

- 1 -



166166



G00002

Recovery of Glycerol

Field of Invention:

The invention relates to a process for recovering glycerol from a glycerol residue and/or the like glycerol-containing compound from an oleochemical plant.

Background of Invention:

Oleochemicals are chemicals derived from oils and fats. In the processing of these basic oleochemicals, there are a number of by-products and some comprise of glycerol residue and/or the like glycerol-containing compounds. Examples of significant plants which include glycerol residue as a by-product are those involved in the manufacture of methyl esters, fatty acids and fatty alcohols. The refining process of glycerine as schematically shown in Figure 1 is likewise included.

The general composition of glycerol residue is presented in Table 1;

	Range	Mean
Glycerol (%)	15-35	23
Soap (%)	10-40	25
Sodium Chloride (%)	30-60	44
Ash (%)	50-70	50
Free fatty matters (%)	0.5-8	3
Water (%)	1-10	6
pH (20%)	10-12	11.7
Appearance	Light to dark brown powder or paste	

Table 1

Glycerol residue has been generally classified as a waste and its disposal has posed a problem in the industry. It is therefore desirable to provide a means or a process, which allows glycerol and/or other desired components from the glycerol residue to be recovered and consequently, provides a process for "treating" such glycerol residue to a more disposable form.

Glycerol (boiling point: 290°C) is used in several fields of applications such as in the manufactures of (i) solvents or drugs carrier in pharmaceutical products; (ii) humectants in cosmetics and tobacco industry and (iii) antifreeze or heat transfer agents and, (iv) soaps.

In view of the numerous applications of glycerol, it is an object of the invention to provide a process for the recovery of glycerol from glycerol residue and/or the like glycerol-containing compounds.

Summary of the Invention

In accordance with the invention, there is provided a process for the recovery of glycerol from glycerol residue and/or the like glycerol-containing compounds, said process including the steps of

- (a) acidification of the glycerol residue and/or the like glycerol-containing compounds within an effective amount of water to obtain a glycerol-rich mixture;
- (b) removal of water from the glycerol-rich mixture and followed by an addition thereto an effective amount of solvent;
- (c) removal of any formed precipitate resulting from the glycerol-rich mixture; and finally followed by
- (d) removal of the added solvent from glycerol-rich mixture, thereby yielding the desired glycerol concentrate.

The invention provides glycerol concentration of 45-69% and may further be purified to a higher concentration of more than 98.5% by vacuum distillation.

Detailed Description of Invention

The invention is applicable for the purpose of recovering glycerol from any glycerol residue and/or the like glycerol-containing compounds, particularly from an oleochemical plant.

In accordance with the invention, there is provided a process for the recovery of glycerol from glycerol residue and/or the like glycerol-containing compounds, said process including the steps of,

- (a) acidification of the glycerol residue and/or the like glycerol-containing compounds within an effective amount of water to obtain a glycerol-rich mixture. The acidification separates the glycerol from the fatty acids and inorganic matters present in the glycerol residue and/or the like glycerol-containing compounds. During and after the acidification to the desired pH, an oil-rich layer and an insoluble matter were usually observed on

top of the aqueous solution. Examples of applicable acids are those selected from the group of mineral acids such as e.g. H_2SO_4 , HCl and/or the like;

- (b) removal of water from the glycerol-rich mixture of step (a) and followed by an addition of an effective amount of organic solvent to effect salt precipitation. Rotary evaporation is one of the preferred methods of removing the water. Another preferred method of removing the water is distillation under mild vacuum (10^{-1} to 10^{-2} torr) at temperature between 60°C to 100°C . The selection of solvents is based on the insolubility of inorganic salts present in the mixture to allow most of the salts to precipitate. Examples of applicable solvents are hexane, methanol, ethanol, chloroform, ethyl acetate, propanol, butanol and/or the like. These are organic solvents.
- (c) removal of any formed precipitate from the glycerol-rich mixture such as by suction using a Buchner funnel. The removed precipitate is generally observed to be whitish in color while the filtrate is of dark brown solution; and finally followed by
- (d) removal of the added solvent from the glycerol rich-mixture in vacuo, thereby yielding the desired glycerol concentrate. Rotary evaporation is one of the preferred methods of removing the solvent. Another preferred method of removing the solvent is distillation under mild vacuum (10^{-1} to 10^{-2} torr) at temperature between 60°C to 100°C .

