PRODUCTION AND USE OF MODIFIED STARCH AND STARCH DERIVATIVES IN CHINA

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ABSTRACT

Due to rapid economic development and increasing market demand after the 1980s, research on the production of modified starch and starch derivatives developed very quickly in China. This paper describes the present situation and the development potential of modified starch, starch sweeteners, saccharide alcohol, degradable starch plastics, oligo-saccharides, and lactic acid made from cassava starch in China, including the production and the use of the most popular products. Progress made and future planning for the development of these products will also be discussed.

I. Industrial Development of Starch in China

In recent years the production and application of starch, modified starch and starch derivatives developed very fast, in line with the overall development of the Chinese economy (**Table 1**).

The development of starch derivatives depends mainly on the rapid development of the starch industry. From 1989 to 1998, total production of Chinese starch increased about 2.7 times, from 1.12 to nearly 3 million tonnes. The scale of the starch factories has also increased considerably, while their numbers have decreased (**Table 2**).

Production of cassava starch showed a similar trend. Guangxi is the largest cassava producing province in China, with cassava production there accounting for more than 50% of total national production. The cassava planted area, total fresh cassava root production and starch output are shown in **Table 3.**

As indicated in **Table 3**, from 1989 to 1998 the cassava planted area increased 24%, the yield 72%, fresh root production 113%, and cassava starch production 170%.

II. Modified Starch and its Applications in China

1. The present situation of Chinese modified starch

Recently, the modified starch industry in China has developed very rapidly (see **Table 1**); modified starch production in 1998 was 7.5 times greater than in 1989. This has been the result of the following factors:

1. Production of starch in China has increased very rapidly, so the starch factories had to search for new markets.
2. The demand for modified starch from various industries increased very quickly.
3. With the opening up and reform of the Chinese scientific system, a more creative technological development framework was established, resulting in new progress being made in research, development and utilization of modified starch.
4. As new foreign technologies were introduced, demand for modified starch

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increased.

5. New enterprises have high quality requirements, so demand for modified starch with high added value increased.

Table 1. Production (in '000 t) of starch, modified starch, crystal glucose and liquid glucose in China from 1989 to 1998.

	Starch	Modified starch	Crystal glucose	Liquid glucose
1989	1,117	21.6	109.4	144.5
1992	1,200	34.8	134.0	70.8
1993	1,600	54.0	149.0	85.0
1994	2,470	59.8	198.8	138.3
1995	2,600	80.9	220.9	108.1
1996	2,645	73.4	196.4	168.6
1997	2,589	91.3	145.8	170.1
1998	2,978	162.0	157.4	256.0
% increase since 1989	167	650	44	77

Table 2. The scale of the starch industry in China.

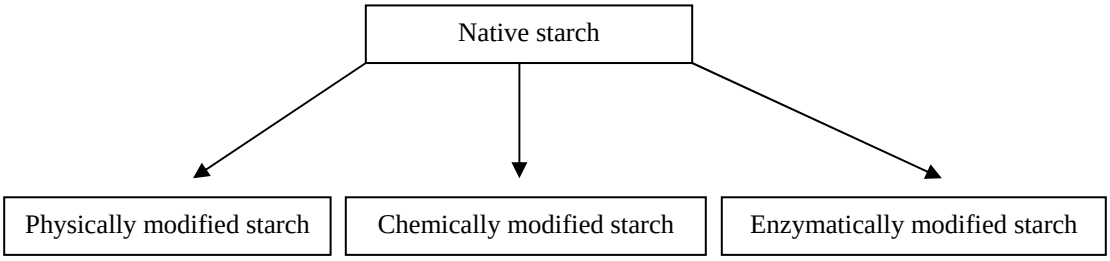
	1989	1993	998
Numbers of starch factories	388	243	157
Total annual capacity (million tonnes)	1,167	1,520	2,978
Average capacity (t/year)	2900	6255	
Number of factories of >100,000 t/year capacity	14	37	67
Number of factories of >200,000 t/year capacity	0	0	2

Table 3. Cassava planted area, total fresh root production and starch production from 1989 to 1998 in Guangxi province of China.

