric constant while simultaneously being polar enough
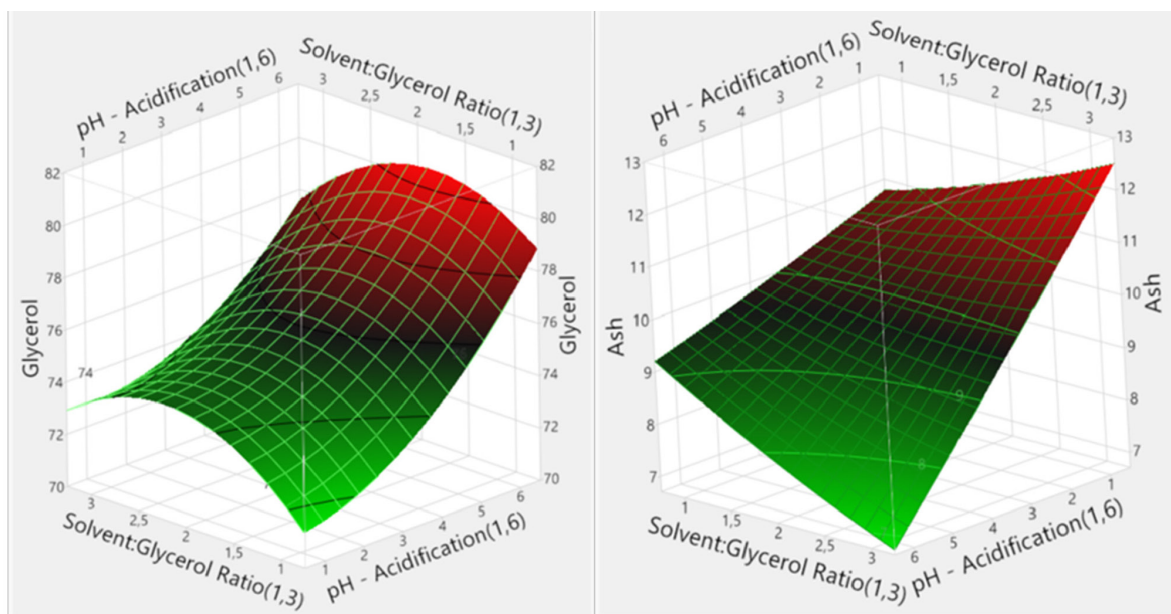
Figure 5. Response surface for the glycerol purity (left) and ash content (right), varying the solvent:glycerol volume ratio and pH of acidification.
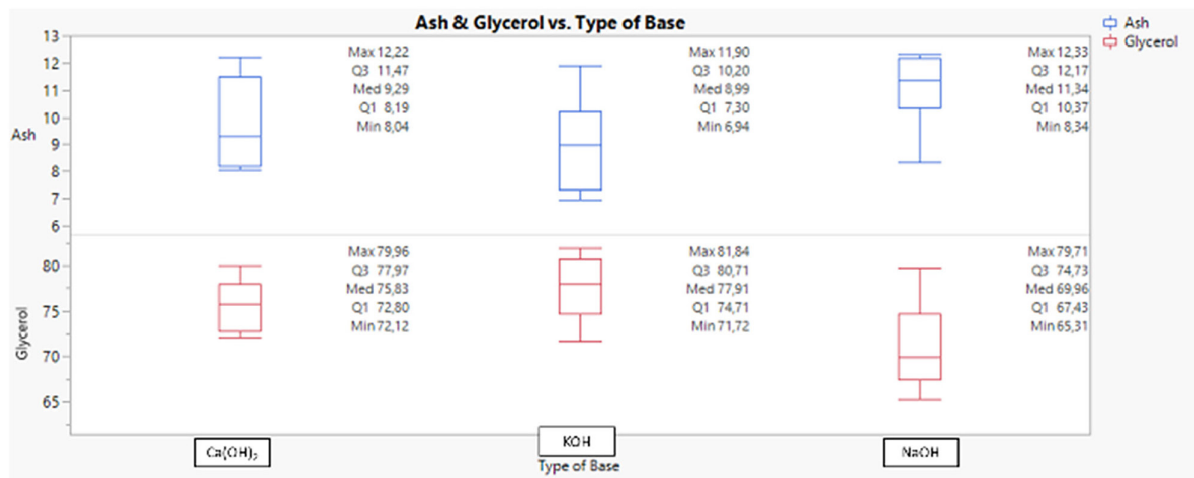


Figure 6. Graphical representation of the influence of the type of base on the ash and glycerol content.

to be miscible with water and glycerol to force a reduction in the dissociability of salts (as in the case of isopropyl alcohol compared to water).[54]

## Optimal purification route

The results obtained through the custom design and response surface methodology were used to determine the best possible set of factors to predict the highest glycerol purity and lowest ash content, as discussed in the methodology section. Figure 7 shows the prediction profiler with the

adjusted maximal desirability. The model predicted a final glycerol purity of 81.8% wt and ash content of 7.05% wt.

