TECHNICAL SCIENCES

RECENT ADVANCES IN MODIFICATION OF STARCH AND ITS APPLICATIONS IN CHINA FOOD INDUSTRY

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Abstract

Starch has great potential for use as a renewable biological material. However, native starch has limitations in use due to its disadvantages, so to expand its properties and possibilities of application, starch modification is carried out by chemical, physical and enzymatic methods.

Among the various methods of modification, physical holds a special place.Physical modification refers to the use of physical techniques such as thermal fields, force fields, electromagnetic fields to change the original morphology, structure and properties of starch granules, thus change the rheological properties and digestibility.

This review sheds light on many of the modern methods found in starch modification, their advantages and disadvantages. Particular attention is paid to the technology of production of modified starch by the method of extrusion. The applications of modified starch in the food industry and the market for modified starch in China have also been investigated.

Keywords: starch, chemical modification, physical modification, enzymatic modification, application

Introduction

Starch is the main component of fruits, seeds, tubers and roots of green plants. Rice, corn, potatoes, taro, bananas and other crops contain a lot of starch, which is widely grown in the world. In 2013, global starch production was about 68.8 million tons, of which corn starch was about 61 million tons, accounting for 89% of the total. In 2017, China's starch production reached 26.12 million tons, accounting for 36% of the world's total starch production. The annual output of starch in the EU is more than 4 million tons, mainly potato starch, wheat starch, corn starch, while the Southeast Asian countries mainly produce cassava starch. With the advantages of being renewable, non-toxic, biodegradable and of relatively low cost, starch has attracted a substantial research and commercial interest as food materials and other green chemical basic raw materials. However, Starch does not have physical and chemical properties suitable for certain type of processing in its native form due to their poor shear and thermal stability and high degree of retrogradation. Its insolubility in cold water, thermal and mechanical properties limitations, instability of its pastes and gels, poor dispersivity and poor filming property limit its widespread commercial application in textile, papermaking, medicine, food and other industries. In order to maximize the application of starch in foodstuff and other industries, starches are frequently modified by chemical, physical, and enzymatic processes to promote and enhance the physiochemical and physic-mechanical properties [1].Chemical modification is the most widely explored modification method due to the non-destructive nature of a select few of the processes and potential increases in the functionality of the modified starch. Chemical modification is extensively implemented, but there is also a mounting significance in the physical modification of starch, especially in food applications. Physical modification of starch is accomplished by moisture, heat, shear, milling, microwave, or radiation and this modification has been gaining wider acceptance because of the absence of chemical reagents in the modified starch. Enzymatic modification, accomplished by adding enzyme preparations, has attracted great attention for its safe, environmentally friendly and highly controllable nature with few by-products under mild conditions. The enzyme preparations used for bioenzymatic modification are pullulanase, amylosucrase, transferase and branching enzyme, among which branching enzyme is the most widely used [2].

Modification of starch is an ongoing process which can design a huge market for many new functional and value added properties resulting from these modifications. The most important advantage of modification is that the starch is considered to be a natural material and a highly safe ingredient.

Starches have been modified by adopting various methods of modification over the last few decades in order to acquire the desired industrial applications. A number of review articles on the subject of starch modification are available. However, there has been an intense interest among the researchers in recent years to develop novel methods for starch modification. This article is designed to be a critical overview for the science community on how to employ different modification methods to obtain a modified starch with well-designed composition and morphology. The application of modified starch in food industry and its market in China are also analyzed in this paper.

