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# Purified Glycerine from Biodiesel Production as Biomass or Waste-Based Green Raw Material for the Production of Biochemicals

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**Abstract:** Glycerine (glycerol) is a polyol consisting of three carbon atoms bonded to hydroxyl groups. It is a by-product of the transesterification of triglycerides, such as animal fats, vegetable oils, or used cooking oils during the biodiesel production process. Crude glycerine is subject to purification processes resulting in distilled glycerine containing at least 99.5% glycerol. Currently, produced high-quality distilled glycerine is used in the food, pharmaceutical, and cosmetic industries. Recently, technologies for converting glycerol to other chemicals through catalytic processes have been intensively developed, e.g., production of bio-based 1,2-propanediol. In the near future, glycerol will certainly become a promising renewable raw material in many modern biorefineries for the synthesis of biofuels, chemicals, and bioenergy production. This paper presents the possibility of using ion exchange resins to remove impurities with trace amounts of sulphur and nitrogen compounds from crude and distilled glycerine, produced during the biodiesel production process from used cooking oils. It was determined that using ion exchange resins at the preliminary purification stage (before distillation) was ineffective. Using cationite resins to purify distilled glycerine produced from waste materials enables the removal of impurities in the form of sulphur and nitrogen compounds.

**Keywords:** glycerine; biodiesel; biofuels; bio-based chemicals; purification of glycerine; used cooking oils; ion exchange resins

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## 1. Introduction

Glycerine (glycerol or propane-1,2,3-triol) is a polyol containing three carbon atoms bonded to hydroxyl groups. It is a hygroscopic liquid that mixes with water in any ratio. Glycerine is a by-product of the production of fatty acid methyl esters (FAMEs) during the transesterification of triglycerides such as animal fats or vegetable oils [1]. Used cooking oils (UCOs) can also be used as an alternative raw material for the production of FAMEs and glycerine [2]. Triglycerides react with methanol, producing glycerine and FAMEs in a mass ratio of approximately 1:10 [3]. Crude glycerine is also obtained as a by-product from the hydrolysis of fats during soap production [4]. Glycerol can also be produced in other processes, e.g., from petrochemical raw material (epichlorohydrin and propylene). However, these processes are not used in a large industrial scale for the production of propane-1,2,3-triol. As a result of the development of modern biorefineries and the increase in the volume of biodiesel produced, the glycerine supply is increasing every year [5]. Crude glycerine is subjected to purification processes resulting in distilled glycerine containing at least 99.5% of glycerol. Currently, high-quality distilled glycerine in accordance with the European and American Pharmacopoeia (EP/USP grade) [6,7] is produced and used in the food, pharmaceutical, and cosmetic industries [8]. In recent years, there has been a strong development of processes for the conversion of glycerol

to other bio-based products, e.g., 1,2-propanediol [9], epichlorohydrin, acrolein, or 1,3-propanediol [10], and even bio-based hydrogen [11]. The bacteriological conversion of glycerol to fuels and chemicals has been also confirmed by research [12,13]. An essential and developing issue is the catalytic conversion of glycerine to olefins [14,15]. The use of glycerine in catalytic processes and conversion to other compounds places new quality requirements on this raw material. Great emphasis is placed on developing environmentally safe (eco-friendly) processes and the use of by-products/waste for the production of organic substances [16]. The production of second-generation biodiesel from waste cooking oil is a promising solution towards improving energy security [17], minimising waste, and promoting a circular economy [18,19]. Compared to FAMEs produced from vegetable oils, FAMEs from UCOs (also called UCOMEs) are characterised by a significantly higher $CO_2$ emission reduction rate. In 2021, with the entry of Directive 2018/2001 (RED II) into force on the promotion of energy from renewable sources, including in particular those derived from non-food and waste raw materials, the raw materials indicated in Annex IX of the directive are increasingly used in chemical production [20]. In the case of the production of FAMEs, the waste raw materials used are UCOs and category II animal fats. The largest manufacturers on the European market produce over 0.7 million tons of second-generation (2G) biodiesel. The demand in Europe for 2G esters in 2025 is forecasted at a level exceeding 5 million tonnes. Glycerine in this process is obtained as a by-product, classified as a product produced from waste raw materials. This glycerine is of lower quality to the product obtained from pure vegetable oils, which currently precludes its use without additional purification in many applications [21]. The expected development of the biodiesel market will result in an increase in the amount of glycerine produced from other waste-based raw materials than before.

The purification process of crude glycerine from biodiesel production used by many manufacturers can be divided into three primary stages [22]. The first stage involves the removal of residual glycerides, free fatty acids, soaps, and catalyst residues, which can be removed, e.g., by precipitation as a result of neutralisation. The next stage is to remove methanol and water from the glycerine stream by distillation. The final stage is vacuum distillation and sorption using activated carbon to remove trace impurities. The glycerine produced in this way, called "distilled glycerine", is a product with applications in the food, pharmaceutical, cosmetic, and feed industries. Other methods of glycerine purification include sorption on ion exchange resins and activated carbon [23], membrane filtration methods [24], extraction [25], and derivatization [26]. Producers of high-quality distilled glycerine use purification technologies consisting of several unit stages based on the above-mentioned processes to remove unwanted impurities and increase the usability of glycerine for catalytical processes and final applications. The most frequently used unit process in any glycerine purification technology is vacuum distillation. The vacuum distillation process is very effective in obtaining high-quality distilled glycerine. A frequently used process at the final stage in glycerol purification technologies is adsorption with activated carbon. This process is mainly used after vacuum distillation to improve the final colour of the product. Currently it is very important to implement a process to remove trace amounts of sulphur, chlorine, and nitrogen impurities from glycerine produced from waste materials.

Impurities such as fatty acids, inorganic salts, and inorganic bases and acids can be removed from crude glycerine by sorption on ionites [27]. Ion exchange resins are polymers that can replace the ions present in solution with protons (cationites) and hydroxyl ions (anionites) [28]. Anionites have positively charged functional groups, e.g., quaternary amine groups $–R_3N^+$, which form ionic bonds with anions (in the active state with hydroxyl ions). In contrast, cationites have negatively charged functional groups (e.g., $–SO_3^-$ sulfonic groups). Some technologies use ion exchange processes at one stage, for example, between the neutralisation and distillation stages [29]. Based on an analysis of the literature data on ion exchange resins in glycerine purification processes, it can be concluded that they can remove contaminants of the inorganic salt [30].

