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A Review-Resistant Starch as Functional Food

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Abstract

Starch is a carbohydrate which is a glucose polymer, and consists of amylose and amylopectin. The utilization of indigenous starch is still very limited because its physical and chemical properties are less suitable for widespread use. Therefore, starch will increase its economic value if modified its properties through physical, chemical, or a combination of both. Modified starch aims to alter the chemical and / or physical properties of starch naturally by breaking the molecular structure, rearranging the molecular structure, oxidation, or substitution of the chemical group on the molecule. One type of modified starch is starch resistant starch (RS). RS is a starch-resistant starch which is defined as a starch fraction that is resistant starch to the hydrolysis of the amylase digestive enzyme and the treatment of polonaise in vitro. Resistant consists of RS1 (starch which is physically difficult to digest as in the maturation of imperfect milling), RS2 (raw starch), RS3 (retrogradationstarch), and RS4 (the result of chemical modification, such as the formation of cross linking). As the functional food of the hospital serves as a fiber fortification material, reducing calories and oxidizing fat, so RS is very important for health.

Keywords: *Starch, resistant starch, starch modification, functional food*

Introduction

The development of science and technology currently expects food to function as a health and fitness maintainer. Where feasible, food should be able to prevent, cure or eliminate the negative effects of certain diseases. This fact demands that food no longer merely fulfills the basic needs of the body that is nutritious and tasty, but also can be functional. Foods can be said to be functional if they contain components (both nutrients and non-nutrients) that are beneficial to organ functions in the body relevant to maintain health or have beneficial physiological effects (Roberfroid, 2000).

It used to be believed that the starch we consume can be perfectly digested in the small intestine. This understanding changed after many researchers revealed and found that the presence of starch in the colon. The fraction of starch that reaches the colon is known as resistant starch.

Formerly it was said that starch is a complex carbohydrate of the main calorie source of vegetable food ingested perfectly in the human small intestine. This opinion arises because it is known absorbed by the human small intestine and grouped into dietary fiber(American Association of Cereal Chemist, 2001). The facts show that resistant starch to alpha-amylase enzyme attacks is different. Some researchers also report that saliva and pancreas can produce enzyme amylase capable to digest starch. Along with the development of science and technology and the number of studies on starch both in vitro and in vivo note that not all starch consumed will be digested perfectly.

The resistant starch is defined as a starch of starch degradation that cannot be starch types retrograde during storage after gelatinization(Jayakody *et al.*, 2005). This indicates that the starches contain a portion that cannot be properly gelatinized and it is suspected that this section is a resistant starch

The presence of resistant starch in foodstuffs can enhance the physiological effects of the food. One of the physiological properties of resistant starch is its ability to be fermented by beneficial intestinal bacteria(Johnson and Soutgate, 1994). In the small intestine the resistant starch is not absorbed so it remains intact up into the intestine and will be fermented by beneficial bacteria such as Bifidobacteria and

Lactobacilli, so the resistant starch also has the potential of being a prebiotic (Haralampu, 2000). According to Gibson and (Roberfroid, 2000) Roberfroid (1995)?, prebiotics are defined as indigestible foodstuffs capable of functioning as substrates for growth or selection of beneficial bacteria growing in the human gut.

It is characterized by the presence of starch in digested (food waste) in the colon. This starch fraction is now referred to as a resistant starch (RS).The term "resistant starch" was first presented byEnglyst*et al*(1982) to describe a small portion of starch resistant to the treatment of α-amylase and pullulanase hydrolysis in vitro during a 120-minute incubation(Sajilata *et al*., 2006)........? tdk ada di daftar pustaka However, because the starch that reaches the colon may be fermented by the micro biota of the colon. Currently RS is defined as the fraction of starch that cannot be digested in the small intestine. RS can also be defined by its physiological and analytical properties. RS is physiologically defined as the amount of starch and the result of starch digestion that is not absorbed in the healthy individual's intestine. Analytically RS is defined as a starch that is resistant to dispersion in boiling water and hydrolysis of pancreatic amylase with pullulanase, but can be dispersed by KOH and hydrolyzed by amyloglucosidase (Englyst *et al*., 1987).

