The catalysts for synthesis of citrate esters plasticizers and the application of citrate esters plasticizers

Chen Ming[1, a, *], Li Shanshan[2, b]

1. Yantai University, Yantai264005, Shandong, China
2. Yantai Newccess New Material Technology Co., Ltd., Yanta, 264005, Shandong, China

a. ming.chen3691@gmail.com, b. susan.lishanshan@yahoo.com
***Corresponding Author**

Abstract: The latest research progress in citrate esters plasticizers at home and abroad was introduced. The advance in the catalysts for the syn thesis of citrate esters plasticizers and the application of citrate esters plasticizers were reviewed in detail. The catalysts for the synthesis of citrate esters included sulfonic acid, solid super acid, heteropolyacids, ionic liquids and inorganic salts. The citric acid ester plasticizers were applied in the fields of food packaging, children's toys and medical instrument. The development prospects of citric acid ester plasticizers were outlined.

Key words: fine chemical engineering, citrate ester, plasticizer

1. Introduction

China is the world's largest plasticizer producer, with an annual output of about 5 Mt, accounting for more than half of the global plasticizer production. The types of plasticizers are mainly divided into phthalate esters, phosphate esters, benzoate esters, aliphatic dibasic esters, and citrate esters, among which, phthalate ester plasticizers are the most widely used, accounting for about 80% of the total plasticizer production. They are mainly used in rubber and plastic products of polyvinyl chloride resin, significantly improving the plasticity of polyvinyl chloride and other polymers, and are widely used in food packaging, children's toys, vinyl flooring, medical materials, and toiletries, etc. However, phthalate ester plasticizers are not stable in polymer products and will slowly migrate into the surrounding environment with the influence of environmental factors, polluting the surrounding air, water, food, and soil. Studies have shown that phthalate ester plasticizers can affect the reproductive development of animals and are related to male obesity, diabetes, thyroid diseases, and have the potential for carcinogenicity. Many countries have strictly limited the use of phthalate ester plasticizers, and China will gradually cancel its application in food packaging materials, medical equipment, and children's products, which has greatly reduced its available range. Therefore [1-3], the development of low-toxicity and environmentally friendly plasticizers is imperative.

Citrates are the esterification products of citric acid and alcohols under certain conditions, mainly divided into citrates and acyl citrates, with advantages of low toxicity, good compatibility, strong plasticizing ability, good weather resistance, and excellent antibacterial properties, and the raw materials (citric acid, n-butanol, acetic acid, etc.) are all non-toxic, harmless, and renewable resources, with excellent market prospects. The synthesis of citrate esters initially used concentrated sulfuric acid as a catalyst, which has the advantages of low production cost, good effect, mild reaction, and easy control, but due to the drawbacks of multiple side reactions, difficult separation, a large amount of acidic waste liquid, environmental pollution, and corrosion of equipment, with the continuous increase in energy consumption and the continuous improvement of environmental awareness, the development of a more efficient and green catalyst has become a trend.

This paper mainly introduces the research progress of catalysts for the synthesis of citrate ester plasticizers and the application of citrate ester plasticizers.

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2. Catalysts

2.1. Sulfuric Acid

Sulfuric acid catalysts mainly include p-toluenesulfonic acid and aminosulfonic acid, both of which are organic acid catalysts. Among them, p-toluenesulfonic acid catalyst is an organic strong acid, compared with concentrated sulfuric acid catalyst, it has the advantages of high activity, small amount required, less side reactions, reduced "three wastes", less corrosion to equipment, and less environmental pollution [4]. Luo Wei and others [5] used p-toluenesulfonic acid as a catalyst, citric acid and n-butanol as raw materials, under the conditions of a molar ratio of acid to alcohol of 1:4, a catalyst amount of 0.2 g, a reaction temperature of 120°C, and a reaction time of 4 hours, the conversion rate reached 96.3%, and the catalyst can be reused. Ye Yuanyuan and others [6] used p-toluenesulfonic acid as a catalyst, with citric acid and 2-heptyl heptanol as raw materials, to conduct the synthesis study of tri(2-heptyl heptanol) citrate. The results showed that under the conditions of a molar ratio of citric acid to 2-heptyl heptanol of 3.7:1 and the reaction system temperature not exceeding 140°C, the yield of citrate ester was greater than 99.5%, and it has a good plasticizing effect on polyvinyl chloride, with excellent performance of high temperature resistance and volatility resistance.