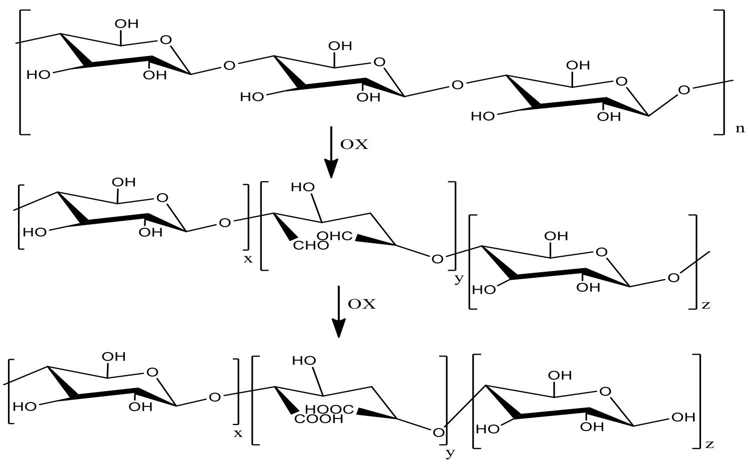
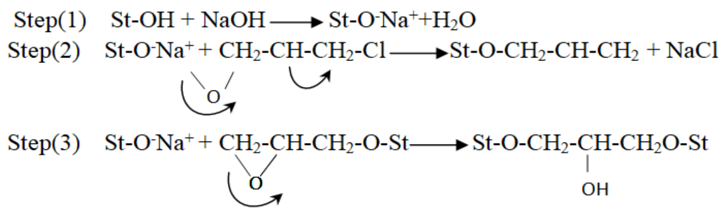
1. Preparation of modification starch

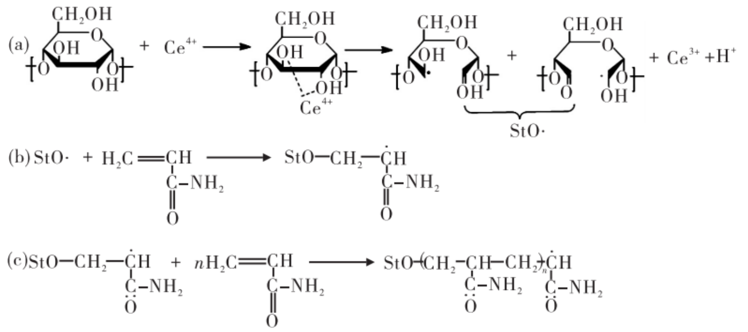
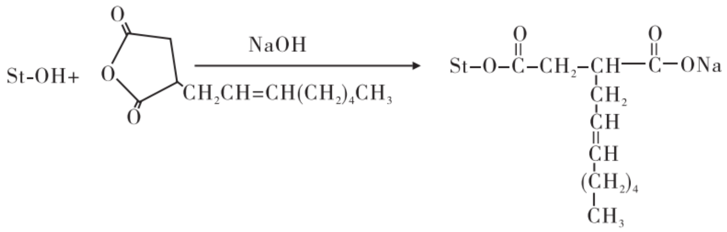
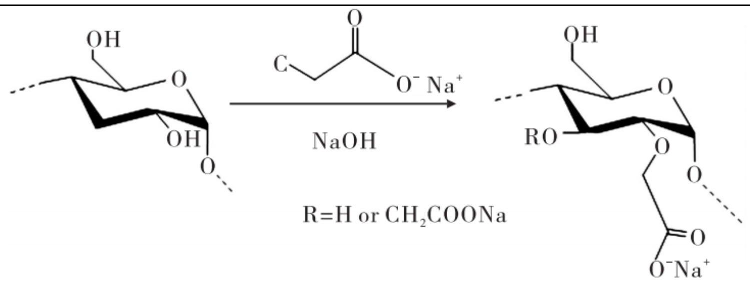
1.1 Chemical modification of starch

Chemical modified starch refers to the use of the active hydroxyl groups in the starch molecular structure to react with various chemical functional groups， generally including oxidation, cross-linking, grafting, esterification, etherification and composite modification [3]. By introducing new chemical functional groups and generating new chemical bonds or changing the size of starch molecules, the water solubility， adhesive property, viscoelasticity, and other properties can be improved， thereby extending its application. The summary of chemical modification is given in table 1.