Glycerine from the transesterification of UCOs/waste oils or animal fats may contain an increased amount of impurities, mainly metals, sulphur, chlorine, and nitrogen, compared to glycerine from vegetable oil processing. This is related to the variable quality of UCOs and waste animal fats used to produce FAMEs and glycerine [31]. The research presented in this paper was aimed at comparing the impurities present in glycerine of different origins and the verification of the purification process sorption on ion exchange resins and activated carbon.

The purity of glycerine is crucial for its selective further conversion to other bio-based products. Therefore, in order to prepare the raw material for the dedicated process, it is necessary to use an effective purification stage adapted to the quality of the raw material and the quality requirements of the glycerine produced from waste materials. The conversion of glycerol to high-quality products can be carried out by processes such as oxidation, carbonylation, reforming, acetylation, etherification, esterification, dehydration, hydrogenation, and fermentation [32–34].

Currently, glycerine contaminated with sulphur and nitrogen compounds cannot be used in the catalytic processes mentioned above due to the poisoning of the used catalysts. During the analysis of the scientific literature and the study of the state of the art, no works related to the assessment of impurities in the form of sulphur, nitrogen, and chlorine compounds in glycerol were found. Thus, no studies were found that were aimed at reducing impurities causing deactivation of the catalysts used in glycerine synthesis processes. Due to the very strong development of processes for glycerol conversion into many other bio-based products, and the increasingly frequent use of catalytic processes, it is crucial to verify the quantity of impurities limiting the lifetime of the catalysts used and implement processes that allow a reduction in certain impurities to safe levels. The implementation of an innovative glycerine purification process can significantly affect the market of bio-based chemicals, the production of which is currently favoured. Increasing amounts of glycerine can be used in the production of chemicals, which are currently produced from petroleum-derived raw materials. A strong development of glycerine purification processes is necessary, along with the increase in biodiesel production, especially from waste such as UCOs [35].

## 2. Materials and Methods

### *2.1. Materials and Sample Preparation*

The experiments were conducted on samples of distilled glycerines present in the Polish and European markets and the crude glycerines subjected to preliminary purification. Samples derived from the biodiesel production process where they are used as raw materials, vegetable oils, UCOs, and mixtures of vegetable oils, UCO and IInd category animal fats (Table 1).

**Table 1.** Glycerine samples.

| Number of Sample | Origin of Sample |
|---|---|
| Veg_1<br>Veg_2<br>Veg_3 | Vegetable oils |
| Mix_4<br>Mix_5<br>Mix_6<br>Mix_7<br>Mix_8<br>Mix_9 | Mixed:<br>min. 90% vegetable oils, max. 10% UCO and<br>II category animal fats |
| UCO_10 | UCO |

Samples were described in accordance with the guideline: "veg" means vegetable-based material, "mix" means mixed based materials (vegetable, UCOs, and animal fats), and "UCOs" means UCO-based material.

Samples veg_1, veg_2, veg_3, and mix_4 are commercially distilled glycerines, while samples mix_5, mix_6, mix_7, mix_8, mix_9, and UCO_10 are distilled glycerines obtained from crude glycerines in laboratory conditions. The crude glycerines were characterised by significant levels (up to 20% (m/m)) of impurities in the form of organic compounds other than glycerol (MONG). These glycerines were subjected to multi-stage purification processes based on the standard processes used in industry technologies, including:

- Separation of impurities by sedimentation.
- Reaction with an alkaline agent (strong base) at 80 °C for 1.5 h.
- Filtration of the reaction mixture under reduced pressure.
- Removal of water on a vacuum evaporator at 20 mmHg.
- Vacuum distillation at 1 mm Hg.
- Sorption on activated carbon.

The properties of distilled glycerines have been presented in Table 2.

**Table 2.** Results of analyses of distilled glycerine samples.

| | | Density at 15 °C | Glycerol Content | Sulphur Content | Nitrogen Content | Chlorine Content | Water Content |
|---|---|---|---|---|---|---|---|
| **Origin of the Sample** | **Sample No** | **kg/m$^3$** | **%(m/m)** | **mg/kg** | **mg/kg** | **mg/kg** | **mg/kg** |
| Vegetable oils | Veg_1 | 1264.0 | 99.9 | <1.0 | <1.0 | <1.0 | 820 |
| | Veg_2 | 1263.8 | 99.9 | <1.0 | <1.0 | <1.0 | 800 |
| | Veg_3 | 1263.7 | 99.8 | <1.0 | <1.0 | <1.0 | 2600 |
| Mixed | Mix_4 | 1263.5 | 99.8 | 3.5 | 3.2 | <1.0 | 76 |
| | Mix_5 | 1263.2 | 99.9 | 2.5 | 5.8 | <1.0 | 1600 |
| | Mix_6 | 1263.4 | 99.7 | 3.2 | 3.6 | <1.0 | 1400 |
| | Mix_7 | 1261.2 | 98.9 | 3.1 | 5.3 | <1.0 | 11,000 |
| | Mix_8 | 1263.7 | 99.9 | 2.7 | 5.5 | <1.0 | 883 |
| | Mix_9 | 1263.6 | 99.8 | 2.5 | 4.8 | <1.0 | 3000 |
| UCO | UCO_10 | 1263.4 | 99.7 | 1.7 | 17.0 | <1.0 | 870 |

Based on the analysis of the results presented in Table 2, it can be concluded that distilled glycerines obtained by standard industrial processes contain less than 1 mg/kg chlorine regardless of their origin. The sulphur and nitrogen content of distilled glycerines is closely related to the origin of the raw materials from which they were produced. Vegetable-based glycerines are virtually uncontaminated with sulphur, nitrogen, and chlorine compounds and do not require additional purification processing. They are quoted as reference samples in the paper. The level of individual impurities does not exceed 1 mg/kg. Glycerines derived from mixed raw materials (10% UCOs and animal fats, 90% vegetable oils) are characterised by elevated sulphur and nitrogen content. The sulphur content is 2.5–3.5 mg/kg, and the nitrogen content is 3.2–5.8 mg/kg. Glycerine derived from UCOs has a significant nitrogen content of 17 mg/kg. These impurity levels preclude glycerine produced from waste raw materials in catalytic conversion processes to other bio-based products due to the potential risk of catalyst poisoning. Sample Mix_7 had an increased water content when compared to the different samples. Glycerine purification tests using ionites were carried out for samples mix_4, mix_5, mix_6, mix_7, mix_8, mix_9, and UCO_10.

