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Preparation of glyoxal from ethylene glycol

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Abstract: Glyoxal is a versatile compound that has attracted the attention of researchers and various industries due to its wide range of applications. From textiles to pharmaceuticals, from adhesives to cosmetics, glyoxal has found its place in countless products we use every day. China is at the forefront of this important chemical manufacturing industry, ensuring sufficient supply of downstream applications in various industries worldwide. The downstream applications of glyoxal cover numerous industries such as textiles, pharmaceuticals, and water treatment. Its versatility makes it an important component of various industries, which rely on its unique characteristics to enhance performance and functionality. Thanks to its excellent properties and extensive applications, glyoxal continues to play an important role in many industrial processes. This article will mainly explore some methods for the production of acetaldehyde from ethylene glycol in gas-phase catalysis, including subsequent impurity removal.

Keywords: ethylene glycol; glyoxal; gas phase; catalyzer

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1. Introduction

As of April 30, 2020, the total capacity of China's ethylene glycol enterprises has increased to 13.735 million t/a, of which 4.89 million t/a is made of coal, accounting for 35.6%; 7.619 million t/a of petroleum production, accounting for 55.5%; MTO (methanol to olefins) method and monomer ethylene method account for 9%. The polyester production capacity has increased by 250000 tons, and the production capacity base has been revised up to 58.82 million tons [1]. Glyoxal, also known as oxalic aldehyde, can undergo addition or condensation reactions with alcohols, amines, aldehydes, carboxyl compounds, etc. It has a wide range of applications in textiles, building materials, leather, medicine, and other fields [2]. Glyoxal has active chemical properties and can undergo addition, condensation, or crosslinking reactions with alcohols, amines, aldehydes, carboxyl compounds, cellulose, polyvinyl alcohol, and urea. It has a wide range of applications in textiles, printing and dyeing, building materials, leather, medicine, and other fields, with broad prospects for development and utilization [3]. The synthesis of resin adhesives using low toxicity, green environmental protection, and easily decomposable glyoxal instead of formaldehyde has become a new hot spot in the industry [4]. Glyoxal, as a non ironing finishing agent for cotton fabrics, forms cross-linking with fibers through condensation, thereby achieving the purpose of non ironing finishing [5]. Ethylene glycol can also be used in pharmaceuticals, polyvinyl chloride paints, adhesives, synthetic resins, cosmetics, lubricants, imaging and developing fluids, electrolytes, brake fluids, etc., with a wide range of applications [6]. Ethylene glycol is an important component of electrolyte used in electrolytic capacitors. Currently, the annual usage of ethylene glycol in capacitor electrolyte is at least 5000t [7]. With China's accession to the WTO, the market is gradually opening up, and the application fields of glyoxal are also expanding. Some fields have high quality requirements for products, and high concentration and high purity glyoxal needs to be imported from abroad every year. In order to enhance the competitiveness of domestic enterprises, enterprises using ethylene glycol production should focus on improving product quality, especially the ability to remove formaldehyde, while controlling costs [8].

Ethylene glycol (EG) is an important organic chemical raw material, mainly used in the production of polyester fiber (PET), plastic, rubber, polyester paint, adhesives, surfactant, ethanolamine and explosives, etc., can also be used as a solvent, lubricant, plasticizer and antifreeze. The chemical nature of ethylene glycol is more active, can occur esterification, etherification, alcoholization, oxidation, condensation and other reactions [9,10]. Combining ethylene glycol and glyoxal can improve the fabric strength [11].

Global ethylene glycol about 25 million t surplus trend. However, the output in Asia cannot meet the requirements. China's ethylene glycol has been in short supply for a long time. Shanxi Province plans to produce 1.2 million tons of ethylene glycol [12,13,14].

2. Progress in production technology

So far, the production methods of glyoxal are relatively rich, mainly including acetylene oxidation method, ethylene oxidation method, oxalic acid reduction hydrolysis method, ethylene glycol gas phase oxidation method [15] and acetaldehyde nitric acid oxidation method [16]. Among them, gas phase oxidation of ethylene glycol and acetaldehyde nitric acid oxidation are more used in industry [17].