2.2. Solid Superacid

Solid superacid catalysts have higher acid strength, higher selectivity, and are easy to separate after the reaction, with less environmental pollution and no corrosion to equipment, but there are disadvantages such as easy deactivation, surface carbon deposition, poor stability, and short service life during the reaction process. Chen Shufen and others [7] first synthesized a solid superacid catalyst $SO4^{2-}$/La2O3-ZrO2-HZSM-5, and analyzed the influence of calcination temperature, catalyst amount, reaction time, and reaction temperature on the conversion rate. The results showed that the catalyst obtained by calcination at 500°C for 3 hours had the best activity, with a conversion rate of up to 91.5%. Ma Huiqin [8] respectively used Fe2O3-ZrO2, ZrO2-Al2O3, ZrO2-SnO2, and ZrO2-CeO2 as the base, $SO4^{2-}$ as the promoter, to prepare four different solid superacid catalysts, and modified the catalyst with La^2 to synthesize citric acid tributyl ester, achieving very good plasticizing effects.

2.3. Heteropoly Acids

Heteropoly acids are a class of metal-oxygen cluster compounds formed by oxygen atoms bridging metal atoms, which have both acid catalytic performance and redox catalytic performance. Heteropoly acid catalysts have stable structure, high reaction activity, good selectivity, small corrosion to equipment, and no environmental pollution, and are a promising class of green catalysts. Edneia Caliman and others [9] loaded $H_3PW_{12}O_{40}$ on the carrier niobium oxide, and found that a new compound was formed between the heteropoly acid and the carrier, which can provide more active proton sites than $H_3PW_{12}O_{40}$, and only has B acid acidity, which has higher activity in catalyzing esterification reactions. Jiang Guangping and others [10] prepared ($[PyPS]_3PW_{12}O_{40}$) three heteropoly acid salts, and used them as catalysts for the synthesis of citric acid tributyl ester. Among them, $[MIMPS]_3PMo_{12}O_{40}$ had the best catalytic effect, and when the catalyst amount was 5% of the mass of citric acid, the esterification rate could reach 98.3%. The catalyst had good reusability, and after being reused 5 times, the esterification rate still remained above 94%.

2.4. Ionic Liquids

Ionic liquids have the advantages of low melting point, low saturated vapor pressure, high acid catalytic activity, and good solubility, and their acidity and structure can be adjusted by changing the ions, belonging to adjustable catalysts. Yin Yanbai and others [11], in the study of the esterification reaction of citric acid and butanol, used N-methyl imidazole hydrogen sulfate ionic liquid as a catalyst, with a fixed catalyst amount of 15% of the total mass of the reactants, and through multiple repeated experiments, the optimal reaction conditions were obtained: a reaction temperature of 110°C, a reaction time of 7 hours, a molar ratio of alcohol to acid of 6:1, and toluene as the water-carrying agent. Under these conditions, the conversion rate of citrate ester was greater than 97%, and the catalyst could be reused. Guo Kangbin [12]

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and others used $[NH(CH_2)_5CO]HSO$ ionic liquid as a catalyst, with citric acid tributyl ester and acetic anhydride as raw materials to synthesize acetyl tributyl citrate, and explored the influence of the molar ratio of raw materials, reaction temperature, reaction time, and catalyst amount on the acetylation reaction. Under the optimal conditions, the yield rate reached 98.7%, and the catalyst could be reused.