According to (Berry, 1986), starch can be classified into 3 types based on the starch response when incubated with enzymes. The first type of starch is Rapidly Digestible Starch (RDS). RDS is a type of starch that can be fully hydrolyzed by the amylase enzyme into glucose molecules within 20 minutes. The second type is Slowly Digestible Starch (SDS). As with RDS, SDS can be fully hydrolyzed by amylase enzymes, but for some reason, the hydrolysis takes longer. The third type of starch is the Resistant starch (RS) which is a small fraction of the starch that is resistant to hydrolysis by enzyme α-amylase and enzyme pulbulase given in vitro. The RS is not hydrolyzed after 120 minutes of incubation(Englyst et al, 1992).

According to Sajilata *et al*., 2006 that RS can be grouped into 4 fractions of the hospital that is resistant to digestion because it is physically protected (RS1); RS resistant to digestive enzyme because it is in granular form. (RS2); the primary hospital containing amylose is retrograde during the cooling of the gelatinization starch. (RS3), this form is the most resistant RS fraction; and RS formed by chemical bonds other than α- (1-4) or α- (1-6) (RS4). RS1 is in whole grains. RS2 is found in raw starch granules (bananas) that have a compact structure so that enzyme access is blocked. RS3 is present in most heated, moist-heated foods. RS4 is found in modified starch produced by various chemical treatments.

RS1 physically can be obtained directly, as in grain or legumes and grains that are not processed.

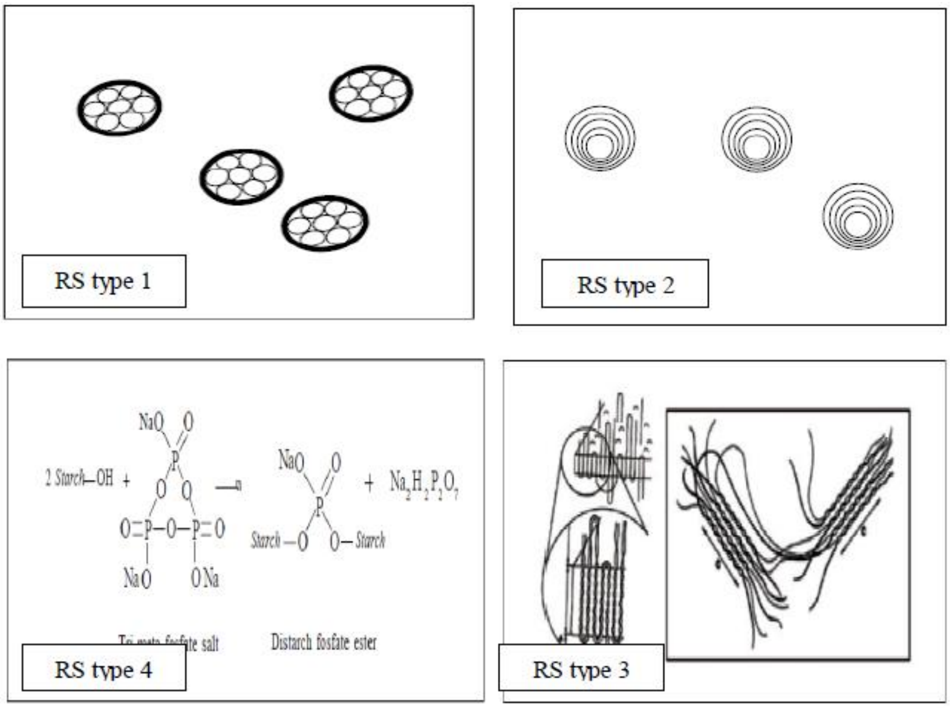

Figure1. *Resistant Starch Type 1, 2, 3, 4 (Salijataet al 2006)*

RS1 is physically trapped in the starch matrix, protein or plant cell walls. RS1 physically can be obtained directly, as in grain or legumes and grains that are not processed. RS2 starch granules resistant to digestion by enzymes α-amylase contained in the pancreatic islets. RS2 is naturally present in the granular structure, such as uncooked potato, also on flour banana and corn flour that contains lots of amylose. RS3 is starch retrogradation, non angular or starch for food. RS3 formed for processing and cooling, such as in bread, corn flakes and potatoes are cooked or refrigerated, or retrogradation amylose maize. RS4 is a chemically modified starch by acetylation and hydroxipropilase or cross linked starch that can stand digested. RS4 i.e. hospitals that have a bond other than α-1,4- and α- 1,6-D-glucosidic (Shi *et al*. 2006)tdk ada dlm daftar pustaka.