To validate these results, a final 25th run was necessary, which was conducted using the same feedstock as in the previous runs, with the predicted conditions of a pH of 8 for saponification, a pH of 6 for acidification, and a 3:1 solvent-to-glycerol volume ratio. The resulting flowsheet can be seen in Fig. 8 with the relevant mass balance of the entire process.

The result of the run under optimized conditions provided a glycerol purity of 84.61% wt and an ash content of 6.53% wt. These results were even higher than expected. Ash removal
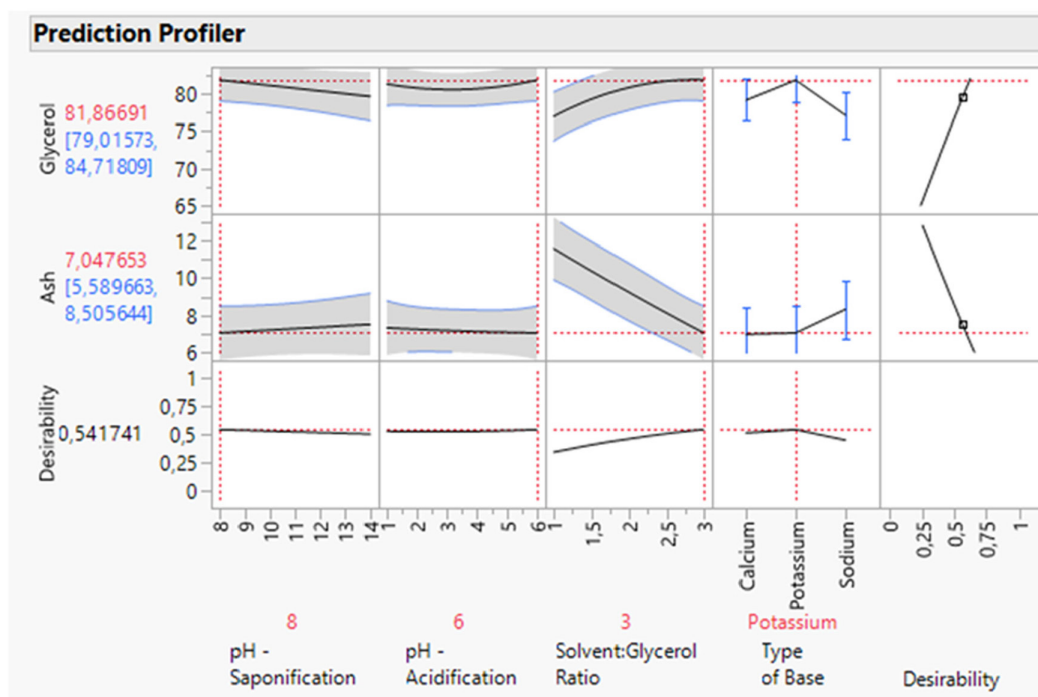
Figure 7. Prediction profiler of JMP, used to determine the optimum factor combination for the highest glycerol purity (% wt) and lowest ash content (% wt).
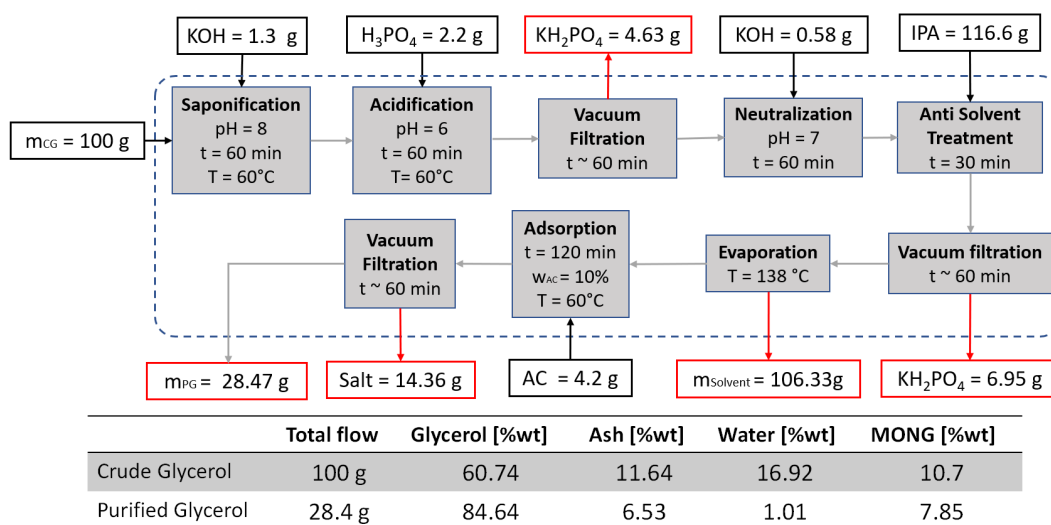


| | Total flow | Glycerol [%wt] | Ash [%wt] | Water [%wt] | MONG [%wt] |
|---|---|---|---|---|---|
| Crude Glycerol | 100 g | 60.74 | 11.64 | 16.92 | 10.7 |
| Purified Glycerol | 28.4 g | 84.64 | 6.53 | 1.01 | 7.85 |

Figure 8. Flowsheet of the optimized crude glycerol purification process.

accomplished a remarkable 84.03% with a glycerol recovery of about 40% considering the scale of the experiment (100 g batch) and considering the exceptionally low quality of the feedstock derived from a multifeed waste-based biodiesel refinery.