Table 1

The summary of chemical modification

Type of chemical modification	reaction mechanism	Application
Oxidation	 (n=x+y+z) The semi-crystal structure of starch was destroyed by oxidation modification, and the uniform amorphous polymer matrix was obtained.	Widely used in papermaking, textile, construction and food industry.
Cross-linking	 The use of a cross-linking agent to form a diester bond or a diether bond between an alcoholic hydroxyl group on a starch molecule, introducing a new chemical bond, and staggering and connecting molecules in starch particles to make two or more starch molecules.	Widely used in adhesive production.

Grafting	 The initiation sites of graft copolymerization in starch molecules are mainly C_1-C_2 terminal group and C_2-C_3 ethylene glycol group.	Widely used in the fields of superabsorbent materials, degradable plastics and films, food and packaging.
Esterification	 Esterification is a modification method that improves the properties of starch by introducing new functional groups through the esterification reaction of hydroxyl groups in starch molecules with other substances.	Widely used In food, medicine, textile, papermaking and other fields.
Etherification	 Etherified starch is produced by replacing the alcoholic hydroxyl groups in starch with etherified compounds.	Can be used in food, textile and packaging production fields.

1.2 Physical modification of starch

Physical modification is an appealing process, as it does not involve the use of chemicals, which could contaminate the starch especially when the modified starch is to be utilized for food contact or in the biomedical industry. Moreover, such modification processes are relatively inexpensive compared to other techniques. Physical modification refers to the use of physical techniques such as thermal, force, electromagnetic fields to change the original morphology, structure and properties of starch granules, thus change the rheological properties and digestibility. During the physical modification process, the hydrogen bonds between starch molecules are broken, the crystalline region of starch is damaged, the ratio of amylose to amylopectin is changed, the molecular chains are broken or aggregated, and the molecules are rearranged. Starch modified by physical means can be classified into hydrothermal treatment [4], microwave treatment [5], ionizing radiation treatment [6], ultrasonic treatment [7], ball milling treatment [8], and extrusion treatment [9].

1.2.1 Hydrothermal modification of starch

Hydrothermal treatment is a technique that modifies starch while keeping the granular structure intact. This treatment requires the starch molecules to be kept in the mobile state above the glass transition temperature (Tg) and below the gelatinization temperature (Tgel) [10].Techniques for hydrothermal modification are annealing (ANN) and hydrothermal treatment (HMT). Both techniques require temperature and moisture level for the duration of the treatment to achieve modification [11]. While HMT requires low levels of moisture, typically carried out in excess water content of >65 % w/w [4].

1.2.2 Microwave modification of starch

Microwave, as a kind of non-ionizing radiation, has the ability to change the structural characteristics of materials during processing. This non-ionizing radiation may be applied to a wide range of materials such as ceramic and it components, metals, conductive materials or polymers. Microwave treatment enables saving time, energy and costs, but more importantly - it changes properties of the irradiated materials. For years the researchers from all over the world have reported on many studies focused on starch treated by microwaves [12]. Irradiation of starch with microwaves leads to changes in granule morphology and crystallinity, which in turn affects its functional properties, such as solubility, swelling powder, gelatinization or retrogradation [12].

Norbert Mollekopf et al. investigated potato starch (18% moisture, dry basis) with vacuum microwave power ratings of 600, 1,000, and 1,500 W at a reduced pressure of 5,000 Pa (absolute) and observed the drying rate. The results showed a sudden increase in the capacity, indicating a reduction in gelatinization temperature of starch. This may be attributed to the change in nature of starch from crystalline to amorphous as shown by X-ray diffractograms and to the cracks developed on the granule surface during treatment seen in the scanning electron microscope images. This modified starch can serve well in the paper and food industry [13].

Izabela Przetaczek-Rożnowska et al. discussed how microwave radiation and mineral additives affect selected physical and chemical properties of potato starch. The data obtained prove that the microwave radiation and saturation with minerals affect the rheology and thermal characteristics of the samples under examination. Both the degree and the vector of the transformation depend on the microwave output and the mineral component introduced. Generation of radicals depends on starch degradation at high temperature while microwaves affect the number of the radicals formed. Amounts of the heat-generated radicals depend on the microwave output and the type of metal ions introduced into the starch structure [5].