The tests used ion exchange resins (ionites) (Table 3, Figure 1).

In addition, granular activated carbon with the following properties was used in the tests: iodine number: 1.000 ± 50 mg/g, granulation 12 × 40 mesh (0.425–1.7 mm), moisture content max. 0.5%, bulk density 440 kg/m$^3$, hardness min. 90%, pH 9–11.

**Table 3.** Ion exchange resins' characteristics.

| Ion Exchange Resin | Designation | Particle Density [kg/m$^3$] | Water Content [%m/m] | Total Exchange Capacity [eq/L] |
|---|---|---|---|---|
| Strong acid cation exchanger, gel form, $H^+$ form | Kat_1 | 1190 | 48–58 | ≥1.80 |
| Strong acid cation exchanger, gel form, $H^+$ form | Kat_2 | 1130 | 62–72 | ≥1.10 |
| Strong acid cation exchanger, highly porous type, $H^+$ form | Kat_3 | 1190 | 45–55 | ≥1.50 |
| Strong base anion exchanger, gel form, $Cl^-$ form | Anio_1 | 1100 | 45–51 | ≥1.25 |
| Strong base anion exchanger, gel form, $Cl^-$ form | Anio_2 | 1070 | 49–59 | ≥1.20 |

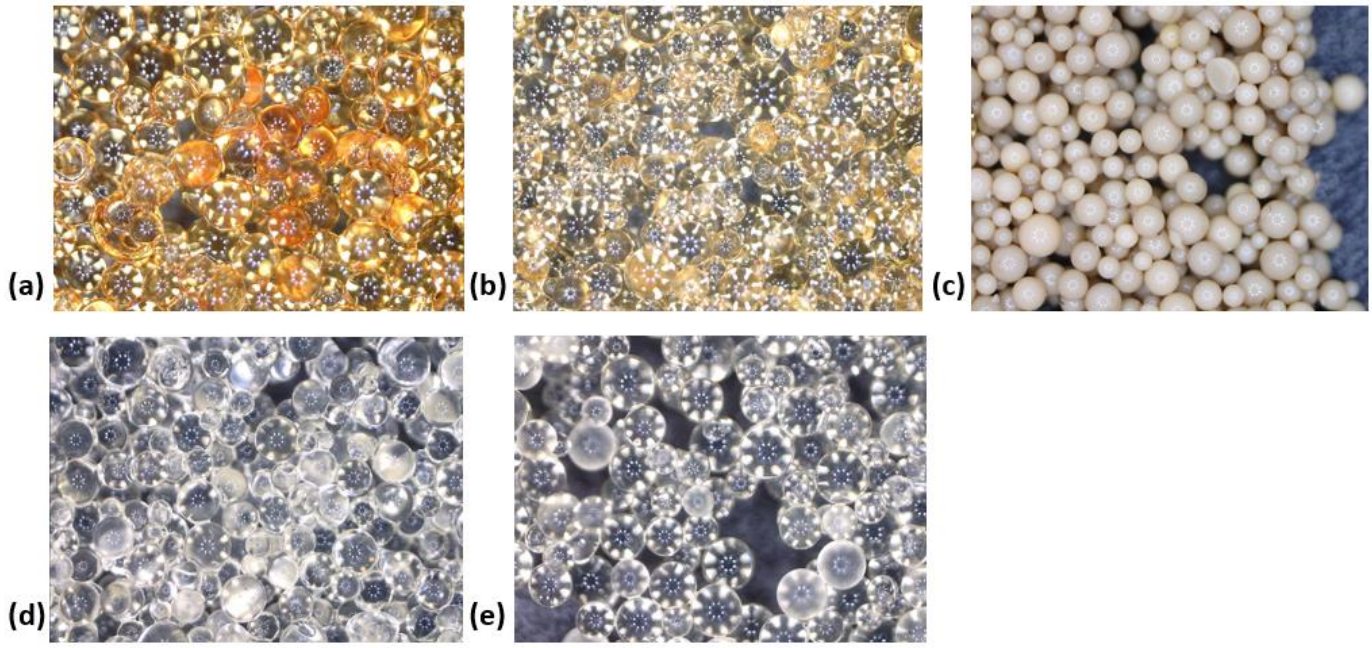



**Figure 1.** Ion exchange resins at 40× magnification (**a**) Kat_1, (**b**) Kat_2, (**c**) Kat_3, (**d**) Anio_1, (**e**) Anio_2.

### *2.2. Glycerine Purification Tests with Ion Exchange Resins*

Distilled glycerine samples Mix_4-Mix_9, and UCO_10 were subjected to purification using ion exchange resins. The test equipment consisted of a glass column heated by a heating tape and a vacuum pump temperature control system (Figure 2). The column was filled with a 10 cm tall ionite bed. The volume of glycerine in contact with the ionite was approximately 9 cm$^3$. Process conditions:

- Temperature: 60 °C,
- The flow of glycerine through the ionite bed at a rate of approx. 2–5 cm$^3$/min forced by a vacuum generated by a diaphragm pump,
- The column had a stabilisation time of approx. 20 min,
- The contact time between the glycerine and the ionite was approximately 2–5 min.

### *2.3. Analytical Methods*

The analytical methods listed were used to quantitatively analyse the impurities in the raw material samples and the products obtained during the tests (Table 4).