2.5. Inorganic Salts

Inorganic salt catalysts mainly include chlorides and sulfates, with common chlorides being aluminum chloride, iron chloride, and titanium chloride, and common sulfates being hydrated iron sulfate, titanium sulfate, zirconium sulfate, and sodium bisulfate, etc. Yang Hongqin [13] used the impregnation method to prepare a supported zirconium sulfate catalyst, and its activity was evaluated. The results showed that using HMS and MCM-41 as carriers could fully improve the catalytic efficiency of zirconium sulfate. The supported catalyst $Zr(SO_4)_2 \cdot 4H_2O/HMS$, after calcination at 180°C, was used to catalyze the synthesis of citric acid tributyl ester. Under the optimal conditions, the esterification rate and yield were 92.8% and 92.3%, respectively, but there were disadvantages such as poor reusability of the catalyst and severe loss of zirconium ions. Zhang Xiayan and others [14], with citric acid and iso-octanol as raw materials, used inorganic salt potassium bisulfate as a catalyst, with a catalyst amount of 3% of the total mass of the reactants, reacted at 150°C for 2 hours, and the esterification rate was greater than 96%. This inorganic salt catalyst had high catalytic activity and good recyclability, and after being used 6 times, the esterification rate still reached 90.85%, which was easy to separate from the product and had less corrosion to the equipment.

In addition, molecular sieves [15-16], lipases [17-18], titanium-pillared bentonite [19], dibutyltin oxide [20], modified zeolites [21], and resin [22-23], etc., can all catalyze the reaction of citric acid and n-butanol to produce citrate esters, and the development prospects are broad.

3. Application of Citrate Ester Plasticizers

Citrate ester plasticizers have excellent properties such as cold resistance, heat resistance, light resistance, and water resistance, and are non-toxic, harmless, green, and environmentally friendly, with a wide range of applications. As plasticizers, they can be widely used in polyvinyl chloride, polyethylene, polypropylene, and cellulose esters, with a maximum addition amount of up to 40%. They can significantly reduce the melt viscosity and processing temperature, increase the flexibility and elongation at break of the polymers, and improve the impact resistance and low-temperature flexibility of the polymers. Acetylated citrates, which are produced by acetylation of citrate esters, not only have the good properties of the original citrate ester plasticizers but also have further improved volatility and water sensitivity after the hydroxyl groups are capped by acyl groups, resulting in a lower water extraction rate. Plastic products made with acyl citrate plasticizers have excellent processing performance, good heat sealing, and are easy to reprocess, mainly used for the plasticization of polyvinyl chloride materials.

3.1. Food Packaging

As a new type of green environmental plasticizer, citrate esters have been recognized by the FDA as non-toxic plasticizers [24]. At present, the use of phthalate plasticizers in food packaging materials is strictly prohibited, and many developed countries have allowed the use of citrate ester plasticizers in food packaging materials. Taking polyvinyl chloride food packaging film as an example, after being plasticized with citrate esters, polyvinyl chloride has the advantages of good air permeability, good transparency, and no peculiar smell when in contact with greasy foods, as well as superior thermal stability. Food packaging materials prepared with citrate ester plasticizers, in addition to being breathable and tough, also have good printability, strong sealing, and excellent degradability, making them the best choice for plasticizers in food packaging materials in the future.

3.2. Children's Toys

Phthalate ester plasticizers are environmental hormones used in children's toys. Phthalate ester plasticizers can be extracted from the material, posing a serious threat to the health and growth of children [25]. Non-toxic citrate ester plasticizers prepared for children's toys have good resistance to plasticizer

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extraction, reducing health problems caused by plasticizers entering the children's body. Plastics plasticized with citrate esters have good processing performance, which is convenient for processing into various types of toys. Therefore, citrate esters are an excellent choice as plasticizers for children's toy materials.

3.3. Medical Instruments

Most medical instruments such as infusion tubes, blood bags, and medical packaging bags use polymer materials, but most polymer materials have added plasticizers in the polymerization molding process formula. Citrate ester plasticizers are non-toxic and harmless, with good plasticizing effects, and can significantly improve the performance of materials. In foreign countries, citrate ester plasticizers were used in the medical field experiments at an earlier stage, and it was found that they extended the service life of medical products. Their good biocompatibility can be used as plasticizers for polymers such as medical sutures and artificial organs.

4. Conclusion and Prospects

China's citric acid production ranks second in the world, with high output and advanced technology, providing abundant raw materials for the development of downstream products such as citrate esters. However, the types of downstream products related to citric acid in China are few, and the added value is low. The research on the preparation of citrate esters from citric acid mainly focuses on a few varieties in low molecular products. Therefore, increasing the depth and breadth of research, improving product added value, and taking a path of combining production, teaching, and research will be the future development direction.

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