According to another aspect of the invention, the following steps may be carried out prior to carrying out steps (a)-(d);

- (i) addition of an effective amount calcium salt to the glycerol residue and/or the like glycerol-containing compounds in water to obtain a pre-treated glycerol-rich compound. The purpose of adding the calcium salts is to remove the fatty acids present in the glycerol. Examples of calcium salts which are applicable are, CaO , $\text{Ca}(\text{OH})_2$ and CaCl_2 ; and
- (ii) removal of any formed solid precipitate via filtration using a Buchner funnel and optionally followed by a complete removal of water from the pre-treated glycerol-rich compound via rotary evaporation in vacuo.

The glycerol concentrate as derived from the foregoing processes may further be purified to a higher concentration of more than 98.5% by vacuum distillation at 130°-220°C. Identification and characterization of glycerol may be carried out via the following standard procedures generally conducted in an oleochemical plant:-

- (i) IR spectrometry to indicate the hydroxyl functionality and the organic moiety;
- (ii) Glycerol content;
- (iii) Moisture Content;
- (iv) Ash content;
- (v) Salt content;
- (vi) Acidity;
- (vii) Refractive index; and
- (viii) GC chromatography.

The invention shall be illustrated via the following examples:-

Example 1

(1) Recovery of glycerol from glycerol residue

A glycerol-rich mixture is obtained by acidifying 2 kg of glycerol residue with H_2SO_4 in 3L of water until pH 0-7 is reached. Any formed solid precipitate is subsequently filtered off. Water is then removed from the glycerol-rich mixture and subsequently replaced with 3L of methanol. Any salt precipitated is removed by filtration. The added methanol is then removed from the glycerol-rich mixture thereby obtaining the desired glycerol concentrate. The concentration of the glycerol concentrate obtained ranged from 45-69%.

Example 2

(2) Recovery of glycerol from glycerol residue

A glycerol-rich mixture is obtained by dissolving of 500g of glycerol residue in 1L of water and subsequently adding thereto, 50g CaCl_2 to remove the fatty acids present in the glycerol residue. The glycerol-rich mixture is then heated to 80°-90°C for an hour and any formed solid precipitate is removed. The glycerol-rich mixture is subsequently acidified with H_2SO_4 to pH0-7 and followed by complete removal of water by rotary evaporation. 1.5L of methanol is then added. Any solid precipitate formed in the glycerol-rich mixture is then removed followed by the removal of methanol in vacuo to obtain the desired glycerol concentrate. The concentration of the glycerol concentrate ranged from 45-69%.

Example 3

(3) Purification of glycerol concentrate

The glycerol concentrate, as recovered from Examples 1 and 2 is subjected to vacuum distillation at 130°-220°C to obtain a clear fraction of purified glycerol. The concentration was found to be more than of 98.5%.