Year	Planted area ('000 ha)	Yield (t/ha)	Fresh root production ('000 t)	Starch production ('000 t)
1989	210.6	8.24	1,734.9	
1990	219.3	8.82	1,934.5	122.5
1991	221.5	9.00	1,993.8	168.2
1992	213.3	9.95	2,121.4	191.0
1993	219.7	11.43	2,511.7	230.0
1994	229.6	12.15	2,789.3	258.2
1995	272.9	13.68	3,733.5	273.0
1996	288.9	13.41	3,873.7	321.2
1997	273.3	14.22	3,886.1	385.0
1998	260.5	14.21	3,701.6	330.3

2. Types of Chinese modified starch

Modified starch can be divided into three main groups according to the modification process utilized. These three groups are further subdivided according to processes and products as shown in **Figure 1** and **Table 4**.



1. Pyrodextrin
   -white dextrin
   -yellow dextrin
   -soluble dextrin
2. Pregelatinized starch
   -α-starch
3. Fractionated starch
   -amylose
   -amylo-pectin

1. Oxidized starch
2. Esterified starch
3. Etherified starch
4. Graft co-polymerized starch

1. Enzyme degradation starch
   -maltodextrin
   -cyclodextrin

Figure 1. Modified starch processing technologies and products.

3. Current and future applications of modified starch

Chinese modified starch has a very good development prospect (**Table 5**). The paper and cardboard industry of China in 1996 consumed 300 thousand tonnes. Moreover, for the paper making industry in China, unlike in most other countries, wood pulp is a minor raw material while the main raw materials are straw pulp and bagasse. The fiber of straw pulp is shorter and is of lower strength so it needs more modified starch. The proportion of modified starch used in the American paper making industry is 2%. It is estimated that the consumption of modified starch in China's paper making industry will be above 700,000 tonnes. Other industries, such as textile, food, medicine and materials used for construction and for environmental protection, consume also a lot of modified starch.

4. Advantages and development prospects of modified cassava starch

Cassava starch is characterized by low pasting temperature, high viscosity and easy enzymatic hydrolysis. Pregelatinized starch and cationic starch made from cassava starch has special quality advantages.

Table 4. Principal modified starch products in China, their production process and application.

Product	Production process	Application
Yellow dextrin	Heat for roasting	Casting, construction materials
White dextrin	Heat for roasting	Binding agent in medicines
Pregelatinized starch	Dried and milled by drum	Feed, casting, construction materials
Oxidized starch	Oxidized by oxidizing agent	Binding agent for cardboard, textile, food
Acid- hydrolyzed starch	Hydrolyzed by acid	Food, sizing for textile, paper making
Starch acetate	Esterification by acetic acid	Paper making, textile, casting, food, snack food
Cationic starch	Etherification by trimethyl amine	Paper pulp additive coating
Complex modified starch		Paper pulp additive coating
Carboxymethyl starch	Etherification by chloroacetic acid	Lubricant for oil drilling medicine, construction materials
Hydroxy-propyl starch		Food, candy
Cross-linked starch		Food, medicine, textile, chemical industry
Graft co-polymerized starch	Graft co-polymerized by acrylo-nitrile	High water-absorbent materials, such as disposable diapers, female napkins, textile sizing material

Table 5. The current situation and future markets for Chinese modified starch ('000 tonnes).