Unlike all previous studies reporting glycerol purification, this work has optimized glycerol purity and ash content while taking into account the impact on glycerol recovery, which is relevant to assess the industrial feasibility of this purification process. Such optimization makes the overall study more challenging; however, it provides meaningful input for process scale up and implementation.

The glycerol recovery is strongly affected by the losses of liquid during the entire process (e.g. due to material that

is sticking in the separatory funnels, beakers, or Buechner flasks). Recovery of glycerol and MONG was limited to 36.85% because a large amount of MONG is recovered in the plant and it has low methanol content.

As mentioned above, the custom-designed runs were conducted using the feedstock from Stanlow as the base scenario. To check whether the purification process can be applied generally to other crude (waste) glycerols as well, the same optimum factors of pH and glycerol-to-solvent ratio were used to treat the glycerol from Motherwell and Amsterdam. The flowsheets of both experiments can be seen in the Appendix. Unlike the glycerol from Stanlow, the two other feedstocks yielded a distinct top hydrophobic organic

layer, which could be separated by gravity. Looking at the results in Table 9, it was possible to confirm that such a set of operating conditions is relevant to achieve the glycerol purity and ash content in the same ranges thus confirming the validity of the process and universal behavior for such low-grade feedstocks.

It can be concluded that the purification process yields, in general, purities over 80% wt on a dry basis (81.49% wt for Motherwell and 86.23% wt for Amsterdam), which is very consistent with other physiochemical routes developed by other research studies, presented and summarized in Table 3. Nevertheless, the recoveries for Motherwell and Amsterdam are significantly lower than those for Stanlow. This is due to the high amount of nonpolar MONG that is being decanted after the acidification which does not exist when using the Stanlow glycerol (due to its nature of a monophasic mixture instead of an emulsion). The mass of nonpolar MONG content that is being removed after the acidification using the glycerol from Motherwell and Amsterdam accounted for approximately 20% wt, which is relevant in the overall mass balance. Furthermore, the ash content increased slightly relative to the mass. Nevertheless, the process that has been developed can be used to treat any kind of crude (waste) glycerol in a comparatively mild pH, making it attractive for the industry in terms of material usage and corrosiveness. Attarbachi et al.[43] presented the experimental validation of the physiochemical treatment in a larger batch reactor, yielding a glycerol recovery of 61.7% and ash removal of 78.9%. The study also reports the economic performance for an industrial-scale application in terms of the cost of purified glycerol 19.19 €/ton and energy demand (137 kWh/ton of purified glycerol) (Figure 9).

| Table 9. Final composition and yields for the glycerol purification process. | | | |
|---|---|---|---|
| Composition $t=1$ | Stanlow | Motherwell | Amsterdam |
| Glycerol (% wt) | 84.61 | 79.78 | 79.50 |
| Ash (% wt) | 6.53 | 4.9 | 6.3 |
| Water (% wt) | 1.01 | 2.1 | 7.8 |
| MONG (% wt) | 7.85 | 13.22 | 6.4 |
| Liquid (g) | 28.47 | 18.17 | 17.99 |
| Glycerol (g) | 24.09 | 14.50 | 14.30 |
| Ash (g) | 1.86 | 0.89 | 1.13 |
| Water (g) | 0.29 | 0.38 | 1.40 |
| MONG (g) | 2.23 | 2.40 | 1.15 |
| Glycerol (% wt) on a dry basis | 85.47 | 81.49 | 86.23 |
| Glycerol recovery (%) | 39.66 | 31.74 | 22.85 |
| Glycerol + MONG recovery (%) | 36.85 | 32.48 | 19.73 |
| Ash removal (%) | 84.03 | 89.39 | 82.06 |
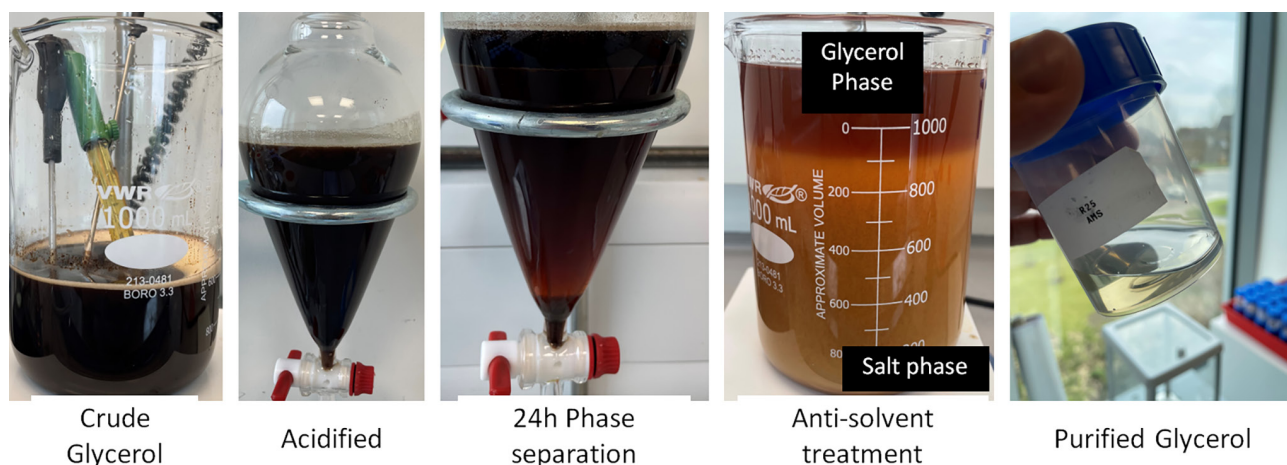