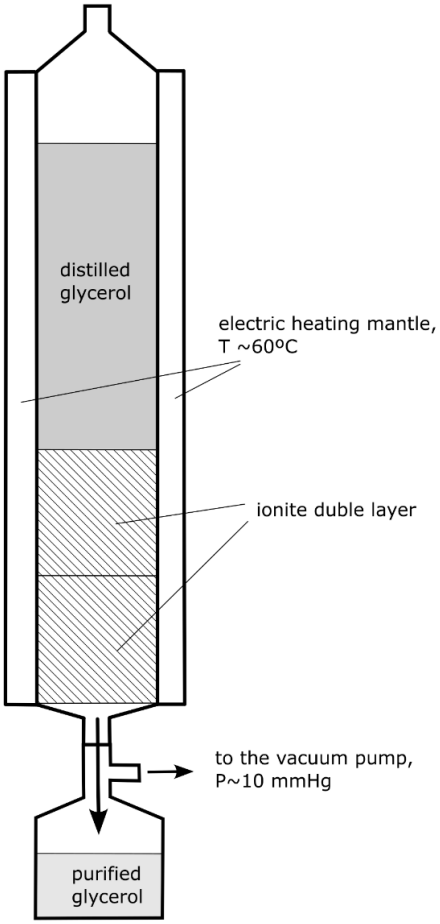



**Figure 2.** Scheme of the purification column of glycerine with the use of ion exchange resins.

**Table 4.** Methods of examining the samples.

| No. | Parameter | Unit | Description of the Method | Procedure/Standard |
|---|---|---|---|---|
| 1. | Density at 15 °C | $kg/m^3$ | the oscillating method with U-tube | PN-EN ISO 12185:2002 [36] |
| 2. | Water content | mg/kg | coulometric titration by the Karl Fischer method | PN-EN ISO 12937:2005 [37] |
| 3. | Glycerol content | %m/m | gas chromatography with GC-FID flame ionization detection | GC method [1] |
| 4. | Sulphur content | mg/kg | ultraviolet fluorescence method | PN-EN ISO 20846:2012 [38] |
| 5. | Nitrogen content | mg/kg | oxidative combustion with chemiluminescence detection | ASTM D 4629-17 [39] |
| 6. | Chlorine content | mg/kg | oxidative microcoulometric method | PN-EN 14077:2008 [40] |

[1] Determination by gas chromatography with flame ionization detection GC-FID. A capillary column with a thick film of the stationary phase Carbowax 20 M. Flame ionization detector FID operating at 250 °C. The sample was introduced through the injector at 250 °C to the column with a temperature program in the range of 110–300 °C. Calibration technique: internal standard method, using reference material: 1,3-propanediol. Carrier gas: argon.

## 3. Results and Discussion

Glycerine samples of mixed origin and from UCOs were selected for testing with ion exchange resins to verify the possibility of reducing the impurities affecting the elevated sulphur and nitrogen content.

### *3.1. Test of Ion Exchange Resin with Crude Glycerol*

As part of the assessment of the feasibility of using ion exchange resins to purify crude glycerine, a test of contacting the Mix_4 sample before distillation with the Anio_2 anionite was performed. The sample was pre-treated by separating suspended impurities in the sedimentation process. The Mix_4 sample was then contacted with the anionite in compliance with the procedure described in Section 2.2. After passing approximately

200 $cm^3$ of sample through the column, a decrease in flow rate was observed followed by complete blockage. After dismantling the system, it was observed that the anionite grains were stuck together by a thick, dark and water-insoluble liquid. The test was repeated using Mix_5 crude glycerine and Kat_1 ionite. The test results were comparable—complete blockage of the flow was observed after passing approximately 180 $cm^3$ of the sample. Based on infrared spectral analysis, it was proven that the filter-blocking substance was mainly a mixture of esters and free fatty acids (FFAs).

Using ionites at the preliminary purification stage (before distillation) is ineffective because the impurities present in the glycerine are released as a separate phase therefore blocking the flow of glycerine through the ionite bed. This calls into question the feasibility of the process for removing impurities such as fatty acids or inorganic salts from crude glycerine using ion exchange resins described in the literature [41].

### *3.2. Test of Anion Exchange Resin with Distilled Glycerol*

Tests were undertaken to assess the feasibility of using an ion exchange resin of the anionite type using two resins, Anio_1 and Anio_2, with a sample of Mix_4 distilled glycerine. The tests were performed in compliance with the procedure described in Section 2.2. The samples obtained during the tests were tested and the results are presented in Figure 3. It was observed that there was a contamination of the distilled glycerine with chloride ions and a slight increase in the concentration of nitrogen compounds. For this reason, using the tested anionites to purify distilled glycerine should be considered ineffective.