Application of modified starch products	Current production	Current domestic market volume	Expected future domestic market volume
1. Textile	50	100	120
2. Paper	40	350	700
3. Food	3	200	400
4. Medicine	10	20	40
5. Agriculture	-	100	200
6. Casting	-	37	75
7. Animal feed	-	100	200
8. Construction materials	-	50	80
9. For oil drilling	-	30	50
10. For fine chemicals	-	10	30
Total	**103**	**997**	**1895**

1. *Pre-gelatinized starch*

About 10,000 tonnes of pregelatinized starch are being produced annually in Guangxi. The quality of pregelatinized starch from cassava starch is better than from maize starch, resulting in good market demand and a 10% higher price compared with that made from maize starch.

2. *Cationic starch*

Approximately 10,000 tonnes of tri-methyl amine cationic starch are being produced annually in Guangxi. The cationic starch made from cassava starch has a low viscosity, and a high degree of substitution, making it especially suitable for the sizing and coating of high-speed paper making machines. Recently, the Guangxi Nanning Cassava Technical Development Center in co-operation with the Mingyang Starch Factory, succeeded in the development of a solid process for cationic starch production. The degree of substitution of the product is higher than that of the original wet process, there is no pollution, and the production cost is 20% lower, giving it a strong competitive advantage.

Besides, Guangxi also produces oxidized starch, starch acetate, amphoteric starch, yellow dextrin, starch phosphate etc.

III. Starch-based Sweeteners

China has a 3000 year history in the production of sweeteners made from starch. Ancient China was the first to invent the production of sugar from raw materials of plants, especially the production of maltose from rice starch. Starch-based sweetener production started with the manufacture of malt syrup. At present, China produces several kinds of starch-based sweeteners as indicated below:

1. Glucose syrup

After starch is hydrolyzed either by enzymes or acid, malt syrup is obtained, which is divided into high-DE, medium-DE and low-DE syrups according to their different DE-values as shown in **Table 6**.

2. Maltose

Table 7 shows several types of maltose syrups produced in China.

Fresh wheat bran contains a considerable amount of β-glucosidase, an enzyme which can decompose starch molecules to produce maltose; this technology is used for producing maltose syrup in China.

3. Glucose

Table 8 lists the principle types, characteristics and uses of glucose produced in China. So far, China has mainly four production technologies of glucose, as indicated in **Table 9**.

4. Conversion and isomerization sweeteners

In the Chinese market, we have four types of fructose-glucose products, as shown in **Table 10**.

Table 6. Glucose syrups of different DE values.

Product	DE value[1)]	Degree of hydrolys	Main ingredients	Product form	Useage
Malt dextrin	10-15	low	low molecule dextrin malt polymaltose iso-maltose glucose	powder liquid	milk powder, substitute solid drink, oral soluble dosage food
Malt syrup	25-35	medium	maltose glucose maltotriose	liquid 70-80^{o} Bx	confectionery
Glucose syrup	42-55	medium	glucose maltose	liquid 70-84^{o} Bx	confectionery
Liquid glucose	75-94	high	glucose maltose malt poly-saccharide salt	liquid 70^{o} Bx	syrup, food, anti-freeze, sorbitol
Mother liquid of glucose	75-80	high		liquid 60^{o} Bx	caramel-coloring, anti-freeze, sorbitol

[1)]measure of the ratio of reduceable saccharide over total saccharide.

Table 7. Types and characteristics of maltose produced in China

Product	Maltose content (%)	Characteristics	Usage
Maltose	<50	liquid, sweet, sensitive to moisture	daily food
High-maltose syrup	50-75	liquid, sweet, sensitive to moisture	special food
Super-high-maltose syrup	75-95	liquid, sweet	special food
Crystal maltose	>90	strong water absorption	special food
Crystal anhydrous maltose	>90	highly soluble	dehydrating agent
High purity maltose	>99	high purity	injection solution

Table 8. Main types of glucose in the Chinese market.

Product	Specification	Price (Yuan/t)	Usage	1996 Production('000 t)
Medical anhydrous glucose	China Pharma-copoeia 1995	5200	injectable solution	20
Medical glucose	China Pharma-copoeia 1995	4500	injectable solution	120
Oral glucose	China Pharma-copoeia 1995	4200	food; sorbitol for production of Vitamin C	50
Industrial glucose	Industrial grade	3900	general industrial use sorbitol production	40
Industrial total powder sugar	DE 90	3000	industrial use	20

Table 9. China's glucose production technology.