1.2.3 Ultrasound modification of starch

Ultrasonic treatment can degrade starch and other high molecular weights, which mainly depends on two aspects. On the one hand, ultrasonic treatment is used to accelerate the friction between solvent molecules and polymer molecules, which causes the C-C bond to break, a process known as mechanical bond breaking. On the other hand, due to the cavitation effect of ultrasonic waves, the free radicals of macromolecular substances undergo a redox reaction of free radicals macromolecules, which can generate a high-temperature and high-pressure environment, resulting in bond fracture. Cavitation is the formation of cavities filled with gas or vapor as the pressure decreases, and their collapse as soon as the pressure increases again.

When the cavitation bubbles generated by ultrasonic waves burst, high pressure changes will occur, and the nearby water layer will become a local high-speed jet, thus resulting shear force can damage the polymer chain and destroy the starch particles [14].In addition, the water in the cavitation bubbles will be partially decomposed into excited OH- and H +, which are released from the cavitation bubbles and react with molecules in the surrounding liquid to cause polymer destruction.

Some known applications of high power ultrasound in food processing include the following: extraction (release of plant material), emulsification, homogenization, crystallization (formation of smaller ice crystals in freezing),filtration, separation, viscosity alteration, defoaming, and extrusion [14].To further investigate how controlled ultrasound treatments affect the morphology, physical property and fine structure of rice starch granules, the starch suspended in water was treated with different ultrasonic power levels(150, 300, 450 and 600 W) at 25 °C for 20 min. XRD, FT-IR and Raman spectroscopy results indicated that ultrasound slightly destroyed the amorphous region of starch granules, while the A-type crystalline pattern remained unchanged. The result of chain length distributions showed that the fine structure of rice starch was not significantly changed by ultrasound treatment. SEM and particle size distribution demonstrated that ultrasound induced fissures and pores on the granule surface and elevated the homogeneity of granules, with minimum effect on the granule size. In addition, DSC and RVA results showed that after ultrasound treatments, the peak and breakdown viscosity increased, while the peak time, pasting temperature and gelatinisation enthalpy decreased [15].

1.4 Enzymatic modification of starch

The content of enzymatic modification of starch is based on the source and characteristics of starch, using different amylase to achieve the effect of changing the granular structure of the starch and the properties of the paste, so as to change the processing properties of the starch, improve the nutritional value, and broaden the application field of starch, increase the added value of raw starch. The enzymes used in enzymatic modification are pullulanase, amylosucrase, transferase and branching enzyme, among which branching enzyme modification is the most widely used [2,16,17,18]. The summary of enzymatic modification is shown in table 2.

Table 2

The summary of enzymatic modification

Reaction method	Reaction mechanism	Common enzyme agent
Liquefaction	Theα-1, 4-glycosidic bonds within the starch molecules are hydrolyzed in a random manner to produce linear and branched oligosaccharides with varying lengths.	Medium-temperature α-amylase High-temperature α-amylase
Saccharification	The non-reductive ends of α-1,4 glucan molecules such as starch and dextrin are continuously hydrolyzed by glucose or maltose.	**Glucoamylase** **β-amylase**
Debranch	The α-1,6 glycosidic bonds within the α-1,4 glucan molecule can be specifically hydrolyzed.	Pullulanase Isoamylase Amylopulanase
Transglycosidation	The process of transferring sugar groups from one glycoside to another.	Cyclodextrin glucosyltransferase α-glucosidase
Isomerization	The reaction of substrate molecules to form isomers under the action of catalyst	Glucose isomerase Starch branching enzyme Trehalose synthase

2. Application of modification starch in China food industry

Modified starch has the texture characteristics of many products, and is widely used in food industry as thickeners, stabilizers, gelling agents, adhesives, etc. Modified starch plays an important role in the food industry. It is widely used in flour products, bakery products, frozen products, beverages, dairy product, meat products and other food products. The commonly used modified starch in food processing is cross-linked esterification starch, hydroxypropyl starch, hydroxypropyl cross-linked starch, etherified starch, etc.

