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MODIFICATION OF CASSAVA STARCH

Summary

Cassava (*Manihot esculenta* Crantz) is an important food crop in many tropical countries in Africa, South America and Asia. However, in Thailand, this crop has been well recognized as more than a subsistence crop. It is important commercially as the raw material for a large and complex industrial system that has a significant impact to the country's economics. The roots of this crop contain high a starch content and approximately half of the total roots produced (20 million tons) are used for the starch industry. Cassava starch has many remarkable characteristics including high paste viscosity, high paste clarity and high freeze-thaw stability, which are advantageous to many industries. In particular, the native starch with high purity can be readily modified by physical, chemical and enzyme process to many diversified products to improve the starch functionality and, consequently, encourage more industrial application. This paper aims to describe the unique modification of cassava starch produced at the industrial level in Thailand with respect to technological aspect and product quality.

Introduction

Cassava (*Manihot esculenta*) is an important food crop in tropical countries such as Brazil, Nigeria, Indonesia and Thailand. The roots of cassava are rich in starch and consumed as human food or animal feed. Only a small amount of roots is converted into other industrial products. Thailand is the only country where most of the roots are processed into chips, pellets and starch. Against the total world root production of 175 million tons (Table 1), Thailand produces about 18 million tons. Ten million tons are converted to starch, producing approximately 2 million tons starch/year, and the rest to chips and pellets. As the leader of cassava starch production (Figure 1), Thailand is also the only country where modified starches from cassava are produced in large

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scale. Around 50% of the starch (native and modified) are employed locally in the food and non-food industries, the remainder is exported. This commodity generates significant revenue for the country (Table 2) and the future is promising. Growth of the starch industry sector is, in part, a substantial driving force that has generated large-scale cassava planting for commercial purpose in Thailand. From the experience in Thailand, this paper describes the unique modification of cassava starch.

Table 1

World production of cassava roots in 2001.

Country	Volume (million tons)
Nigeria	33,854,000
Brazil	24,481,356
Thailand	18,283,000
Congo	15,959,000
Indonesia	15,800,000
Ghana	7,845,440
Tanzania	5,757,968
India	5,800,000
Mozambique	5,361,974
China	3,750,900
Other	38,723,751
Total	175,617,389

Source: [1].

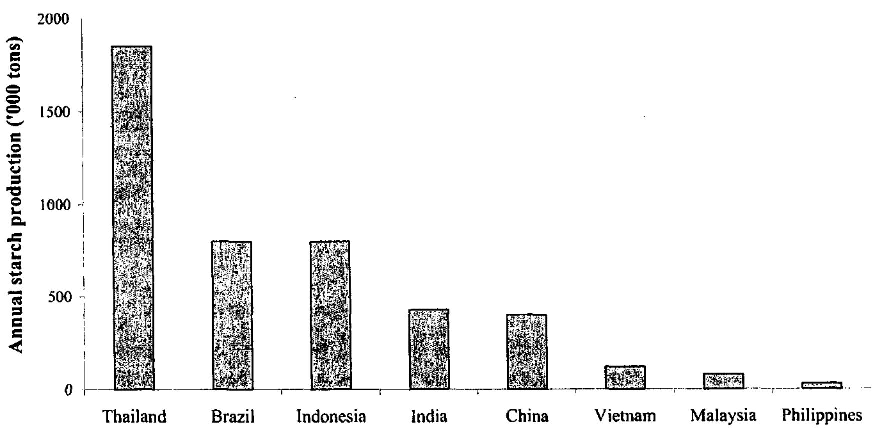


Fig. 1. Cassava starch production in various countries.
Source: [3, 6].

Table 2

Export volume and value of Thai cassava starch.

Cassava starch	Volume (tons)			Value (million Baht*)		
	1999	2000	2001	1999	2000	2001
Native starch	699,175	1,044,087	724,393	4,817.43	6,148.86	5,241.89
Modified starch	331,604	365,571	344,738	5,606.95	6,257.29	6,063.75
Sago pearl	15,508	15,470	14,455	164.64	150.14	150.49
Total	1,046,287	1,425,128	1,083,586	10,588.84	12,556.29	11,456.13

*1 USD = 45 Baht
Source: [6].

Modification

Native Starch

The term "native starch" is defined as the product extracted from cassava roots, which is called "starch" – not "flour" by the modern separation process [4]. The standard for starch content in native cassava starches is not less than 96% (dry basis). For modification purposes, native starch of the specification summarized in Table 3 is used.