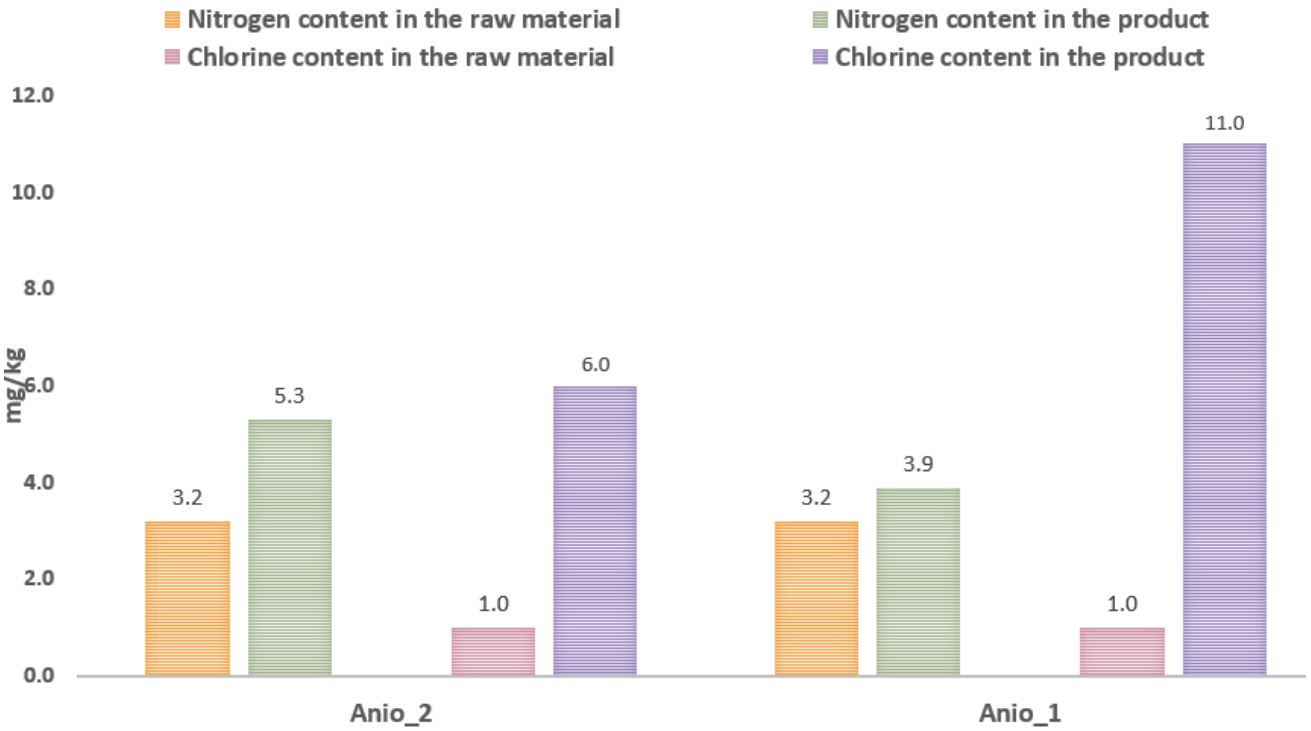



**Figure 3.** Results of tests with the use of anion exchange resin and glycerine mix_4.

### *3.3. Test of Cation Exchange Resin with Distilled Glycerol*

In the subsequent testing stage, the possibility of using cation exchange resins to remove impurities, in the form of a sulphur and nitrogen compounds, from distilled glycerine was verified. Nine tests were performed using different raw materials and ion exchange resins. Table 5 presents the test characteristics. The testing procedure is described in Section 2.2.

**Table 5.** Test description of cation exchange resin with distilled glycerol.

| Test No. | Cation Exchanger | Glycerine Sample |
|---|---|---|
| Test_1 | Kat_1 | Mix_4 |
| Test_2 | Kat_1 | Mix_5 |
| Test_3 | Kat_1 | Mix_6 |
| Test_4 | Kat_1 | Mix_7 |
| Test_5 | Kat_2 | Mix_7 |
| Test_6 | Kat_1 | Mix_8 |
| Test_7 | Kat_2 | Mix_9 |
| Test_8 | Kat_1 | UCO_10 |

During test No. 9 (cation exchanger: Kat_3, glycerine sample: Mix_7), we did not yield a sample for further testing. The column was blocked during the process. Kat_1 resin was the basic material (representative of strong acid cation exchangers in gel form) used for the tests. In order to confirm the efficiency of purification by strong acid cation exchanger in gel form, the same type of exchanger (Kat_2) was used—one test with the same sample and a second test with another sample.

The physicochemical properties of the purified distilled glycerines are shown in Figures 4–6.

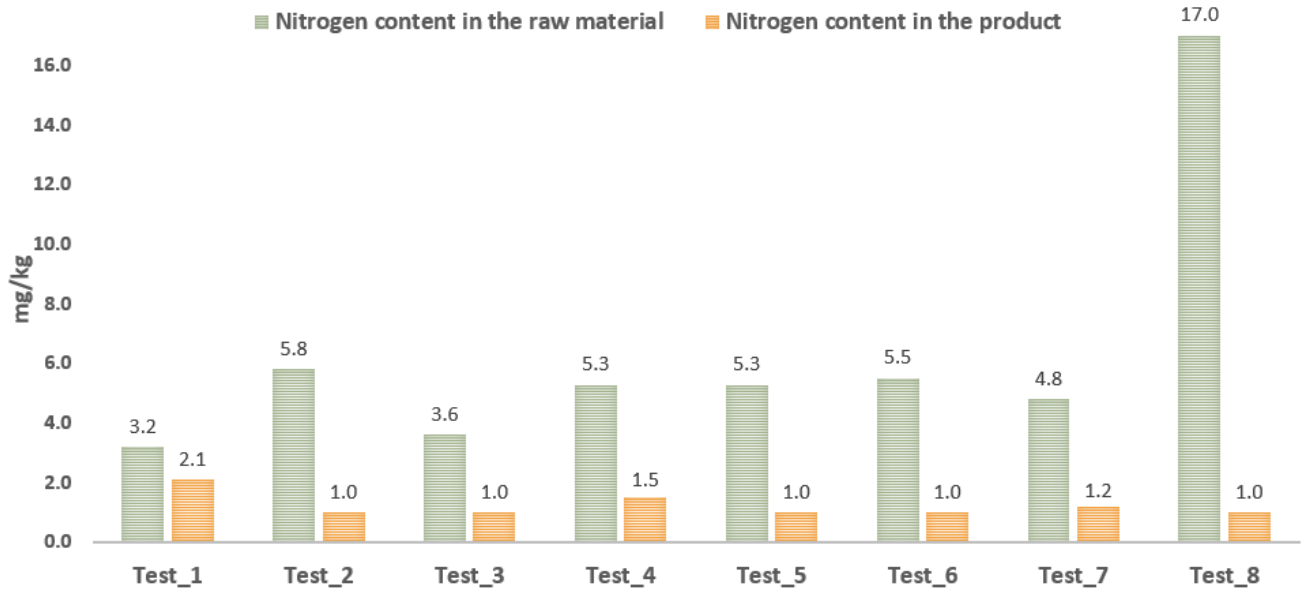



**Figure 4.** Nitrogen content in the raw materials and products.

As a result of the test, a significant level of nitrogen reduction in the samples after the purification process was achieved. Cationites have a high potential for reducing impurities from nitrogen compounds. This is due to the amino groups in a protonated form in the structure of compounds that compromise glycerine impurities. The most significant reduction was observed in the sample from UCOs, with as much as a 17-fold reduction in nitrogen content during the test. In seven cases, the nitrogen results in the product samples did not exceed 1.5 mg/kg; in only one test, the result was 2.1 mg/kg. Based on the obtained data, the great potential of implementing a process using cationites in distilled glycerine purification technology can be observed.

Cationites were found to have some affinity for removing impurities in the form of sulphur compounds from glycerine (Figure 5). This is most likely related to the affinity of structures containing C-S(II) bonds to the polymer matrix in the tested cationites. In most cases, a reduction in sulphur content to less than 2 mg/kg was achieved. Only in one of the tests was the reduction in sulphur content negligible. The potential of implementing a glycerine purification process using cationites to reduce impurities in the form of sulphur compounds is apparent.