Colloid starch can improve the gel characteristics of jelly, making the mouth feel fuller and chew more elastic. When modified starch is added to the dough, the dough has better viscoelasticity, dough is easier to shape, and the texture of the noodles is delicate. Adding modified starch to daily food can increase the fiber content of food, which is beneficial for weight loss, prevention and treatment of hemorrhoids, and promotes calcium absorption. It can also be used for dietary therapy for patients with hyperlipidemia, hyperglycemia, and gallstones.

2.1 Application of modification starch in flour products

Compared with raw starch, pregelatinized starch has good dispersibility, high swelling degree and high viscosity. Modified starch plays an important role in food industry.

After adding pre-gelatinized starch, the dough formation time and stabilization time can be reduced to increase its degree of weakening, while reducing the stretch area and tensile force of the dough. We know that the viscoelasticity of pregelatinized starch is very good. When added in an appropriate amount, it can reduce the noodle breaking rate and cooking time, especially when 10% cassava phosphate cross-linked starch is added. Guo Yu [19] studied the effect of pre-gelatinized starch on frozen noodles, and found that because of the good freezing stability of pre-gelatinized starch, the hardness, elasticity and shear force of noodles increased with the increase of the added amount.

Li Yaoyao's [20]study results showed that the solubility, swelling power, light transmittance, and the content of rapidly digestible starch (RDS) of sweet potato starch lower than native starch and decreased with the increase of the initial water content after heat treatment. Heat treatment reduced the rate of starch retrogradation. Acid treatment combined with wet heat treatment significantly improved the solubility, SDS and RS content of sweet potato starch, and the RS content in Acid-HMT-4 reached 27.87%, which was higher than that of the heat treated samples.

2.2 Application of modification starch in bakery products

Frozen dough has some disadvantages, such as poor stability, small volume of finished products, short shelf life, etc. Because of its good water retention, the addition of esterified starch can effectively disperse free water and prevent the formation of large ice crystals on the gluten network damage. Adding a certain amount of modified starch into bread can delay the aging of the bread, especially the effect of hydroxypropyl starch has the most obvious effect, and it can also improve the texture of the bread. Appropriate amount of hydroxypropyl starch and acetate starch can make bread softer.

Min Dandan[21]investigated the effects of HMW- SD (high relative molecular weight spring-dextrin) and LMW-SD (low relative molecular weight spring-dextrin) addition on the dough properties by rapid viscosity analyzer (RVA), farino graph and extensor graph instruments. The results showed that both HMW-SD and LMW-SD had no significant effect on flour pasting temperature, and could decrease the peak viscosity, valley viscosity, final viscosity, recovery value and disintegration value of flour. Along with increasing two kinds of SD addition, the water absorption and formation time of dough increased, and the degree of weakening decreased.

2.3 Application of modification starch in beverages

Hydrophilic starch can form very stable and very small colloids under homogeneous and stirring conditions. It can be used as an emulsion stabilizer instead of gelatin, gum arabic, and casein in the food industry. Modified starch (such as pure gum) is used in the production of soft drinks, which has the effect of stabilizing and thickening, and can improve the taste. Such as the production of carbonated beverages, the addition of pure rubber can improve the lubricity and thickness of the beverage, and give the beverage gloss. In solid beverages, adding pre-gelatinized starch, maltodextrin, or esterified starch can significantly improve the rehydration of solid materials, increase the viscosity after preparation, and make the taste delicate.

Zhang Jiayan [22]investigated the effect of cross-linked starch on the stability of starchy turbid juice beverage, Cross-linked starch prepared by using different concentrations of cross-linking agent (6%, 8%, 10%, 12%, 14%) were applied to sweet potato juice beverages, and the turbidity, rheological properties, stability, zeta potential and centrifugal precipitation rate of the sweet potato juice beverage were determined. Maize beverage can be improved with 0.8% hydroxypropyl composite modified starch,0.8% acetylated modified starch, and hydroxypropyl octenyl succinic acid esterified starch, and lowered centrifugal sedimentation [23].