Production process	Main procedure						
	Mixing	Acid liquification	Enzymatic liquification	Acid sacchari-fication	Enzymatic sacchari-fication	Decoloration and filtering	Concen-tration
Acid process	✓	✓		✓		✓	✓
Enzymatic process	✓		✓		✓	✓	✓
Acid-enzymatic process	✓	✓			✓	✓	✓
Enzymatic acid process	✓		✓	✓		✓	✓

Table 10. Various fructose-glucose products produced in China.

Product name	Viscosity	Fructose content (%)	Sweetness compared to sucrose	Usage
Fructose-glucose syrup	70 Bx	42	0.9	food
High-fructose syrup	75 Bx	55	1.1	soft drinks
High purity fructose syrup	80 Bx	90	1.6	special drinks
Crystaline fructose	solid	>98	1.8	special food/drinks

5. Oligo-saccharides

1. Oligo-iso-maltose

The enzyme transglucosidase (TG) interacts with maltose and glucose, resulting in an inversion reaction, which produces iso-maltose, panose, iso-malto-triose, etc.

Oligo-iso-maltose can not be digested and fermented by yeast, but it can be used by *Bifdobacterium bifidium* to enhance its reproduction; this is good for the intestinal bacterial colonies and elevates the proportion of favorable colonies resulting in a more healthy functioning of the digestive system.

This kind of oligo-iso-maltose has been produced in the starch industry; the procedure is as follows: 1) liquify starch milk with the use of α-amylase; 2) saccharify with the combination of β-amylase and glucose group invertase; β-amylase yields maltose, invertase yields iso-maltose and panose through the linking of α-1,6 link yields glucose and maltose. 3) refine and concentrate to 75%. A colorless, transparent solution is obtained which contains the following substances (dry weight basis): 16.9% iso-maltose, 12.5% panose, 3.4% iso-malto-triose, 6.7% maltose and 40.5% glucose. The content of iso-

maltose can be elevated to as high as 85% with resin chromatography while glucose is removed.

2. *Oligo-fructose*

Oligo-fructose is one of the edible enhancement and function foods. Because the bio-reactions of oligo-fructose are almost the same as short-link soluble cellulose, it can be used as a source of edible cellulose. In China, oligo-fructose is now produced on an industrial scale and marketed. The first production line of 3000 t/year was set up in Yunnan province. Researchers of Guangxi University used the immobile enzyme to successfully produce oligo-fructose; a 1000 t/year production line has been built.

Besides oligo-iso-maltose and oligo-fructose, new types of oligo-saccharides such as oligo-saccharide, oligo-mannose, etc. have also been researched.

IV. Hydrogenated Sweeteners

1. Sorbitol

Sorbitol is the main raw material for production of vitamin C. It is also a favored sweetener for diabetic patients and can function as an effective moisture absorbent; it absorbs water strongly, so it has been used widely in the production of toothpaste and cosmetics.

The present diversity and characteristics of various sorbitol-based products in China are shown in **Table 11**.

2. Mannitol

Mannitol is the only polylol which is solid under normal conditions. It is a favored medicine for diuretic and dehydration problems. Mannitol is one of the essential medicines in all hospitals. In industry, mannitol is the main raw material for producing polyester and polyether, which in turn are essential raw materials for production of foamed plastic.

At present, mannitol in China's market is mainly derived from seaweed with an annual production capacity of 8,000 tonnes. The cost is high and the production process is out of date. In recent years we have developed a new technology, which uses either sucrose or glucose to manufacture mannitol, and we have begun industrial production. Hydrolysis of sucrose can yield the inversion sugars fructose and glucose, which in turn produce 25% mannitol and 75% sorbitol, respectively, when hydrogenated.