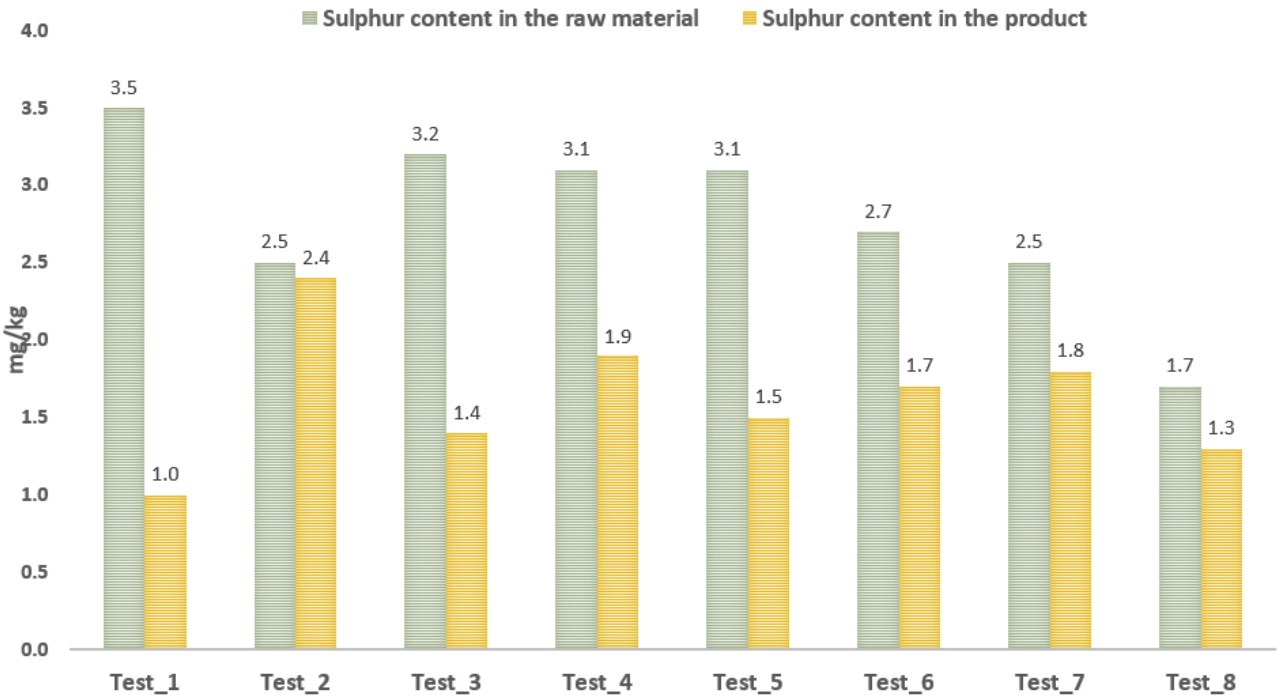



**Figure 5.** Sulphur content in the raw materials and products.

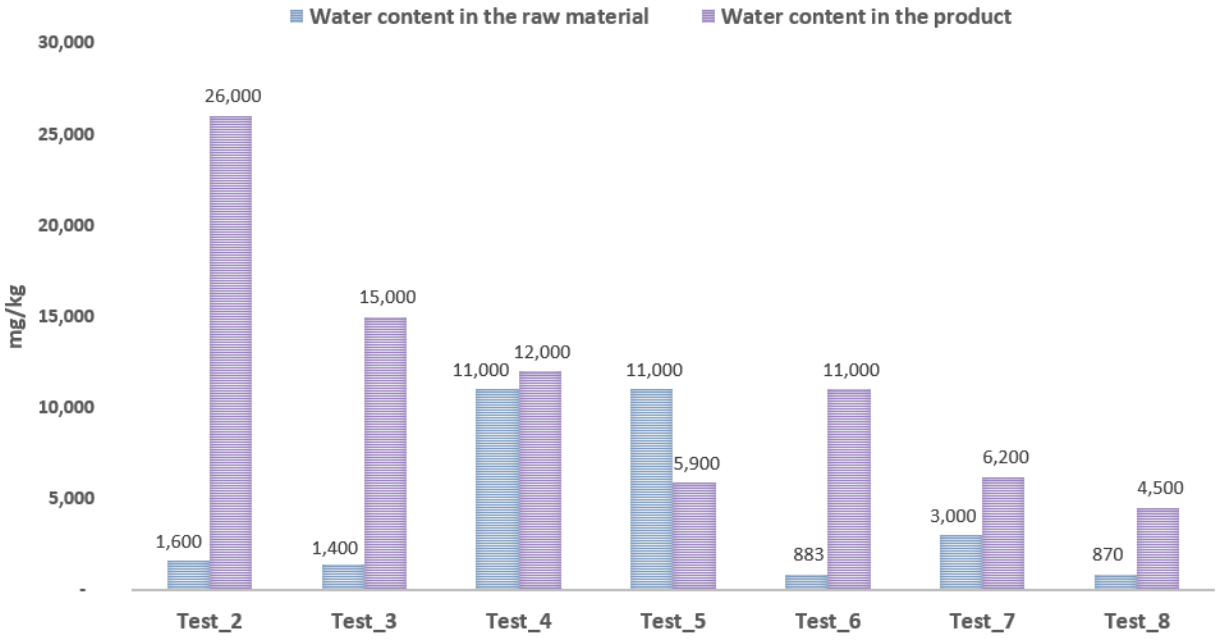



**Figure 6.** Water content in the raw materials and products.

In an additional assessment of water content, a significant increase was observed in the samples obtained from the performed tests (Figure 6). There was a noticeable increase in the water content of product samples to around 0.5–1.5% and even 2.6%, which is up to several times higher than the water content of the raw material. This suggests using steam stripping after sorption on cationite in distilled glycerine purification technology. The steam stripping process is a standard process used in industrial glycerine technologies.

Test No. 9, utilising Mix_7 distilled glycerine and Kat_3 cationite, did not yield a sample for further testing as the column was blocked during the process. The test was repeated with the same result. It was determined that cationite in the form of a porous material (Kat_3) is not dedicated to the purification process of glycerines, in contrast to

cationites in the form of gel grains (Kat_1 and Kat_2). After removal of cationite from the purification column swelling of the material was observed, which was the reason for blocking of the flow during tests.