Table 3

Standard Specification of native cassava starch for modification purpose

Property	Specification
Moisture content (% maximum)	13 %
Ash (% maximum)	0.2 %
Fiber (cm^3 per 50g wet starch, maximum)	0.2
pH	5.0 to 7.0
Whiteness (Kett scale, minimum)	90
Viscosity (Barbender Unit, minimum)	600
Sulfur dioxide content (ppm, maximum)	100
Residue (ppm, maximum)	300

Modification of cassava starch in Thailand

The starch modification sector is one of the most important industries in Thailand. This industry began as the production technology of cassava starch developed from small- to large-scale and starch quality improved. One of the main driving forces was the high market demand; both domestically and internationally, for the diversified cassava-based products produced by the modification technology. The modified cassava starch and derivatives currently produced at the commercial scale can be categorized based on the technology approach as summarized in Figure 2.

Physical modification

This group of modified starches involves the treatment of cassava starch by physical means such as shear force, blending and thermal treatment. A combination of heat treatment and shear force has been used to produce many extruded products and snacks. The well-known products for cassava starch are alpha starch and heat-moisture treated starch obtained by a thermal process.

Alpha starch

Alpha starch or pregelatinized starch began to be a major industry in the late 1980's during the eel-farming boom when farms required a cold water soluble binder. Alpha starch from cassava gives specific properties such as high transparency, absence of foreign odors, good color carrier properties and high viscosity. The total production capacity for all alpha starch in Thailand is about 50,000 tons/year. The manufacturing process involves drying of 30–40% (dry solid) cassava starch slurry on a roller drum drier heated to 160–170°C by direct steam (Figure 3). Presently alpha starch is produced as food grade, and is used in many industries (Table 4).

Table 4

Specification of food-grade alpha starch produced from Thai cassava starch

Property	Specification
Moisture content (% maximum)	13
pH	4.5-7.0
Viscosity (Barbender Unit*, minimum)	800**
Ash (% maximum)	0.2
Pulp (cm^3, maximum)	0.2
Cyanide (ppm)	nil
Residues (ppm, maximum)	300
Whiteness (Kett scale, minimum)	90
Sulfur dioxide content (ppm, maximum)	30

*Using 6% starch (dry basis)

**Upon the customer's request and application

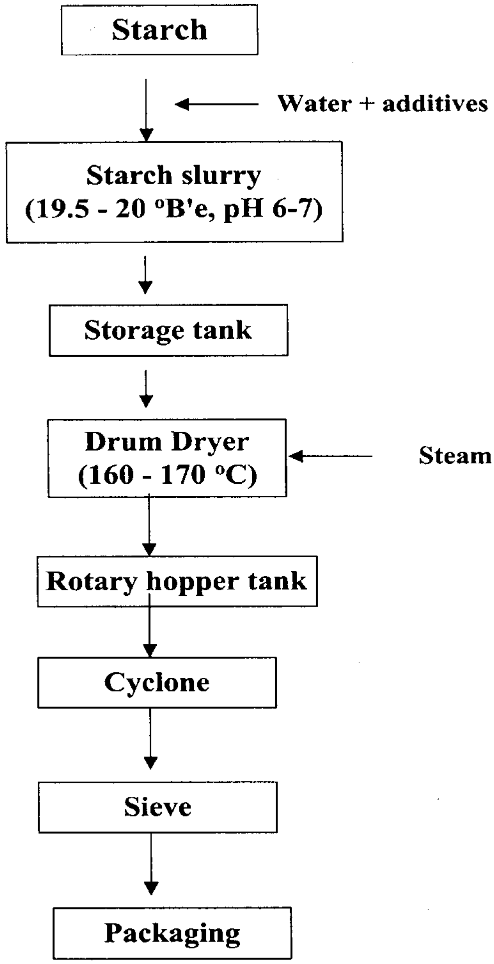


Fig. 3. Alpha starch process.