CLAIMS

1. A process for the recovery of glycerol from glycerol residue and/or the like glycerol-containing compounds, said process including the steps of
 - (a) acidification of the glycerol residue and/or the like glycerol-containing compounds within an effective amount of water to obtain a glycerol-rich mixture;
 - (b) removal of water from the glycerol-rich mixture and followed by an addition thereto of methanol, ethanol, hexane, chloroform, ethyl acetate, propanol or butanol as an effective amount of solvent;
 - (c) removal of any formed solid precipitate resulting from the glycerol-rich mixture; and finally followed by
 - (d) removal of the added solvent from the glycerol-rich mixture in vacuo, thereby yielding the desired glycerol concentrate.
2. A process for the recovery of glycerol of claim 1, wherein the acidification of step (a) is carried out with any acid selected from the group of mineral acids to pH 0-7.
3. A process for the recovery of glycerol of claim 1, wherein the added solvents comprise those of any organic group which are polar.
4. A process for the recovery of glycerol of claim 1, wherein steps (a)-(d) are carried out at room temperature to 90°C.
5. A process for the recovery of glycerol of claim 1, wherein steps (a) and (c) are carried out at atmospheric pressure.
6. A process for the recovery of glycerol of claim 1, wherein the recovered glycerol concentrate is further subjected to vacuum distillation at 130°-220°C for purification.
7. A process for the recovery of glycerol from glycerol residue and/or the like glycerol-containing compounds, said process including the steps of
 - (i) adding an effective amount of calcium salt to the glycerol residue and/or the like glycerol-containing compounds to obtain a pre-treated glycerol-rich compound; .
 - (ii) removal of any formed solid precipitate and optionally followed by a complete removal of water from the pre-treated glycerol-rich compound;

- (iii) acidification of the pre-treated glycerol-rich compound within an effective amount of water to obtain a glycerol-rich mixture;
 - (iv) removal of water from the glycerol-rich mixture and followed by an addition of methanol, ethanol, hexane, chloroform, ethyl acetate, propanol or butanol as an effective amount of solvent to the glycerol-rich mixture;
 - (v) removal of any formed solid precipitate and; and finally followed by
 - (vi) removal of the added solvent from the glycerol-rich mixture in vacuo, thereby yielding the desired glycerol concentrate.
8. A process for the recovery of glycerol of claim 7, wherein the acidification of step (iii) is carried out with any acid selected from the group of mineral acids to pH 0-7.
9. A process for the recovery of glycerol of claim 7, wherein the added solvents comprise those of any organic group which are polar.
10. A process for the recovery of glycerol of claim 7, wherein steps (iii)-(vi) are carried out at room temperature to 90°C.
11. A process for the recovery of glycerol of claim 7, wherein steps (i), (ii),(iii) and (v) are carried out at atmospheric pressure.
12. A process for the recovery of glycerol of claim 7, wherein the recovered glycerol concentrate is further subjected to vacuum distillation at 130°-220°C for purification.
13. A process for the recovery of glycerol of claim 1, wherein the removal of water in step (b) is carried out by rotary evaporation.
14. A process for the recovery of glycerol of claim 1, wherein the removal of water in step (b) is carried out by distillation under mild vacuum (10^{-1} to 10^{-2} torr) at temperature between 60°C to 100°C.
15. A process for the recovery of glycerol of claim 7, wherein the removal of water is carried out by rotary evaporation.

16. A process for the recovery of glycerol of claim 7, wherein the removal of water is carried out by distillation under mild vacuum (10^{-1} to 10^{-2} torr) at temperature between 60°C to 100°C.
17. A process for the recovery of glycerol of claim 1, wherein the removal of the added solvent in vacuo in step (d) is carried out by rotary evaporation.
18. A process for the recovery of glycerol of claim 1, wherein the removal of the added solvent in vacuo in step (d) is carried out by distillation under mild vacuum (10^{-1} to 10^{-2} torr) at temperature between 60°C to 100°C.
19. A process for the recovery of glycerol of claim 7, wherein the removal of the added solvent in vacuo in step (vi) is carried out by rotary evaporation.
20. A process for the recovery of glycerol of claim 7, wherein the removal of the added solvent in vacuo in step (vi) is carried out by distillation under mild vacuum (10^{-1} to 10^{-2} torr) at temperature between 60°C to 100°C.
21. A process for the recovery of glycerol of claim 1, wherein the preferred solvent in step (b) is either methanol or ethanol.
22. A process for the recovery of glycerol of claim 7, wherein the preferred solvent in step (iv) is either methanol or ethanol.