3. Preparation by the oxidation method

The gas phase oxidation method of ethylene glycol has become the development direction of high-quality glyoxal production process because of its simple process equipment, environmental friendliness, high concentration of the initial product, easy post-treatment and suitable for continuous production. Alcohol using air catalytic oxidation to produce the corresponding aldehyde is the most commonly used method for industrial production of aldehydes. The same with methanol to produce formaldehyde, ethanol for acetaldehyde similar devices and catalyst with ethylene glycol to produce ethylene glycol is also feasible ethylene glycol due to the relatively high molecular weight and high boiling point, so the difficulty to achieve high temperature gas phase oxidation and dehydrogenation is more difficult to break chain and coke. In addition to glyoxal, the reactants also have organic acids (mainly formic acid), formaldehyde and unreacted ethylene glycol. These substances can be separated by different separation means and devices [18]. The key to the oxidation preparation method is to find suitable catalysts for the reaction [19].

Ethylene glycol gas phase oxidation method is the traditional production method of glyoxal, which is widely used by glyoxal manufacturers in China. After ethylene glycol preheat and gasification, it is mixed with circulating gas into the catalytic reactor for the reaction at 650-670°C. The product is cooled by water to form an aqueous solution of glyoxal. Then, glycolal is obtained through subsequent treatment of decolorization and vacuum filtration. The one-way conversion rate of ethylene glycol is 80% -85%. With tail gas cycle to adjust the oxygen content, products containing glyoxal concentration is generally 30% -40%, the method of raw materials ethylene glycol, short process, the process is simple, deficiency is the product quality is poor, contains a certain amount of formaldehyde, alcohol and acid, such as magazine, need further purification treatment, to meet the quality requirements of medicine and other industries [20]. Process glycol after preheating into the vaporizer, air and circulating gas, inert gas after metering, preheating after mixing with ethylene glycol gas into the mixing filter, purification mixing, above the temperature into °C oxidation catalytic bed reaction, control the reaction temperature, reaction gas absorption, extraction content control, crude acetaldehyde, into human extraction tower for extraction, settlement after separation of formaldehyde and other by-products, separation of glyaldehyde into the human decolorization kettle, with activated carbon, after vacuum filter acetaldehyde product, the yield is about, one-way conversion rate is about. The process is widely used in China, production technology is relatively mature, raw material ethylene glycol, the process is short, simple, but also has high energy consumption, low yield, poor product quality defects, the content of formaldehyde products as high as, make the purpose of the product by a certain restrictions, need further purification, can be used in medicine, daily chemical industry, at the same time due to the high price of raw material glycol, increase the product cost [21]. Compared with this method of nitric acid oxidation method, the disadvantage are low content, high impurity content (formaldehyde content 6%~7%). Therefore, the glyoxal products produced by this method are limited in some uses, especially in the pharmaceutical industry. At present, most of the glyoxal used in the pharmaceutical industry in China still needs to be imported. There are also methods of tetrachloroethane and smoke sulfuric acid reaction, ozone oxidation acetylene or benzene, oxalic acid and its derivatives are reduced to glyoxal, but these three processes have not been further developed, no industrial production. At present domestic b awake method and ethylene glycol method with low yield, products containing high impurities, high energy consumption, manufacturer's priority is to actively adopt new technology and new technology, introducing foreign advanced technology or organization research, reduce consumption, improve product quality, expand the application of products, so as to reduce the imports of the product [22].