## 4. Conclusions

As a result of the conducted tests, it was concluded that:

- Glycerines as a by-product of biodiesel production, obtained from vegetable raw materials, do not contain significant amounts of impurities in the form of sulphur, chlorine, and nitrogen compounds.
- Glycerines obtained from mixed raw materials (vegetable oils, UCOs and animal fats) do not contain significant amounts of impurities in the form of chlorine compounds. Still, they are contaminated with sulphur and nitrogen compounds. Glycerine obtained from UCOs has high levels of impurities in the form of nitrogen compounds.
- The use of ion exchange resins at the preliminary purification stage (before distillation) is ineffective because the MONG-type impurities present in the glycerine are released as a separate phase which block the flow of glycerine through the ionite bed.
- Using anionites to purify distilled glycerine of waste origin is not recommended due to the introduction of impurities such as chlorine and nitrogen compounds during the process.
- The use of cationites in the purification process of distilled glycerine of waste origin is promising due to the reduction in the sulphur content and the significant elimination of impurities in the form of nitrogen compounds. The disadvantage is that the cationites cause an increase in the water content of the glycerine samples. Following the sorption on the cationite, it is advisable to carry out the standard steam stripping process. Research is required to verify the performance of this process in laboratory conditions.
- The use of cationites which are a highly porous material is not recommended for the purification process of glycerines, in contrast to cationites in the form of gel grains.

Based on the analysis of the presented results, contamination of glycerines produced during biodiesel production from wastes with nitrogen and sulphur compounds is visible. The applied purification technique with the use of cation exchange resin reduced the amount of impurities to an acceptable level. The implementation of this process in standard industrial technologies has great potential to obtain high-quality raw material for further conversion processes into bio-based products. This is a significant step towards the development of modern biorefineries based on advanced biodiesel production processes (second-generation biodiesel from waste defined in Annex IX of the RED II Directive).

It is necessary to prepare a plan of further research in order to select an appropriate process for removing excess water from glycerine after the sorption on cationite. The development of a new technology consisting of the stage of removing sulphur and nitrogen impurities, and excess water from the previous step, will contribute to the development of the bio-based chemical market and the related biodiesel market.

## 5. Patents

Patent Application
Title: Glycerin purification method and glycerin purified by the method
Application number: EP4122907A1

**Author Contributions:** Conceptualization, G.B. and W.K.; methodology, W.K.; formal analysis, J.L.; investigation, G.B.; resources, G.B.; data curation, G.B. and G.S.; writing—original draft preparation, G.B.; writing—review and editing, W.K.; visualization, G.B. and W.K.; supervision, G.S.; project administration, J.L.; funding acquisition, G.S. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References


1. Fauzi, A.H.M.; Amin, N.A.S. An overview of ionic liquids as solvents in biodiesel synthesis. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5770–5786. [CrossRef]
2. Hudha, M.I.; Daryono, E.D.; Rastini, E.K. Potential crude glycerol from Transesterification WCO (Waste Cooking Oil) as an anti-fungisida Spray. *ChemTech Res.* **2017**, *10*, 55–61.
3. Checa, M.; Nogales-Delgado, S.; Montes, V.; Encinar, J.M. Recent Advances in Glycerol Catalytic Valorization: A Review. *Catalysts* **2020**, *10*, 1279. [CrossRef]
4. Hambali, E.; Fitria, R.; Sari, V.I. *Biorefinery of Oil Producing Plants for Value-Added Products, Glycerol and Derivatives*; Wiley: Hoboken, NJ, USA, 2022; p. 24. [CrossRef]
5. Datta, I.; Ghosh, A.; Acharjee, A.; Rakshit, A.; Saha, B. Overview on biodiesel market, Vietnam. *J. Chem.* **2021**, *59*, 271–284. [CrossRef]
6. Council of Europe. *European Pharmacopoeia 10.0*; Council of Europe: Strasbourg, France, 2010; pp. 2765–2767.
7. *The United States Pharmacopeia, the National Formulary*; United States Pharmacopeial Convention, Inc.: Rockville, MD, USA, 2009.
8. Fokum, E.; Zabed, H.M.; Yun, J.; Zhang, G.; Qi, X. Recent technological and strategical developments in the biomanufacturing of 1,3-propanediol from glycerol. *Int. J. Environ. Sci. Technol.* **2021**, *18*, 2467–2490. [CrossRef]
9. Konur, O. *Propanediol Production from Glycerol, Biodiesel Fuels—Science Technology Health and Environment*; CRC Press: Boca Raton, FL, USA, 2021; ISBN 9780367456238.
10. Dolejš, I.; Líšková, M.; Krasňan, V.; Markošová, K.; Rosenberg, M.; Lorenzini, F.; Marr, A.C.; Rebroš, M. Production of 1,3-Propanediol from Pure and Crude Glycerol Using Immobilized Clostridium butyricum. *Catalysts* **2019**, *9*, 317. [CrossRef]
11. Berdechowski, K. Analysis of biohydrogen production methods in terms of GHG emission value. *Nafta-Gaz* **2019**, *4*, 230–235. [CrossRef]
12. Zhou, C.H.; Beltramini, J.N.; Fan, Y.X.; Lu, G.Q. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* **2008**, *37*, 527–549. [CrossRef]
13. Chilakamarry, H.R.; Mimi Sakinah, A.M.; Zularisam, A.W.; Pandey, A.; Vo, D.V.N. Technological perspectives for utilisation of waste glycerol for the production of biofuels: A review. *Environ. Technol. Innov.* **2021**, *24*, 101902. [CrossRef]
14. Zakaria, Z.Y.; Linnekoski, J.; Amin, N.A.S. Catalyst screening for conversion of glycerol to light olefins. *J. Chem. Eng.* **2012**, *207*, 803–813. [CrossRef]
15. Bhargava, A.; Shelke, S.; Dilkash, M.; Chaubal-Durve, N.; Patil, P.; Nadar, S.; Marghade, D.; Tiwari, M. A comprehensive review on catalytic etherification of glycerol to value-added products. *Rev. Chem. Eng.* **2022**. [CrossRef]
16. Clauser, N.M.; González, G.; Mendieta, C.M.; Kruyeniski, J.; Area, M.C.; Vallejos, M.E. Biomass Waste as Sustainable Raw Material for Energy and Fuels. *Sustainability* **2021**, *13*, 794. [CrossRef]
17. Zhao, Y.; Wang, C.; Zhang, L.; Chang, Y.; Hao, Y. Converting waste cooking oil to biodiesel in China: Environmental impacts and economic feasibility. *Renew. Sustain. Energy Rev.* **2021**, *140*, 110661. [CrossRef]
18. Velenturf, A.P.M.; Purnell, P. Principles for a sustainable circular economy. *Sustain. Prod. Consum.* **2021**, *27*, 1437–1457. [CrossRef]
19. Rogowska, D.; Berdechowski, K. Ocena wpływu sposobu alokacji emisji w procesie produkcji biopaliwa na wartość emisji gazów cieplarnianych. *Nafta-Gaz* **2013**, *4*, 226–234.
20. Mai-Moulin, T.; Hoefnagels, R.; Grundmann, P.; Junginger, M. Effective sustainability criteria for bioenergy: Towards the implementation of the european renewable directive II. *Renew. Sustain. Energy Rev.* **2021**, *138*, 110645. [CrossRef]
21. Tan, H.W.; Aziz, A.A.; Aroua, M.K. Glycerol production and its applications as a raw material: A review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 118–127. [CrossRef]
22. Ziels, N.W. Recovery and purification of glicerol. *J. Am. Oil Chem. Soc.* **1956**, *33*, 556–565. [CrossRef]
23. Khok, Y.T.; Ooi, C.H.; Matsumoto, A.; Yeoh, F.Y. Reactivation of spent activated carbon for glycerine purification. *Adsorption* **2020**, *26*, 1015–1025. [CrossRef]
24. Chol, G.; Dhabhai, R.; Dalai, A.K.; Reaney, M. Purification of crude glycerol derived from biodiesel production process: Experimental studies and techno-economic analyses. *Fuel Process. Technol.* **2018**, *178*, 78–87. [CrossRef]
25. Maquirriain, M.A.; Neyertz, C.A.; Querini, C.A.; Pisarello, M.L. Crude glycerine purification by solvent extraction. *Braz. J. Chem. Eng.* **2022**, *39*, 235–249. [CrossRef]
26. Borówka, G.; Krasodomski, W.; Semerjak, G.; Lubowicz, J.; Krzak, M. Technologie oczyszczania gliceryny technicznej. *Przemysł Chemiczny.* **2021**, *100*, 163–167. [CrossRef] [PubMed]
27. Ardi, M.S.; Aroua, M.K.; Awanis, H.N. Progress, prospect and challenges in glycerol purification process: A review. *Renew. Sustain. Energy Rev.* **2015**, *42*, 1164–1173. [CrossRef]
28. Dixit, F.; Dutta, R.; Barbeau, B.; Berube, P.; Mohseni, M. PFAS removal by ion exchange resins: A review. *Chemosphere* **2021**, *272*, 129777. [CrossRef]