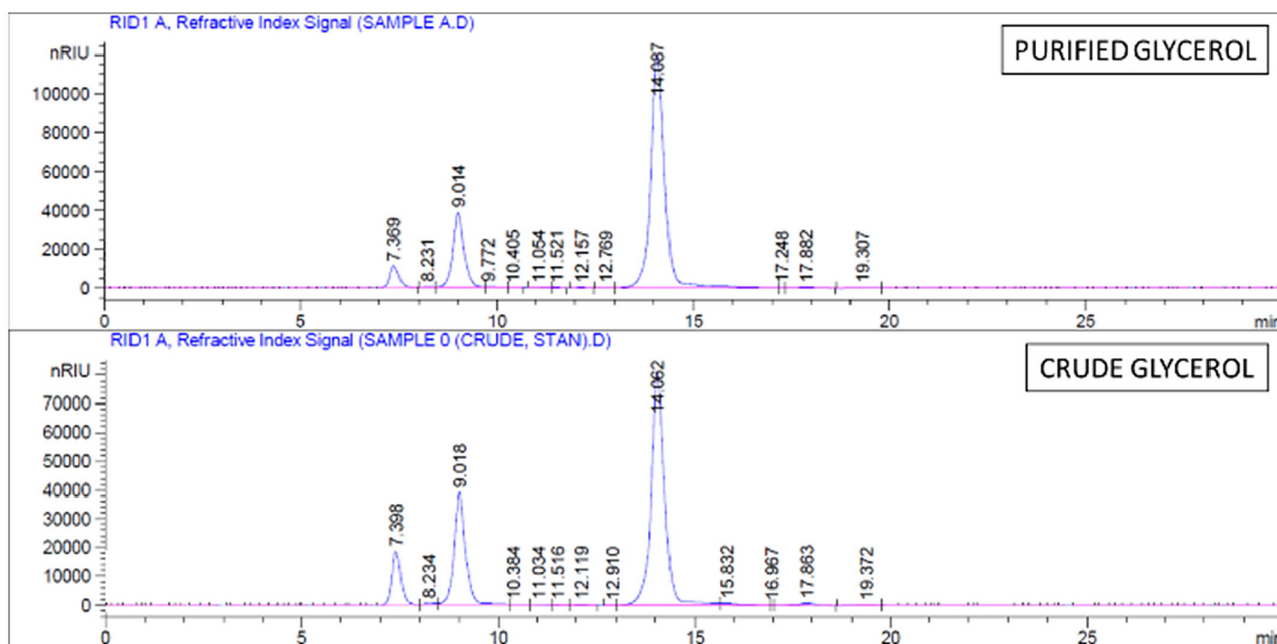Figure 9. Purification of crude glycerol to purified glycerol.

Figure 10. Refractive index detector results for the purified and crude glycerol samples.

**Table 10. New composition of purified glycerol after HPLC compared to titration technique.**

| Component | Composition after HPLC | Titration composition |
|---|---|---|
| Glycerol (% wt) | 89.81 | 84.64 |
| Ash (% wt) | 6.53 | 6.53 |
| Water (% wt) | 1.01 | 1.01 |
| MONG (% wt) | 2.65 | 7.85 |
| Glycerol recovery (%) | 42.10 | 39.65 |
| Ash removal (%) | 84.03 | 84.03 |

The HPLC-RID results for the crude and purified sample are shown in Fig. 10. The peak at min 14 shows the glycerol sample whereas the peak at min 9 shows the citric acid in which the samples have been dissolved. This was confirmed by the internal standards plots, which were also provided by the HPLC.

The results validate the results obtained from the titration, as the purity of the crude glycerol is similar to the purity of the Stanlow feedstock with a slight deviation of about 5%. (Table 10) and also with a slight increase in glycerol recovery.