Heat-moisture treated starch

Heat-moisture treated starch is the oldest physically modified cassava starch. It had been manufactured in early time since the settling pond was used for separation of starch cake. The collected starch cake from the pond containing about 50% moisture content was used as the starting material for making heat-moisture treated starch. After being dried overnight on a hot floor (50 to 80°C), the dried starch was ground, sieved and packed. The product was accepted as flour with special name called *Tao starch*, not cassava starch. This starch is preferentially used as the product improver for many Thai desserts and food recipes replacing the traditional starch extracted from *Tacca* *pinnatifida* (Tao Yai Mom) tubers, which is rare and more expensive than cassava starch. At present, all starch factories operate the modern separation technique instead of settling. The current manufacturing process, then, starts with soaking dried cassava starch overnight in ceramic or cement ponds. The moisture content of starch cake is about 50 % and wet starch is then dried on the hot floor. The produced starch has a remarkably different pasting profile from the native one (Figure 4).

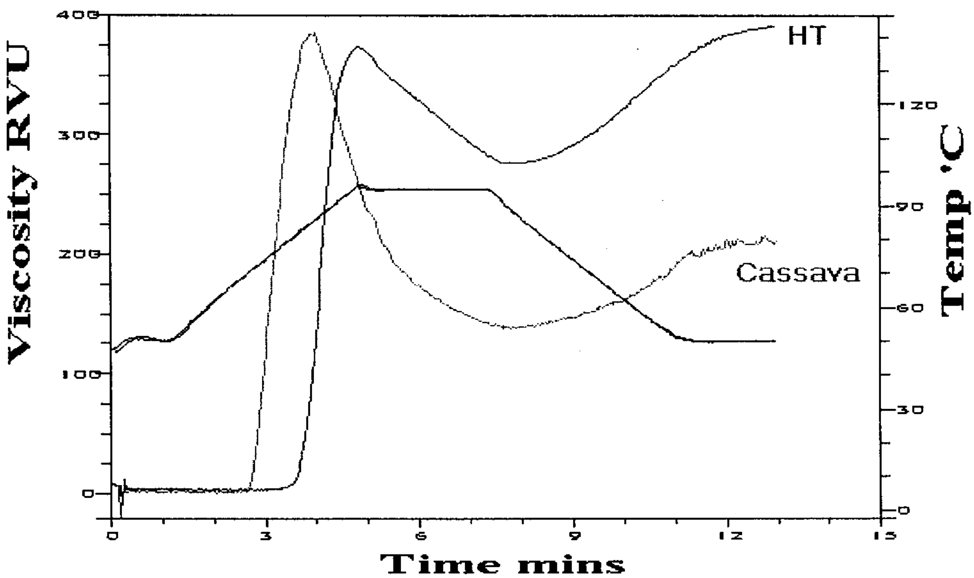
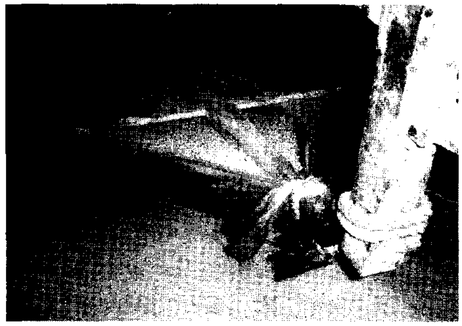


Fig. 4. Paste viscosity profiles as determined by a Rapid Visco Analyzer (using 3g starch of 14% moisture content in 25g of distilled water) of heat-moisture treated (HT) and native cassava starches.

Sago pearl or tapioca pearl

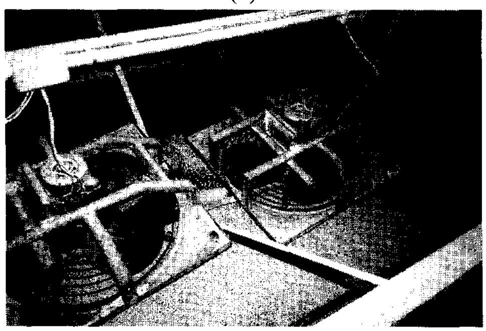
Sago pearl is one of the unique products produced from cassava starch in Thailand. Originally, this pearl was made from starch obtained from the stem of sago (*Metroxylon* spp.) palms which occur naturally only in the Southern part of Thailand. Due to the scarcity of sago starch, the technology of making sago pearls from cassava starch was developed and the product, called tapioca pearls, is used in some food products. The process for producing sago pearl involves heat-moisture treatment and a mechanical process (Figure 5). Similar to heat-moisture treatment, the starch is wetted overnight in ceramic or cement ponds to reach 50% moisture content. Wet starch is shaped to sphere-like by shaking continuously and the products subjected to dry heat process at 250–300°C. The pearls are cooled before being subjected to another drying process at a lower temperature (50–80°C) on the hot floor. The pearls are then graded and packed. When cooked, the pearl has a very unique characteristic as the pearl's surface is soft and transparent but inside is hard and opaque. Nowadays, the amount of starch used in the sago industry is about 60,000 tons per year, accounting for 6% of total domestic cassava starch consumption.