29. Konstantinović, S.S.; Danilović, B.R.; Ćirić, J.T.; Ilić, S.B.; Savić, D.S.; Veljković, V.B. Valorization of crude glycerol from biodiesel production. *Chem. Ind. Chem. Eng. Q.* **2016**, *22*, 461–489. [CrossRef]
30. Isahak, W.N.R.W.; Jahim, J.M.; Ismail, M.; Nasir, N.F.; Ba-Abbad, M.M.; Yarmo, M.A. Purification of crude glycerol from industrial waste: Experimental and simulation studies. *J. Eng. Sci. Technol.* **2016**, *11*, 1056–1072.
31. Goh, B.H.H.; Chong, C.T.; Ge, Y.; Ong, H.C.; Ng, J.H.; Tian, B.; Józsa, V. Progress in utilisation of waste cooking oil for sustainable biodiesel and biojet fuel production. *Energy Convers. Manag.* **2020**, *223*, 113296. [CrossRef]
32. Anitha, M.; Kamarudin, S.K. The potential of glycerol as a value-added commodity. *J. Chem. Eng.* **2016**, *295*, 119–130. [CrossRef]
33. Aroua, M.K.; Cognet, P. Editorial: From Glycerol to Value-Added Products. *Front. Chem.* **2020**, *8*, 69. [CrossRef]
34. Nakagawa, Y.; Tomishige, K. Heterogeneous catalysis of the glycerol hydrogenolysis. *Catal. Sci. Technol.* **2011**, *1*, 179–190. [CrossRef]
35. Miyuranga Viraj, K.A.; Udara Arachchige, S.P.R.; Randika Jayasinghe, A.; Samarakoon, G. Purification of Residual Glycerol from Biodiesel Production as a Value-Added Raw Material for Glycerolysis of Free Fatty Acids in Waste Cooking Oil. *Energies* **2022**, *15*, 8856. [CrossRef]
36. *PN-EN ISO 12185:2002*; Ropa Naftowa i Przetwory Naftowe-Oznaczanie Gęstości-Metodą Oscylacyjną z U-Rurką. The Polish Committee for Standardization: Warszawa, Poland, 2002.
37. *PN-EN ISO 12937:2005*; Przetwory Naftowe-Oznaczanie Wody-Miareczkowanie Kulometryczne Metodą Karla Fischera. The Polish Committee for Standardization: Warszawa, Poland, 2005.
38. *PN-EN ISO 20846:2012*; Przetwory Naftowe-Oznaczanie Zawartości Siarki w Paliwach Do Pojazdów samochodowych-metoda fluorescencji w nadfiolecie. The Polish Committee for Standardization: Warszawa, Poland, 2012.
39. *ASTM D4629-17*; Standard Test Method for Trace Nitrogen in Liquid Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection. ASTM International: Conshohocken, PA, USA, 2017.
40. *PN-EN 14077:2008*; Ciekłe Przetwory Naftowe-Oznaczanie Zawartości Chlorowców związanych Organicznie-Metoda Mikrokulometrii Oksydacyjnej. The Polish Committee for Standardization: Warszawa, Poland, 2008.
41. Carmona, M.; Lech, A.; de Lucas, A.; Perez, A.; Rodriguez, J.F. Purification of glycerol/water solutions from biodiesel synthesis by ion exchange: Sodium and chloride removal. Part II. *J. Chem. Technol. Biotechnol.* **2009**, *84*, 1130–1135. [CrossRef]


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