## Conclusion

This work is the first attempt to develop a systematic, universal, and comprehensive study for the purification of extreme low-quality crude glycerol derived from multifeedstock waste-based biodiesel refineries. The process shows consistent results by increasing the purity of the glycerol from 40% to 60% wt to over 80% wt regardless of the source, type and initial composition reaching a maximum of 89.8%. This approach is valid for several industrial settings, enhancing waste recovery and in line with the sustainability agenda of biobased industries and governments. A mild treatment with KOH (saponification to pH of 8) and $H_3PO_4$ (acidification to pH 6) has shown the best response. A 2-propanol-to-glycerol volume ratio of 3 is generally preferable to achieve high glycerol purity and low ash content. Potassium hydroxide has shown remarkable efficiency in removing the ashes due to its affinity with the inorganic compounds present in the ashes in comparison with calcium and sodium hydroxide. Glycerol recovery has been limited to 40%, which is unprecedented when compared with previous literature studies, which have not mentioned the glycerol recovery of their purification methods. These results have been consistent in the presence of different low-quality feedstocks, thus providing a general platform for hard feedstock purification and oleochemical waste recovery. The results of this study will be further elaborated at a larger scale (20× bigger) in a future work which will also look at the industrial implementation, large-scale assessment, and process techno-economics.

# Abbreviations

| | |
|---|---|
| ACS | American Chemical Society |
| ANOVA | analysis of variance |
| AOCS | American Oil Chemists' Society |
| BS | British Standard |
| CAGR | compound annual growth rate |
| DF | degree of freedom |
| DOE | design of experiment |
| FAME | fatty acid methyl ester |
| FFA | free fatty acids |
| FOG | fats, oils, and greases |
| HPLC | high-performance liquid chromatography |
| ICP-OES | inductively coupled plasma–optical emission spectrometry |
| MONG | matter organic nonglycerol |
| OFAT | one factor at a time |
| PAC | powdered activated carbon |
| POME | palm oil mill effluent |
| RID | refractive index detector |
| RSM | response surface methodology |
| TAG | triacylglyceride |
| UCO | used cooking oil |

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# Author contributions

Taha Attabachi: Conceptualisation; methodology; formal analysis; investigation; visualization; data curation; and writing—Original draft. Martin Kingsley: Writing—review and editing; resources; and supervision. Vincenzo Spallina: Funding acquisition; project administration; supervision; visualization; and writing—review and editing.

# Conflict of interest statement

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.

# References

1. *Biofuels Market Size to Hit Around US$ 201.21 Billion by 2030* [Online]. Available: https://www.precedenceresearch.com/biofuels-market [3 January 2023].
2. Directorate-General for Energy. *Biofuels* [Online] (2020). Available: https://energy.ec.europa.eu/topics/renewable-energy/bioenergy/biofuels_en [29 November 2022].
3. Bhuiya MMK, Rasul MG, Khan MMK, Ashwath N and Azad AK, Prospects of 2nd generation biodiesel as a sustainable fuel – Part: 1 selection of feedstocks, oil extraction techniques and conversion technologies. *Renew Sustain Energy Rev* **55**:1109–1128 (2016). https://doi.org/10.1016/j.rser.2015.04.163.
4. Cárdenas J, Orjuela A, Sánchez DL, Narváez PC, Katryniok B and Clark J, Pre-treatment of used cooking oils for the production of green chemicals: A review. *J Clean Prod* **289**:125129 (2021).
5. Santibáñez C, Teresa Varnero M and Bustamante M, Residual glycerol from biodiesel manufacturing, waste or potential source of bioenergy: a review. *Chil J Agric Res* **71**:469 (2011).
6. Anand P and Saxena RK, A comparative study of solvent-assisted pretreatment of biodiesel derived crude glycerol on growth and 1,3-propanediol production from *Citrobacter freundii*. *N Biotechnol* **29**:199. Available:–205 (2012). www.elsevier.com/locate/nbt.
7. Bhuiya MMK, Rasul MG, Khan MMK, Ashwath N, Azad AK and Hazrat MA, Second generation biodiesel: Potential alternative to-edible oil-derived biodiesel. *Energy Procedia* **61**:1969–1972 (2014). https://doi.org/10.1016/j.egypro.2014.12.054.
8. Fávaro VR, Ezequiel JMB, D'Aurea AP, Van Cleef EHCB, Sancanari JBD, Santos VC *et al.*, Glycerin in cattle feed: Intake, digestibility, and ruminal and blood parameters. *Semin Agrar* **36**:1495–1505 (2015).
9. Tyagi LRKRD and Drogui P, Economic analysis for simultaneous production of microbial lipid and citric acid by oleaginous yeast cultivated on purified crude glycerol. *Biomass Convers Biorefinery* **13**:9141–9154 (2023). https://doi.org/10.1007/s13399-021-01772-8.
10. Kumar LR, Yellapu SK, Tyagi RD and Drogui P, Purified crude glycerol by acid treatment allows to improve lipid productivity by Yarrowia lipolytica SKY7. *Process Biochem* **96**:165–173 (2020). https://doi.org/10.1016/j.procbio.2020.06.010.
11. Pitt FD, Domingos AM and Barros AAC, Purification of residual glycerol recovered from biodiesel production. *South African J Chem Eng* **29**:42–51 (2019). https://doi.org/10.1016/j.sajce.2019.06.001.
12. Attarbachi T, Kingsley MD and Spallina V, New trends on crude glycerol purification: a review. *Fuel* **340**:127485 (2023) Available: https://linkinghub.elsevier.com/retrieve/pii/S0016236123000984 [13 March 2023].
13. Tan HW, Abdul Aziz AR and Aroua MK, Glycerol production and its applications as a raw material: a review. *Renew Sustain Energy Rev* **27**:118–127 (2013).
14. Behr A, Eilting J, Irawadi K, Leschinski J and Lindner F, Cutting-edge research for a greener sustainable future improved utilisation of renewable resources: New important derivatives of glycerol. *Green Chem* **10**:13–30 (2008).
15. Pal P, Chaurasia SP, Upadhyaya S, Agarwal M and Sridhar S, Glycerol purification using membrane technology. *Membr Process* **7**:431–463 (2018).
16. Pott RWM, Howe CJ and Dennis JS, The purification of crude glycerol derived from biodiesel manufacture and its use as
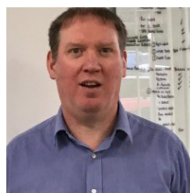
a substrate by *Rhodopseudomonas palustris* to produce hydrogen. *Bioresour Technol* **152**:464–470 (2014). https://doi.org/10.1016/j.biortech.2013.10.094.