(a)



(b)

(c)



(d)

(e)

(f)

Fig. 5. Sago pearl process (a) wetting cassava starch (b) shaping the pearl (c) dry-heat process (d) cooling the pearl (e) sizing the pearls and (f) drying on the hot floor.

Chemical Modification

This group of products is prepared by chemical reaction. The most popular are oxidized starch and acid-modified starch for paper industry. The production of hydroxy – ethylated starch, cationic starch and amphoteric starch from cassava for paper industry is prepared only in a small scale. Starch acetate and phosphate are the most produced products for food industry.

Oxidized starch

Oxidized or chlorinated starch is one of the biggest-volume products produced from cassava starch. The preparation of oxidized starch is normally accomplished by the reaction of starch with sodium hypochlorite (NaOCl) under alkaline conditions. Oxidized starch is used at the size press as a surface sizing on wide range of uncoated free sheets to strengthen the paper surface. Traditionally, it is applied at 40 to 45 tons per ton of paper. Based on estimated paper consumption in Asian countries, an additional demand of about 240,000 tons of oxidized starch is expected each year [7].

Cassava starch, as a dominant source of starch in Asian countries, possesses a strong film, clear paste, good water holding properties and stable viscosity and should be the most suitable material for paper industry in this region.

Characteristics of oxidized cassava starch are influenced by oxidation conditions. Compared to the strong oxidized starches, the mild oxidized starch (prepared by 1,000 ppm active chlorine at pH 10.5) produces a stable high paste viscosity, which is called – Stabilized high viscosity starch [2].

Acid modified starch

Acid modified starch is also a well-known product in many Thai cassava starch factories. This product is normally prepared during the production of native starch. The preparation involves the addition of acid (usually hydrochloric acid) to the starch slurry (≈ 20°Be) at the temperature below the gelatinization temperature. After the reaction is finished and neutralized with soda ash, the starch slurry is concentrated, dewatered and dried. The acid modified starch should give the viscosity less than 30 cPs and pH about 5.0–6.0.

A main characteristic of acid modified cassava starch is the low tendency of the starch to retrograde compared to other starches. The handling of acid modified cassava starch under 70–85° C does not create any film-forming problem in storage tanks.

Starch acetate

Starch acetate is a representative of modified cassava starches for the food industry. The high volume of consumption is in food seasoning and sauce industry. The normal preparation process of starch acetate is the reaction of vinyl acetate monomer (max 7.5% of starch dry weight) to cassava starch under an alkaline aqueous suspension. The standard allowance of acetyl groups in modified starch for food application is 2.5% as the maximum level.

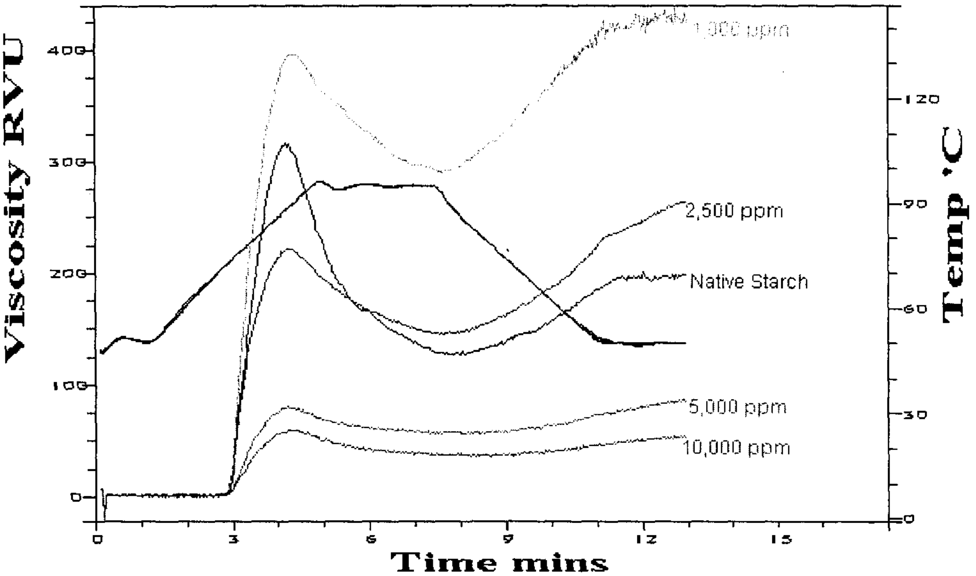


Fig. 6. Paste viscosity as determined by a Rapid Visco Analyzer (using 3g starch of 14% moisture content in 25g of distilled water) of oxidized cassava starches prepared by using different levels of sodium hypochlorite (0 to 10,000 ppm).