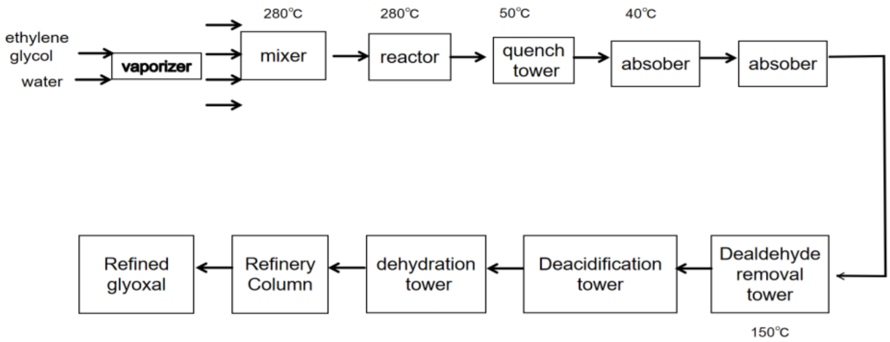

Figure 1. Process diagram of glyoxaldehyde generation by ethylene glycol

3.1. Chemical oxidation method

Ozone oxidation in aqueous solution and ethylene glycol analog diethylene alcohol (DEG) The main products of ozone oxidation are glycolaldehyde, glyoxal, formaldehyde, acetaldehyde and acetic acid, formic acid, pyruvate acid, oxalic acid and glyoxal [23]. The oxidation mechanism of ethylene glycol on the loaded silver catalyst is with phosphate-modified lysates. Earlier, silver loaded on silicate-phosphate carriers was found to have high catalytic activity in selective convection.

Conversion of ethylene glycol to glyoxal. The Ag/SiO_2 (silver loaded on silica) and $Ag/P_2O_5/SiO_2$ (silver base loaded on phosphoric acid-modified silica) model catalytic systems were selected as the test materials. The interaction of alcohols with the surface of the phosphorus-containing catalysts includes interactions in the presence of components of the reaction mixture such as water vapor, oxygen and hydrogen.

By gen, the adsorption and conversion of ethylene glycol on the surface of phosphate-modified Ag catalyst was studied by dehydrogenase formation, and the ratio between the components of the reaction mixture was: $V(CH_2OH)_2$: $V(H_2O)$: $V(O_2)$: $V(N_2)$ =4.2:14.4:5.1:76.2, and the contact time was 0.016~0.080s. It is found that ethylene glycol adsorbs on the surface of the phosphate group, and that water vapor increases the stability of the adsorbed ethylene glycol to 400℃. During the reaction, changing the catalyst dosage and reaction temperature of the reaction can regulate the product distribution and selectivity of the reaction. At 400℃, ethylene glycol into glycolaldehyde, and then glycolaldehyde to glyoxal; during the reaction at 500 to 550℃, ethylene glycol can be directly converted to glyoxal [24].

3.2. Electrochemical oxidation

In 2011, Wang et al. used in situ infrared spectroscopy and electrochemical method to study the mechanism of electrocatalytic oxidation of ethylene glycol on Pd electrode, and explored the adsorption and electrooxidation of ethylene glycol on the surface of polycrystalline palladium in alkaline and acidic media by cyclic voltammetry. The oxidation of ethylene glycol shows that ethylene glycol oxidation requires higher potential in acid solution, and the catalytic performance decreases with the increase of pH, and CO_2 can be selectively obtained; glycolate, glyoxal, glyoxylate, oxalate and formate are mainly obtained in alkaline medium. G Products and intermediates of oxidation on Pd are affected by pH. In alkaline media, the C_2 species (glycolate, glyoxal, glyoxylate, and oxalate) and the C1 species (formate and carbonate) all form at a mutual concentration, depending on the pH. In contrast, CO_2 is selectively produced in an acidic aqueous solution [25].

3.3. Biochemical oxidation method

In 1994, Isobe et al. used two enzymes of ethylene glycol into glyoxal from methanol yeast Candida (Candidasp.) and Pichia (Pichiapastoris). The study showed that adding catalase increased the catalytic effect of alcohol oxidase extracted from Pichiapastoris, 100 mmol ethylene glycol for 10h; 100mmol glycolaldehyde for 100mmol glycolaldehyde. A novel ethylene glycol oxidation reaction was identified from methanol yeast, Candida and Pichia pastoris. Both alcohol oxidases oxidize ethylene glycol to glyoxal by ethylene glycol aldehyde [26].