17. Lopes AP, Souza PR, Bonafé EG, Visentainer JV, Martins AF and Canesin EA, Purified glycerol is produced from the frying oil transesteri fication by combining a pre-purification strategy performed with condensed tannin polymer derivative followed by ionic exchange. *Fuel Process Technol* **187**:73–83 (2019). https://doi.org/10.1016/j.fuproc.2019.01.014.

18. Chol CG, Dhabhai R, Dalai AK and Reaney M, Purification of crude glycerol derived from biodiesel production process: experimental studies and techno-economic analyses. *Fuel Process Technol* **178**:78–87 (2018). https://doi.org/10.1016/j.fuproc.2018.05.023.

19. Yildiz G, Ronsse F, Venderbosch R, van Duren R, Kersten SRA and Prins W, Effect of biomass ash in catalytic fast pyrolysis of pine wood. *Appl Catal B Environ* **168**–**169**:203–211 (2015). https://doi.org/10.1016/j.apcatb.2014.12.044.

20. Dhabhai R, Koranian P, Huang Q, Scheibelhoffer DSB, Dhabhai R, Koranian P *et al.*, Purification of glycerol and its conversion to value- added chemicals: A review. *Sep Sci Technol* **58**:1383–1402 (2023). https://doi.org/10.1080/01496395.2023.2189054.

21. Moklis MH, Cheng S, Cross JS. Current and future trends for crude glycerol upgrading to high value-added products. *Sustainability* **15**:2979 (2023). https://doi.org/10.3390/su15042979.

22. Di Fraia A, Miliotti E, Rizzo AM, Zoppi G, Pipitone G, Pirone R *et al.*, Coupling hydrothermal liquefaction and aqueous phase reforming for integrated production of biocrude and renewable $H_2$. *AIChE J* **69**:e17652 (2022).

23. Tabatabaei M, Aghbashlo M. *Biodiesel from Production to Combustion* (2019). Available: http://www.springer.com/series/11833

24. Thompson JC and He BB, Characterization of crude glycerol from biodiesel production from multiple feedstocks. *Appl Eng Agric* **22**:261–265 (2006).

25. Shanmughom R and Raghu SK, Purification strategies for crude glycerol: a transesterification derivative. *AIP Conf Proc* **2863 2023**:020012 (2023).

26. Hájek M and Skopal F, Treatment of glycerol phase formed by biodiesel production. *Bioresour Technol* **101**:3242–3245 (2010). https://doi.org/10.1016/j.biortech.2009.12.094.

27. Manosak R, Limpattayanate S and Hunsom M, Sequential-refining of crude glycerol derived from waste used-oil methyl ester plant via a combined process of chemical and adsorption. *Fuel Process Technol* **92**:92–99 (2011). https://doi.org/10.1016/j.fuproc.2010.09.002.

28. Javani A, Hasheminejad M, Tahvildari K and Tabatabaei M, Bioresource technology high quality potassium phosphate production through step-by-step glycerol purification: A strategy to economize biodiesel production. *Bioresour Technol* **104**:788–790 (2012). https://doi.org/10.1016/j.biortech.2011.09.134.

29. Mena-Cervantes VY, Hernández-Altamirano R and Tiscareño-Ferrer A, Development of a green one-step neutralization process for valorization of crude glycerol obtained from biodiesel. *Environ Sci Pollut Res* **27**:28500–28509 (2020).

30. Kongjao S and Damronglerd S, Purification of crude glycerol derived from waste used-oil methyl ester plant. *Korean J Chem Eng* **27**:944–949 (2010).