Other modified cassava starches for food products and their regulations

- Monostarch phosphate
  - Preparation: Orthophosphoric acid, Sodium orthophosphate, Sodium tripolyphosphate
  - Product regulation: Phosphate (calculated as phosphorus) not more than 0.4% (0.5% for potato and wheat starch)
- Distarch phosphate
  - Preparation: Sodium trimetaphosphate, Phosphorus oxychloride
  - Product regulation: Phosphate (calculated as phosphorus) not more than 0.04% (0.14% for potato and wheat starch)
- Starch succinate
  - Preparation: Succinic oxide, Octenylsuccinic anhydride
  - Product regulation: Octenyl succinic group not more than 0.3%

- Hydroxyl - propyl starch
  Preparation: Propylene oxide (max 10%)
  Product regulation: Propylene chlorohydrin not more than 1 mg/kg and hydroxy - propyl group not more than 7.0%
- Hydroxy - propyl - distrach phosphate
  Preparation: Sodium trimetaphoaphate, Phosphorus oxychloride and propylene oxide (not more than 10%)
  Product regulation: Propylene chlorohydrin not more than 1 mg/ kg and Hydroxy - propyl group more than 4.0%
- Acetylated distrach phosphate
  Preparation: Phosphorus oxychloride and vinyl acetate not more than 7.5% (in case of acetic anhydride not more than 10%)
  Product regulation: Acetyl group not more than 2.5%
  Phosphate (calculated as phosphorus) not more than 0.04% (0.14% for potato and wheat starch)

Starch hydrolysate and derivatives

This industry sector consumes the biggest volume of cassava starch produced in Thailand. The major product of this group is as a sweetener; important are glucose and fructose syrup. Glucose syrup is further used as the starting material for other industries; the biggest one is monosodium glutamate/ lysine (Table 5).

Table 5

Expected annual demand for cassava starch for the production of sweeteners and MSG/lysine in Thailand.

Products	Quantity of starch used (tons/year)	Product yield (kg/kg of starch)
High fructose (42% dry solid)	54,000	1.00
Glucose syrup	60,000	0.90-0.95
Dextrose monohydrate	20,000	1.75
Dextrose anhydrous	500	0.50
Sorbitol	30,000	1.20
MSG/Lysine	233,000	0.42

Source: [5, 6]

Sweeteners (glucose/fructose/sorbitol)

In Thailand, there are 14 factories manufacturing glucose syrup (two also produce sorbitol) and two large international sorbitol producers (Ueno Co., Ltd., Japan and Lucky Chemical Co., Ltd., Korea). There are two factories producing high fructose syrup (about 54,000 tons per year). All factories prefer to apply the enzyme process for hydrolyzing starch and isomerizing glucose to produce glucose and fructose syrup.

Monosodium glutamate (MSG) and lysine

Highest consumption of native cassava starch in Thailand is by the MSG (four factories) and lysine (one factory) industries. Starch consumption for production of these products is in the proportion of 80:20 by the MSG and lysine industries, respectively. Production of commercial MSG in Thailand utilizes only two carbohydrate sources for inoculation including molasses and cassava starch. To produce one ton of MSG, factories need either about 2.4 tons of cassava starch or 7.0 tons of molasses.

Other starch hydrolysate and derivatives

- Citric acid

There are only two factories manufacturing citric acid in Thailand. One uses cassava pulp from starch factories as the raw material (about 5-6 tons/day) for its solid state (surface) fermentation. The other, recently established, uses cassava chips as the raw material for its submerged fermentation process. About 40 tons of chips are needed to produce 6 tons of citric acid per day.