The oxidation of ethylene glycol mainly includes chemical oxidation, electrochemical oxidation and biocalytic oxidation. Both enzyme oxidation and resting cell catalysis in biological oxidation method have the incomparable advantages of chemical oxidation method, which can avoid environmental pollution to a large extent, meet the requirements of green chemistry, and has a good application prospect. In addition, the oxidation products of ethylene glycol can also synthesize the index and its derivatives, piperazine and its derivatives, vinyl carbonate and its derivatives and other fine chemicals. This paper expects to introduce the review and progress of ethylene glycol oxidation reaction, especially biological oxidation, to provide some new research ideas on the overcapacity of ethylene glycol and the single downstream product structure [9]

4 Catalyst

4.1. Commonly used catalysts in the early stage

Much work has been done on catalyst and product purification. Traditional catalyst is phosphorus and copper catalyst, which has the advantages of wide source, low price and high yield, but many side reactions, poor product quality and high ethylene glycol consumption. In the early stage of ethylene glycol oxidation process, halide was used as an inhibitor, and the equipment requirements are high, and the process is more complex [27].

The reaction yield is low when the metal copper is used as the catalyst without adding other cocatalyst, and the reaction yield is increased by adding copper as the main catalyst with phosphorus. In the case of copper-containing systems, the formation of copper oxides on the catalyst surface leads to a decrease in the catalytic activity [28,29].

4.2. Silver catalyst

$$(CH_2OH)_2 + O_2 \rightarrow (CHO)_2 + 2H_2O \quad (1)$$

$$(CH_2OH)_2 \rightarrow (CHO)_2 + 2H_2 \quad (2)$$

$$H_2 + O_2 \rightarrow 2H_2O \quad (3)$$

Figure 2. The ethylene glycol oxidation reaction [19]

The reaction of alcohol to aldehyde uses silver as catalyst. There are two active centers on its surface, one can catalyze the oxidation of alcohol to produce aldehyde and the other promotes the deep oxidation of alcohol to produce byproduct CO_2 [30]. In the 1980s, the US patent reported that with the crystalline silver catalyst, the reaction yield of glyoxal was 66%, and the spatial and temporal yield rate was 14.6g/(cm^3 h). Xu Hualong of Fudan University chose crystalline silver prepared by electrolysis as the carrier, first high temperature treatment, and then metal deposition. After drying and roasting, crystalline silver of copper silver alloy particles was obtained. Then ethylene glycol, oxygen, water and inert gas are oxidized on the above catalyst to form glyoxal. Using this method, we can directly obtain an aqueous solution of 40% glyoxal with formaldehyde content less than 500ppm and hydroxyacetaldehyde content less than 0.5%. The catalyst obtained by this method is easy to regenerate and can be regenerated by the same method as electrolytic silver. The glyoxal product produced is of high quality [31]. Du Shu et al. found the excellent performance of the silver carrier catalyst in the formation of glyoxal [32]. Deng Jingfa et al. found that phosphorus-containing compounds and silver surface formed a stable surface compound at certain surface positions through strong interaction, eliminating part of the silver surface active center that caused deep oxidation of alcohol. Therefore, the addition of phosphorus increased the selectivity of the reaction [33]. Wuhan university of engineering has developed a new process of composite silver catalytic ethylene glycol production of glyoxal filled with Ag-P-Se / porcelain-plate catalyst catalytic oxidation reaction catalyst activity is high, the yield of glyoxal as high as 85%, impurity formaldehyde less [34] xiao spectrum with metal silver as a catalyst oxidation of ethylene glycol make the yield of glyoxal reached 72.9% [35]. The modification of silver catalyst with SiC extended the catalyst life and prevents the catalyst agglomeration [36].

4.3 Silver, copper-phosphorus catalyst

Selective oxidation of ethylene glycol on silver and copper catalysts is the promising method for the synthesis of glyoxal [23,37].

4.4. Other catalysts

Xu Hualong et al. [38] of Fudan University developed a catalyst for circulating gas purification in the process of glyoxal production by air oxidation. It is composed of lanthanum, cerium, zirconium and roasting at 500-1000°C in copper, silver, manganese, palladium and platinum elements after a period of time of 1000°C. The catalyst has a large specific surface, good thermal stability and a suitable grain scale of active components [39].