31. Ningaraju C, Yatish KV and Sakar M, Simultaneous refining of biodiesel-derived crude glycerol and synthesis of value-

added powdered catalysts for biodiesel production: a green chemistry approach for sustainable biodiesel industries. *J Clean Prod* **363**:132448 (2022). https://doi.org/10.1016/j.jclepro.2022.132448.

32. Xiao Y, Xiao G and Varma A, A universal procedure for crude glycerol purification from different feedstocks in biodiesel production: experimental and simulation study. *Ind Eng Chem Res* **52**:14291–14296 (2013).

33. Ahmad Farid MA, Hassan MA, Roslan AM, Ariffin H, Norrrahim MNF, Othman MR *et al.*, Improving the decolorization of glycerol by adsorption using activated carbon derived from oil palm biomass. *Environ Sci Pollut Res* **28**:27976–27987 (2021). https://doi.org/10.1007/s11356-021-12585-7.

34. Hunsom M and Autthanit C, Preparation of sludge-derived KOH-activated carbon for crude glycerol purification. *J Mater Cycles Waste Manag* **19**:213–225 (2017).

35. Hunsom M and Autthanit C, Adsorptive purification of crude glycerol by sewage sludge-derived activated carbon prepared by chemical activation with $H_3PO_4$, $K_2CO_3$ and KOH. *Chem Eng J* **229**:334–343 (2013). https://doi.org/10.1016/j.cej.2013.05.120.

36. Aziz I, Sulistina RC and Hendrawati AL, Purification of crude glycerol from acidification using tea waste. *IOP Conf Ser Earth Environ Sci* **175**:1–9 (2018).

37. Chen J, Yan S, Zhang X, Tyagi RD, Surampalli RY and Valéro JR, Chemical and biological conversion of crude glycerol derived from waste cooking oil to biodiesel. *Waste Manag* **71**:164–175 (2018). https://doi.org/10.1016/j.wasman.2017.10.044.

38. Dmitriev GS, Zanaveskin LN, Terekhov AV, Samoilov VO, Kozlovskii IA and Maksimov AL, Technologies for processing of crude glycerol from biodiesel production: synthesis of solketal and its hydrolysis to obtain pure glycerol. *Russ J Appl Chem* **91**:1478–1485 (2018).

39. Nanda M, Yuan Z and Qin W, Purification of crude glycerol using acidification: effects of acid types and product characterization. *Austin J Chem Eng* **1**:1–7 (2014) Available: http://flash.lakeheadu.ca/~wqin/website_papers_nov_14/2014_Malaya_Austin_Journal_Paper.pdf.

40. Thanahiranya P, Charoensuppanimit P, Sadhukhan J, Soottitantawat A, Arpornwichanop A, Thongchul N *et al.*, Succinic acid production from glycerol by actinobacillus succinogenes: techno-economic, environmental, and exergy analyses. *J Clean Prod* **404**:136927 (2023). https://doi.org/10.1016/j.jclepro.2023.136927.

41. Thanahiranya P, Sadhukhan J, Charoensuppanimit P, Soottitantawat A, Arpornwichanop A, Thongchul N *et al.*, Sustainability assessment of dihydroxyacetone (DHA) production from glycerol: a comparative study between biological and catalytic oxidation routes. *ACS Sustain Chem Eng* **11**:17425–17439 (2023).

42. Vincenzo Spallina. *Glamour Project* [Online] (2020). Available: https://www.glamour-project.eu/ [27 June 2023].

43. Attarbachi T, Kingsley M and Spallina V, Experimental scale-up and technoeconomic assessment of low-grade glycerol purification from waste-based biorefinery. *Ind Eng Chem Res* **63**:4905–4917 (2023).

44. Animal by-Product Categories, Site Approval, Hygiene and Disposal – GOV.UK [Online]. Available: https://www.gov.uk/guidance/animal-by-product-categories-site-approval-hygiene-and-disposal [20 May 2021].

45. Chiu CW, Dasari MA, Sutterlin WR and Suppes GJ, Removal of residual catalyst from simulated biodiesel's crude glycerol for glycerol hydrogenolysis to propylene glycol. *Ind Eng Chem Res* **45**:791–795 (2006).

46. Hu S, Luo X, Wan C and Li Y, Characterization of crude glycerol from biodiesel plants. *J Agric Food Chem* **60**:5915–5921 (2012).

47. Esteban J, Ladero M, Molinero L and García-Ochoa F, Liquid-liquid equilibria for the ternary systems DMC-methanol-glycerol, DMC-glycerol carbonate-glycerol and the quaternary system DMC-methanol-glycerol carbonate-glycerol at catalytic reacting temperatures. *Chem Eng Res Des* **92**:2797–2805 (2014). https://doi.org/10.1016/j.cherd.2014.05.026.

48. Velez AR, Mufari JR and Rovetto LJ, Sodium salts solubility in ternary glycerol+water+alcohol mixtures present in purification process of crude glycerol from the biodiesel industry. *Fluid Phase Equilib* **497**:55–63 (2019). https://doi.org/10.1016/j.fluid.2019.05.023.