2.4 Application of modification starch in meat products

Using too much raw starch in meat products will make the product rough, inelastic, and poor in taste. The main reason is that starch is gelatinized at high temperature, aging will occur during low temperature storage, while modified starch has relatively low gelatinization. Temperature can gelatinize protein at the same time as protein denaturation, and absorb moisture lost by protein due to heat denaturation in time, making starch granules soft and elastic, and play a dual role of water retention and adhesion. Adding modified starch to meat products can make the meat products have a finer structure, a more compact structure, rich elasticity, and tenderness and taste.

The hardness change of 6% waxy corn starch meatballs was consistent with that of corn starch in different storage cycles, and the cohesiveness was lower than the others. The sensory quality of meatballs could also be improved. In addition, meatballs with waxy corn starch had the best freeze-thaw cycle stability in these different kinds of meatballs [24]. Modified starch can advance the retentiveness and emulsibility of hen surimi, and keep product's good texture and taste [25]

3. Market analysis of modification starch in China

The research and industrialization of modified starch in China started relatively late, and technical research began in the early 1980s，and it was not until the middle and late 1990s that the yield of modified starch began to increase rapidly. The number of modified starch production enterprises in China has been concentrated from more than 300 in the 1990s to about 50 currently. The production capacity of modified starch enterprises in Shandong province and Jilin province accounts for 25% and 23% of the total national production capacity, respectively. The province of Zhejiang, Liaoning, Guangxi, Hebei , and Jiangxi are also important production sites for modified starch. In terms of application fields, 57% of the country's total modified starch is used in the paper, 19% in food, 10% in textile, 3% in chemicals, 3% in pharmaceutical, 4% in packaging and 4% in other industries. Generally speaking, the amount of modified starch used in paper is the largest, and edible modified starch is in second place for its widely application.

According to the "2019-2023 China's Modified Starch Industry Development Trend and Development Prospect Forecast Report" released by Xin-si-jie industry research center, China produced 1.71 million tons modified starch in 2017 , with an increase of 15.3% year-on-year. Because of the decline in the price of raw materials, China's modified starch industry has started to operate adequately, with substantial increase in output and improvement in market prosperity. From the perspective of modified starch production areas in 2017, as shown in table 3, Shandong province produced 620,000 tons modified starch, accounting for 36%; Guangxi province produced 310,000 tons modified starch, accounting for 18%; Zhejiang province produced 210,000 tons modified starch, accounting for 12%; Jiangxi province produced 180,000 tons modified starch, accounting for 11%; Guangdong province produced 130,000 tons modified starch, accounting for 7%. The total output of modified starch in the five major provinces accounts for 84%, and modified starch industry in China has high regional concentration. In 2017, as shown in figure 1, the varieties of modified starch products produced in China with an output more than 100,000 tons included: oxidized starch with a yield of 310,000 tons; compound modified starch with a yield of 230,000 tons; acetate starch with a yield of 230,000 tons; Cationic starch with a yield of 200,000 tons; Phosphate starch with a yield of 120,000 tons. The total output of these five type products accounted for 64% of the total output of the modified starch industry, which is the leading product type in the market.

Table3

Production of modified starch in China, 2017

Province	Yield	Proportion
Shandong	620000 tons	36%
Guangxi	310000 tons	18%
Zhejiang	210000 tons	12%
Jiangxi	180000 tons	11%
Guangdong	130000 tons	7%
Other Provinces	260000 tons	16%