- Maltodextrin

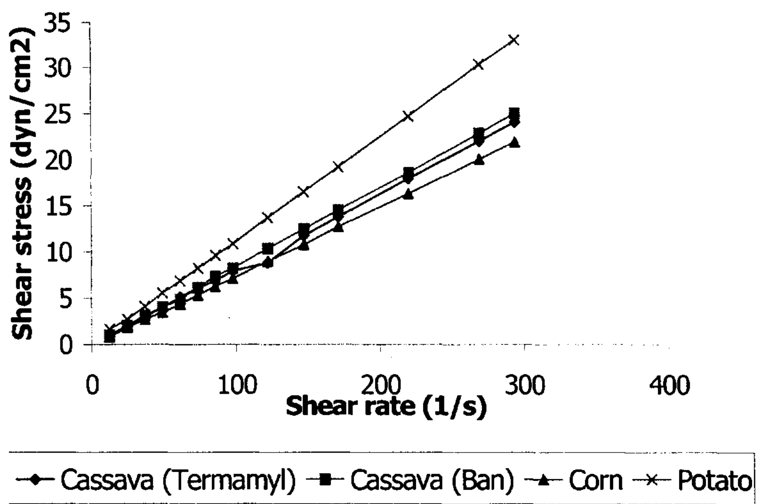


Fig. 7. Shear rate and shear stress of maltodextrin DE 5 (20% solution at 25°C) obtained from cassava starch prepared by two types of enzymes (I and II), corn starch and potato starch.

Maltodextrin produced from cassava starch in Thailand usually has the dextrose equivalent value greater than 10 (DE = 10, 14 and 17). The production of maltodextrin with DE < 10 is still limited to the low yield due to the filtration problem caused by the retrogradation of starch hydrolysate prior to spray drying. The process involves the hydrolysis of cooked starch with microbial enzymes and, when the reaction is terminated, the hydrolysate is filtered and spray-dried. Significant properties such as solubility, viscosity and water adsorption capacity, of cassava-based maltodextrin are much more similar to corn-based than potato-based maltodextrin (Figure 7).

Conclusion

Cassava can be more than a subsistence crop that contributes to the sustainability of millions of farmers. With technology development, the high-starch containing roots of this crop can be converted to starch, an important material for other upstream industries of many value-added products by modification technology.

Reference

[1] FAOSTAT, 2001. http://www.fao.org
[2] Kettlitz B. W., Coppin J.V.J.M: U.S. Pa. 6235894, 2001.
[3] Ostertag C.F.: World production and marketing of starch. In: D. Dutour, G.M. O'Berin and R. Best (Eds). Cassava Flour and Starch: Progress in Research and Development. CIRAD/CIAT, Cali, Columbia. 1996, 105-120.
[4] Sriroth K., Piyachomkwan K., Wanlapatit S., Oates C.G.: Starch/Starke, 2000, **52,** 439-449.
[5] Sriroth K.: Status of the Cassava-Industry Technology in Thailand, National Center for Genetic Engineering and Biotechnology (BIOTEC), Thailand. 1998, 113 p. (in Thai).
[6] The Thai Tapioca Flour Industries Trade Association. 2001. Private communication.
[7] Tupper E.: The paper industry and starch applications. Proceeding of the International Symposium on Cassava Starch and Starch Derivatives. Nanning, Guangxi, China Nov 11-15, 1992, 1995, 37-41.

MODYFIKACJA SKROBI TAPIOKOWEJ

Streszczenie

Tapioka (*Manihot esculenta,* Crantz) jest ważną rośliną uprawianą w wielu krajach Afryki, Ameryki Południowej i Azji. W Tajlandii roślina ta zajmuje poczesne miejsce. Jest ona ważna jako surowiec dla olbrzymiego kompleksu przemysłowego liczącego się w kształtowaniu ekonomii kraju. Korzenie tej rośliny odznaczają się wysoką zawartością skrobi toteż połowa zbiorów (20 milionów ton rocznie) jest przerabiana przez przemysł skrobiowy. Skrobia tapiokowa odznacza się szeregiem użytecznych właściwości takich, jak lepkość kleików, przejrzystość tych kleików i wysoka stabilność na zamrażanie i rozmrażanie, mające znaczenie w wielu zastosowaniach. Szczególnie skrobia natywna o wysokiej czystości nadaje się do modyfikacji fizycznej, chemicznej i enzymatycznej, prowadzących do polepszenia jej właściwości funkcjonalnych i zachęcających do poszerzenia zastosowań przemysłowych. W pracy opisano sposób modyfikacji skrobi tapiokowej wdrożony w Tajlandii na skalę przemysłową.