49. Yuliana M, Trisna L, Sari F and Lunardi VB, Glycerol purification using reactivated spent bleaching earth from palm oil refineries: zero-waste approach. *J Environ Chem Eng* **9**:105239 (2021). https://doi.org/10.1016/j.jece.2021.105239.

50. Eze VC, Harvey AP and Phan AN, Determination of the kinetics of biodiesel saponification in alcoholic hydroxide solutions. *Fuel* **140**:724–730 (2015).

51. Dhabhai R, Ahmadifeijani E, Dalai AK, Reaney M. Purification of crude glycerol using a sequential physico-chemical treatment, membrane filtration, and activated charcoal adsorption. *Sep Purif Technol* **168**:101–106 (2016). https://doi.org/10.1016/j.seppur.2016.05.030.

52. *Fischer Esterification – Carboxylic Acid to Ester Under Acidic Conditions – Master Organic Chemistry* [Online]. Available: https://www.masterorganicchemistry.com/2022/11/16/fischer-esterification/ [2 April 2023].

53. *Dielectric Constant – Chemistry LibreTexts* [Online]. Available: https://chem.libretexts.org/Ancillary_Materials/Reference/Organic_Chemistry_Glossary/Dielectric_Constant [13 March 2023].

54. Dielectric Constant [Online]. Available: https://macro.lsu.edu/HowTo/solvents/DielectricConstant.htm [13 March 2023].

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Martin Kingsley obtained a bachelor's degree in engineering sciences at Edinburgh University before taking a master's degree in analytical chemistry from Teesside University. He has over 25 years' technical experience, including experience in new product development, product quality, biofuels, and lubricants. He is currently the R&D manager at Argent Energy, a waste-based biodiesel manufacturer with sites in the UK and Netherlands.

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**Taha Attarbachi**

Taha Attarbachi completed his bachelor of science degree in process engineering at the Hamburg University of Technology (TUHH). Following this, he completed a double degree in process engineering (MSc) and technology management (MA) at the TUHH and at the Northern Institute of Technology Management (NITHH). He started his PhD in chemical engineering at the University of Manchester in 2020, working on the GLAMOUR H2020 project. He is responsible for the purification of waste material, specifically crude glycerol from second-generation biodiesel refineries, which will be used for glycerol steam reforming purposes and finally turned into sustainable aviation fuel.

# Appendix



| | Total flow | Glycerol [%wt] | Ash [%wt] | Water [%wt] | MONG [%wt] |
|---|---|---|---|---|---|
| Crude Glycerol | 100 g | 62.59 | 6.3 | 17.13 | 15.74 |
| Purified Glycerol | 17.99 g | 79.50 | 6.3 | 7.8 | 6.4 |

Figure A1. Flowsheet for the purification of Amsterdam crude glycerol.



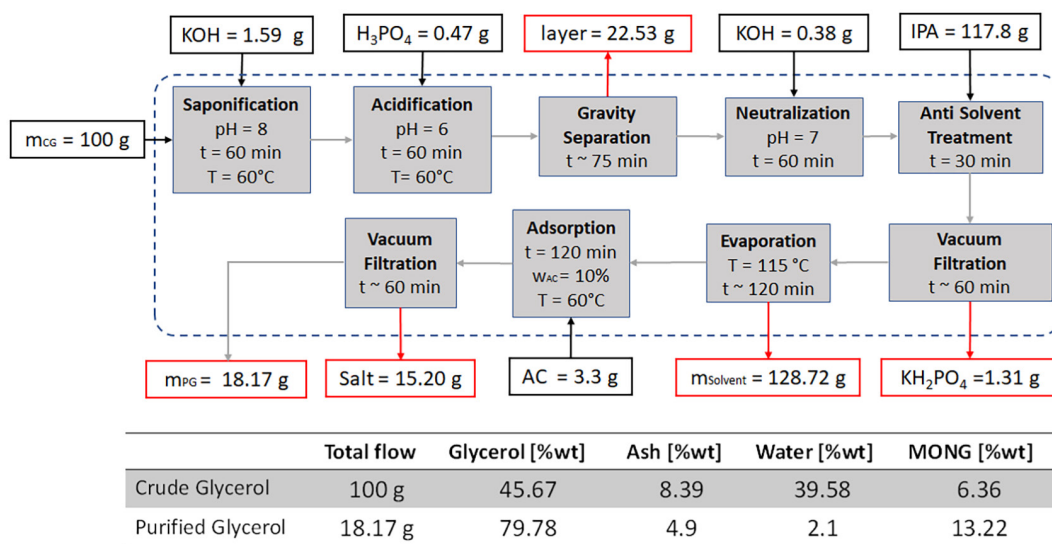| | Total flow | Glycerol [%wt] | Ash [%wt] | Water [%wt] | MONG [%wt] |
|---|---|---|---|---|---|
| Crude Glycerol | 100 g | 45.67 | 8.39 | 39.58 | 6.36 |
| Purified Glycerol | 18.17 g | 79.78 | 4.9 | 2.1 | 13.22 |

Figure A2. Flowsheet for the purification of Motherwell crude glycerol.