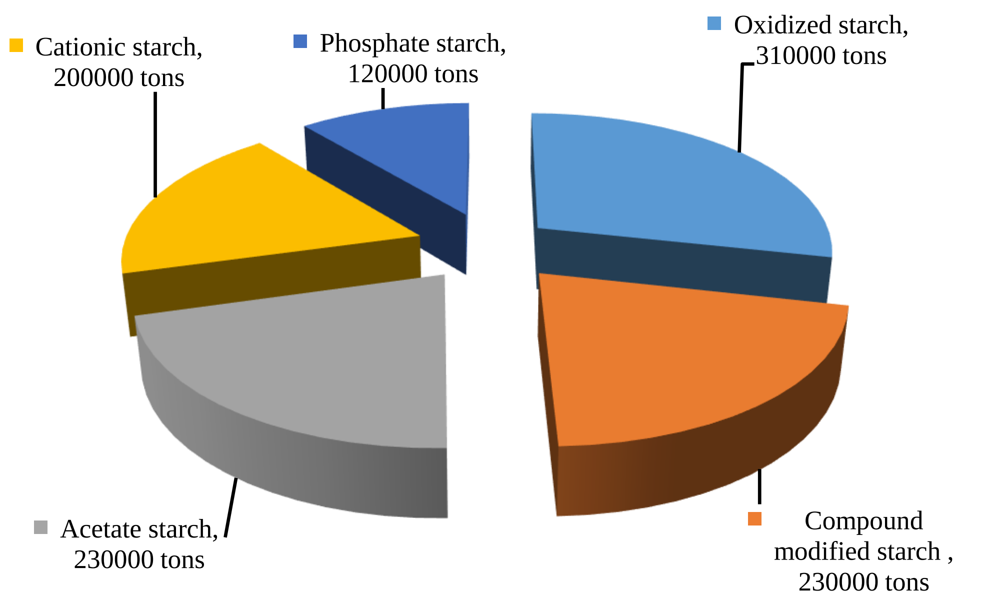


Fig 1. The main types modified starch in China,2017

At present, there are more than a dozen domestic manufacturers of chemically modified starches only used in food with total annual production capacity sales exceeded 150,000 tons. The raw materials of chemically modified edible starch are mainly corn starch, tapioca starch, potato starch and a small amount of waxy corn starch. And these edible starches are mainly used in instant noodles, meat products, frozen foods, sauces and condiments. Tianjin Dingfeng Starch Development Co., Ltd., Fujian Sanming Beststar Starch Co., Ltd. and Jilin Siping Dida Food Co., Ltd. have the largest production capacity, with an estimated output of 120,000 tons. Changchun Dacheng Industrial Group Company Ltd.，Huanglong Food Industry Co., Ltd. Zhucheng Xingmao Corn Developing Co.,Ltd. and other large starch processing enterprise mainly produce edible modified starch with an estimated output of 120,000 tons that are used in meat products and sauces. Physically modified pre-gelatinized starch and biologically modified dextrin, cyclodextrin and other modified starches with annual production and sales volume of 120,000 tons are mainly used in bakery products, instant food, and Medicine and health products. In addition, China imports 50,000 tons of edible modified starch every year. Therefore, it is conservatively estimated that the annual national demands for various edible modified starches are over 400,000 tons.

The average annual per capita consumption of starch in the Unites States is higher than 90kg, Japan is higher than 30kg, EU countries are higher than 25kg, Thailand is 37kg, and China is 8.5kg. And the average annual per capita consumption of modified starch is about 0.8kg in the world, about 10kg in the United States,3.7kg in Japan, 3.1kg in European Union and 1.2kg in China, which exceeds the annual per capita consumption of the world, but far lower than the average annual consumption of Americans. As China's economy grows and the scale of industrial products continues to expand, the demand of modified starch will continue to increase. Modified starch industry is still a developing industry with a broad prospect in China.

4. Conclusion

With the development of economic globalization and the continuous improvement of people's requirements for food safety, taste and flavor, the market prospect of edible modified starch is broad. Though various modification methods are desirable, it is undeniable that the current modification methods still have shortcomings. This requires experts and scholars to continuously explore in order to find better modification methods. Due to its safety and non-toxicity, physical modification methods will be the future research trend of starch modification.

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METHOD OF TEMPERATURE CONTROL AND FORCED COOLING OF THE BARREL OF AN ARTILLERY GUN USING A THERMOELECTRIC GENERATOR

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Abstract

A method of controlling the temperature of an artillery barrel and, if necessary, its forced cooling due to the reverse operation of a thermoelectric generator based on the use of Peltier elements, which is mounted on the barrel of an artillery gun, is proposed.