After special isomerization, part of the glucose can be inverted to mannose and fructose, which can yield 42% mannitol and 58% sorbitol when hydrogenated.

Recently, research on the adoption of a simulated fluid bed to separate mannitol and sorbitol has been successful.

3. Maltol

Maltol is a new type of dietary supplement, produced by hydrogenating maltose. Maltol is a transparent, colorless or lightly yellow solution.

Maltol is non-fermentable, so it may be used to prevent dental decay; it is low in calories, so may be used to prevent obesity; it has good flavor with a sweetness of 90% of that of sucrose; it has high viscosity and may be used as a thickener; moreover, it has high heat and acid resistance, good moisture retention, so may be used for moisture adjustment;

it hardly decomposes by insulin, so it can be used as food for diabetics. About 10,000 tonnes are produced annually in China, mainly using cassava starch.

Table 11. Sorbitol-based products and applications in China's market.

Characteristic	For vitamin C production	For detergent and cosmetics production	For toothpaste production	Injectable Sorbito l	Hard crystal sorbitol	Solid sorbitol	Icy sorbitol
Appearance	colorless and transparent solution	colorless and transparent solution	colorless and transparent solution	white powder	white hard granules	white soft granules	icy
Degree of substitution	45-51	67-73	69-71	99.5	99.5	99.0	98.0
Specific weight (gm/ml)	1.228	1.280-1.316	> 1.285				
Refractive index	1.42	> 1.460	1.459-1.461				
Reducing sugar (%)	> 0.2	0.63	>0.5	0.2	0.3	0.2	0.2
Main usage	raw material for vitamin C	food, cosmetics and detergents	toothpaste	medical injection solution	food gum	chemicals and food	chemicals and food
Relative price[1)]	1.1	1.0	1.0	3.5	2.8	1.6	1.3

[1)]Calculated according to the current market price on a dry weight basis.

V. Degradable Plastics

China proclaimed a law which prohibits the pollution of the environment with disposable plastic packing materials. The annual production of plastic in China is nearly 4 million tonnes. The consumption of plastic is more than 1.4 million tonnes in the packing industry. The potential market for degradable plastic is very big.

So far, domestically produced degradable plastics includes the following two types:

1. Bio-degradable starch resin

By adding starch or modified starch to polyvinyl hydrocarbons, particles of bio-degradable starch are produced. These can be further manufactured into degradable plastic bags, disposable plates, forks and spoons, degradable products for medical care, etc.

2. Bio-and photo-degradable starch plastics

These are mainly used for plastic mulching in agriculture, packing film for food and groceries, packing film for industrial products. These plastics are not only decomposed by bio-degradation, but also by photo-degradation.

Presently, China has more than 50 manufacturers, with an annual production capacity of 100,000 tonnes. Among them, about ten factories introduced production technologies from abroad. But, these degradable plastics are mainly starch plastics which require 7-40% of starch as filling. The base materials are polyvinyl and polystyrene plastics, which are not fully degradable plastics. The plastic mulch produced by this

process is difficult for the farmers to use, because this starch-based plastic has low water resistance, it is rather thick and of high cost. Further research is needed to improve this product.

Recently, some local companies have developed a technology for producing fast-food boxes using starch and plant fiber as raw materials. The technology uses maize cobs, rice bran and sweetpotato as raw materials to manufacture bowls, discs, boxes, spoons etc.. Their hardness and brightness are nearly the same as ceramic. Once used they can be recycled as feed and fertilizer, and will thus not pollute the environment and be a source of waste.

VI. Organic Acids

Besides citric acid and acetic acid, two kinds of organic acids using starch as the raw material have been developed successfully.