Using Pt-Sb2O3/D3520 as the catalyst. The choice of reaction conditions (such as reaction medium, temperature, etc.) directly affects the conversion rate and glyoxal yield. According to the experimental situation, the catalyst needs to be further studied: (1) the separation and purification of reaction products is complicated, with column separation or adsorption separation; (3) the reaction product is easily inactivated, which is one of the reasons for the use of a large number of hospitals; respectively, with appropriate reduction of the system temperature[40].

5. Prognostic treatment

The post-treatment of glyoxal by ethylene glycol production is mainly for the removal of formaldehyde. At present, the industrial application or research methods include water vapor distillation and solvent extraction [41]. The determination of ethylene glycol in glyoxal solution is simple and fast, with good accuracy and high sensitivity. The detection limit of ethylene glycol was 0.10 mg / mL, which showed a good linear relationship in the concentration range of 0.3-2.00mg / mL, and the correlation coefficient (r) was greater than 0.998. Quantitative addition of the target to the blank water sample showed a recovery in the range of 95.06% to 103.40% with the RSD value between 2.56% and 3.32%.

Results show that this method can be applied to the determination of ethylene glycol in glyoxal solution [42].

5.1. Water-vapor steam distillation method

Water vapor distillation is a widely used unit operation in chemical production, using the difference of the properties of different components in the mixture solution. The purification of glyoxal by water vapor distillation is to use the difference between the boiling point of formaldehyde and Z dialal to remove formaldehyde from the aqueous solution of glyoxal. This method can remove about 70% of formaldehyde, which cannot meet the purity requirements of medical glyoxal; the high energy consumption, the long operation cycle (about 20 h), the equipment investment; and the chromatic depth of long distillation increases the discoloration burden in the post-processing process.

5.2. Solvent extraction method

Solvent extraction takes advantage of formaldehyde and glyoxal between the aqueous and solvent phases to selectively remove formaldehyde from the aqueous glyoxal solution [43]. Li Zhou of tsinghua university solvent take formaldehyde, using isooctanol as an extraction agent, xylene as a diluent, containing 40% of 5% formaldehyde glyoxal aqueous solution study, can make the formaldehyde content in the products to below 0.5%, can meet the needs of special industries such as medicine, has the advantages of investment province, low energy consumption, short operation cycle [44]. Tsinghua Unigroup Group corporation has developed a new process of glydialdehyde. The process is mainly with the extraction equipment instead of water steam distillation equipment. Crude glyoxal and solvent into the extraction tank, after extraction of glyoxal into the original process of decolorization kettle, solvent treatment (form a byproduct 2D resin) after aldehyde back to measuring tank, product color and easy decoloring processing, running smoothly, easy to control, the content of formaldehyde, out of formaldehyde and glyoxal can form a by-product 2D resin, not only increase the benefit, and reduce the discharge of waste, significant economic benefits [45].

$$(CH_2OH)_2+1/2\ O_2 \rightarrow 2\ HCHO+H_2O \qquad (4)$$

$$(CH_2OH)_2+5/2\ O_2 \rightarrow 2\ CO_2+3H_2O \qquad (5)$$

$$(CH_2OH)_2+1/2\ O_2 \rightarrow 2\ HOOCCH_2OH+H_2O \qquad (6)$$

Figure 3. Triethylene glycol oxidation side reaction [19]

6. Conclusion

At present, glyoxal manufacturers in China mainly use ethylene glycol catalytic oxidation process, which has the disadvantages of high comprehensive energy consumption, poor product quality and low conversion rate of oxidation reaction. Major manufacturers through strengthening management, optimizing the control system, to eliminate running, running, dripping, leakage and other phenomena, material consumption has no obvious change. In the oxidation process of process production, high system resistance and high circulating fan load cause high power consumption, which affect the total amount of raw materials into the system and reduce the annual production capacity of the whole equipment, the electric energy and excessive water consumption, and the long filter time and poor depeffect due to the defects of the filter. In today's rising energy price, energy consumption accounts for an increasing and larger proportion in the cost. How to transform the existing process, reduce the energy cost and enhance the competitiveness is of great significance.

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