Title: Energy Efficient Process for Producing Dipropylene Glycol and/or Tripropylene Glycol

Technical Field

The present invention pertains to a method for selectively producing dipropylene glycol and/or tripropylene glycol using propylene oxide and propylene glycol as starting materials.

Background Art

Dipropylene glycol (DPG) is a highly versatile compound widely used in a variety of industries, including the production of polyester resins, polyurethane resins, acrylic acid esters, hydraulic oils, antifreeze, cellophane wetting agents, oil-water mutual solvents, printing ink solvents, and as a raw material for cosmetics, perfumes, and toiletries. Similarly, tripropylene glycol (TPG) serves as an essential raw material for polyester resins, polyurethane resins, acrylic esters, and acts as a solvent for water-soluble oils and inks.

Typically dipropylene glycol (DPG) and tripropylene glycol (TPG) conventionally have been made as co-products in the hydration of propylene oxide to make monopropylene glycol (PG, or 1,2-propanediol), with a certain fairly well-defined and limited range of amounts of both being produced according to the amount of water used in the hydration.

The global production capacity of DPG exceeds 2 million tonnes per annum. In the standard industrial process, propylene oxide (PO) reacts with water to form a mixture of monopropylene glycol (MPG) and DPG/TPG, which is later separated by distillation and purification, with MPG being the main product. DPG generally consists of three isomers: 1,1'-oxydi-2-propanol, 2-(2'-hydroxypropoxy)-1-propanol, and 2,2'-oxydi-1-propanol.

As the demand for DPG continues to rise, there is an increasing need to produce DPG as the primary product, rather than as a byproduct. For instance, Patent CN201981142U discloses a method where propylene oxide and propylene glycol are reacted at 130°C in the presence of a catalyst to produce DPG/TPG. Similarly, Patent WO2013111839A1 describes a process for producing DPG and/or TPG by reacting propylene glycol with propylene oxide at a high temperature of 220°C and a pressure of approximately 5 MPa in the absence of a catalyst. However, both processes require elevated temperatures (130°C and 220°C) and pressures, resulting in increased operational costs.

Thus, the current methods for synthesizing DPG and TPG suffer from limitations due to the need for higher temperatures and pressures, leading to higher manufacturing costs. There remains a need for an improved process that addresses these challenges by reducing production costs, enhancing efficiency, minimizing byproducts, and improving the yield of DPG and TPG.

Disclosure of the Invention

The present invention provides a highly selective method for producing dipropylene glycol and/or tripropylene glycol, addressing the above-mentioned issues. The process involves reacting propylene oxide with propylene glycol under mild reaction conditions, specifically at low temperatures between 40°C and 70°C, without the use of water, and optionally in the presence or absence of a catalyst. The method ensures high selectivity and yield while minimizing unwanted side reactions.

Detailed Description of the Invention

The invention provides a method for producing dipropylene glycol and/or tripropylene glycol with high selectivity by optimizing the reaction rate between propylene oxide and propylene glycol. The method achieves efficient production under mild conditions.

1. **Reaction Conditions**
    - **Temperature:** The reaction temperature is preferably between 40°C and 90°C, more preferably between 50°C and 70°C, and most preferably between 60°C and 70°C. A temperature of 65°C or higher significantly enhances the reaction rate, improving the yield of dipropylene glycol and/or tripropylene glycol.
    - **Pressure:** The reaction is conducted at normal atmospheric pressure, ensuring an energy-efficient and cost-effective process.
    - **Catalyst:** The reaction may be carried out in the presence or absence of a catalyst. Suitable catalysts include alkaline or acidic catalysts, such as potassium hydroxide (KOH) or sodium hydroxide (NaOH), though other catalysts may be used depending on specific requirements.

Method

The process begins by adding 100 grams of propylene glycol into a round-bottom flask under a nitrogen atmosphere. Then, 0.3 grams of sodium hydroxide (NaOH) beads are added, and a magnetic stirrer bar is employed to dissolve the NaOH in the propylene glycol. The reaction mixture is cooled using an ice bath, and 100 grams of propylene oxide are slowly added while ensuring the reaction is free from moisture and water. The mixture is gradually heated to reflux, and chilled water is circulated around the apparatus for condensation. The temperature is then slowly increased to 70°C (using either a water or oil bath) and maintained for 6 hours. After the reaction, heating is stopped, and the mixture is cooled. Any excess propylene oxide is neutralized by adding water. The product is then collected in a suitable container, and its composition and purity are confirmed via mass balance analysis and gas chromatography-mass

spectrometry (GCMS). The yield of dipropylene glycol (DPG) and tripropylene glycol (TPG) is typically over 85%, with DPG comprising 50% and TPG comprising 35%.

The propylene oxide and propylene glycol used in this method may be sourced from any known production processes.

Claims

1. A method of preparing dipropylene glycol, tripropylene glycol or a mixture thereof, comprising the steps of:

   i) providing propylene glycol;

   ii) adding propylene oxide to the propylene glycol to form a mixture; and

   iii) heating the mixture at a temperature in the range of 30 °C to 90 °C.

2. The method of claim 1, wherein one or more of steps i) to iii) are performed in an inert atmosphere.

3. The method of claim 1 or 2, wherein one or more of steps i) to iii) are performed in an environment that is substantially free of water.

4. The method of claim 3, wherein the environment comprises less than 0.1% of water.

5. The method of any one of the preceding claims, wherein one or more of steps i) to iii) are performed at a pressure in the range of 1 atm to 3 atm.

6. The method of any one of the preceding claims, wherein the temperature range in step iii) is in the range of 40°C to 90°C, 40°C to 70°C, 50°C to 70°C, or 60°C to 70°C.

7. The method of any one of the preceding claims, wherein the propylene glycol and propylene oxide are present at a mole ratio in the range of 100:1 to 1:100, preferably at a mole ratio of about 1:1 or at a mole ratio in the range of 1:1 to 1:100.

8. The method of any one of the preceding claims, further comprising mixing a catalyst with the propylene glycol in step i).

9. The method of claim 8, wherein the catalyst is a base.

10. The method of claim 9, wherein the base is KOH or NaOH.

11. The method of any one of claims 8 to 10, wherein the catalyst is present at a range of 0.001% to 0.5% by weight of the propylene glycol.

12. The method of any one of the preceding claims, further comprising step ia) of cooling the mixture to a temperature in the range of about 0 °C to about 25°C, more preferably about 0 °C to about 20°C, between steps i) and ii).

13. The method of any one of the preceding claims, further comprising step iia) of refluxing the mixture between steps ii) and iii).

14. The method of any one of the preceding claims, wherein step iii) is performed for a duration in the range of 0.5 hours to 12 hours, preferably 4 hours to 6 hours.

15. The method of any one of the preceding claims, further comprising the step of cooling the mixture after step iii).

16. The method of any one of the preceding claims, comprising the step of adding water to the mixture after step iii).