1. Lactic acid

Lactic acid is an important organic acid; it can be used in the production of beer for adjustment of the pH of the malt, in the pharmaceutical industries and in the production of cosmetics, fine chemicals, tobacco, food and silk. Stearoyl lactate sodium and calcium salts are the most important lactate salts, being a general food additive used throughout the world. Monoglyceride lactate ester is an emulsifier, suitable for producing biscuits, meats, milk products and fruit jams, as well as pectin. In recent years, researchers have developed L-lactic acid, i.e. poly-lactic acid, which is an ideal fully-degradable plastic material, and easier to be produced industrially. Therefore, research on lactic acid in China has developed very fast. Presently, a 10,000 t/year L-lactic acid production line is under construction.

2. Itaconic acid

Itaconic acid and its esters are very good additives and raw materials for the manufacturing of synthetic resins, plastic, rubber, ion-exchange resins, surfactants, anti-rust agents, etc. The enzyme for producing itaconic acid has been produced in Yunnan and Hubei provinces. These factories succeeded in producing itaconic acid from native cassava starch. So far, China has produced more than 5,000 tonnes of itaconic acid.

VII. The Effect of Value-adding of Starch

Cassava is a low-value product. When we produce only native starch, farmers and manufacturers can only get a low income. The increase of product value and the average increase of added value for cassava-based products are shown in **Table 12**. It is based on recent market prices: 600 Yuan/t of dry cassava chips, 1800 Yuan/t of native starch.

As seen in **Table 12**, further processing of native starch into modified starch and its derived products plays a very important role in increasing the value of cassava-based products.

Table 12 The effect of further processing on the added value of cassava-based products.

Product	Consumption of cassava dry chips (t/t)	Cost of processing (Yuan/t)	Sales price (Yuan/t)	Product value/ cassava value	Income increase per tonne of cassava (Yuan/t)
Native starch	1.5	400	1,800	2.00	333
Low-grade modified starch	1.5	800	3,50	3.89	1,200
High-grade modified starch	1.5	1,600	6000	6.67	2,333
Special modified starch	1.5	3,000	12,000	13.33	5,400
Liquid glucose	1.5	1,000	2,700	3.00	533
Crystal glucose	1.5	1,800	5,000	5.5	1,533
High purity maltose	1.5	1,100	4,500	5.00	1,677
Sorbitol 70%	1.3	1,400	4.200	5.38	1,554
Crystal sorbitol	2.0	3,000	14,000	11.67	4,900
Mannitol	2.0	3,000	12,000	10.07	3,900
Maltol 70%	1.5	1,600	6,500	7.22	2,667

VIII. Opportunities and Challenges

Cassava-based modified starch and its derivatives face a great challenge from the competition of maize starch. In 1998, maize starch production was 2.75 million tonnes, accounting for 92% of total starch production in China. Cassava starch production was only 286,000 tonnes, or 9.6% of total starch. The average yield of maize in Jilin province of China has reached above 9 t/ha, while that of dried cassava chips is only 6 t/ha in Guangxi. The scale of maize starch factories in China is larger than that of cassava starch factories. Factories with an annual capacity of one million tonnes of maize starch have been set up in northeastern areas, such as Shandong province of China, while the biggest cassava starch factory can produce only 30,000 tonnes per year. Even though the Guangxi Mingyang Starch Factory is still the biggest modified starch manufacturer in China, it must confront strong competition from maize starch manufacturers.

IX. Proposal

1. Production of modified starch and starch derivatives hold great significance for increasing the value of cassava products, and for improving the economic benefits in cassava production areas. Therefore, strong emphasis should be placed on research and development of modified starch and starch derivatives, in order to develop the cassava economy.
2. For the sake of enhancing the competition of cassava starch and starch derivatives, it is very important to continuously increase cassava yields, so it can compete with maize. Consequently, it is equally important to breed and select good varieties of cassava and to improve the cassava cultivation methods.

3. It is very important to strengthen the collaboration between agriculture and industry, to emphasize the linkage between agricultural and industrial development and research, which are all important factors for developing the cassava economy.