RS1 has a stable characteristic of the process of warming at the moment processing, as well as widely used as an additive to foods traditional. RS2 is a starch which has a granular form and is resistant to digestive enzymes. Chemically, glucose produced by the digestive enzymes in the sample of cooked starch homogeneously and cooked samples can be measured to determine the content of RS2. Examples RS2 starches that are not gelatinization, or which are naturally present in bananas. RS1 and RS2 will leave a residue fiber, and slowly digested in the small intestine. RS RS3 is most often found, is generally a fraction of starch and amylose retro gradation during the cooling process in starch gelatinization. Chemically, starch fractions that are resistant to heating and digestive enzymes, can generally only be dispersed using KOH or dimethyl sulfoxide.

According Asp and Bjorck 1992 that the RS enzyme amylase in the pancreas can be determined by the formula:

RS1 = TS - (RDS + SDS) - RS2 - RS3; RS2 = TS - (RDS + SDS) - RS1 - RS3; RS3 = TS - (RDS + SDS) - RS2 - RS1; RS 4 is formed from a bond other than - (1-4) or - (1-6). Some ways to modify starch are presented in Table 1.

Table1. *Classification of resistant starch (RS) raw materials and factors that influence*

Type RS	Description	Process	Resources	Production process
RS 1	It is physically not digested because it is trapped in an indigestible matrix	Physical treatment	whole grain or destruction results	Milling, chew
RS 2	Resistant granules in non-gelatinized form, having type B crystallinity, are hydrolyzed slowly by α-amylase	Resistant granules, crystals of type B, hydrolyzed by α-amylase	Potatoes, pineapple, legume, corn is rich in amylose	Cooked
RS 3	Retrograde starch, formed when food containing starch is cooked and cooled	Starch retrogradation	Cook potatoes, bread, cornflakes, food to reheat	Setting process conditions
RS 4	Chemically resistant resistant starch	Chemical modification	Bread, cake	Physical and chemical modification

Source:*(Hustiany R, 2006)*

Production Process of Resistant Starch

There are several production process of resistant starch, there are as follows

Physical Process

Process of heating and cooling can affect the characteristics of the RS. RS production process can be performed at temperatures above the gelatinization temperature and Simultaneous dried with a dryer such as a drum-type dryer (drum drier) and extruder. RS optimal production process is at a temperature of starch gelatinization i.e. 120°C for 20 minutes, followed by cooling at room temperature(García-Alonso *et al.*, 1999). Starch gel is then cooled at -20°C and dried at 60°C before being destroyed. Some physical treatment can be performed to produce the RS3. Gelatinization process, propagation, and heat treatment is needed to produce starch which has low calories associated with durability digested during digestion. The temperatures used are generally above the melting point of the crystalline amylopectin and below the melting point of enzymes RS (140°C) to generate the RS3(Haynes *et al.*, 2000).

Using steam (steam cooking) can be used in processing of legume starch which has RS with durability digestibility quite high (19-31%) (Tovar and Melito 1996). The processing of RS with using high-pressure steam will generate RS has a power hold 3-5 times greater digestibility of raw material.

Autoclaving or heating by high pressure steam can improve RS 1% higher than the raw material in wheat (Siljestrom and Asp 1985). The processing by using an autoclave can improve RS wheat from 6.20% to 7.80% after three times the cooking process or cooling(BJöRCK and NYMAN, 1987). Ranhotra *et al*. (1991) state, the process RS autoclaving can increase three times as much on bread flour and four times as much flour pastry products. According to Sievert and Pomeranz (1989), the use of enzymes RS during autoclaving and cooling to produce the highest yield of RS, i.e. 21.30% in amilomaize VII starch (amylose content 70%).

Commercially, manufacture RS using autoclaving can be applied to corn starch, potato or legume, which is one of the products intended for children aged 3-8 years in the form of puree (Siljestrom and Bjorck 1990). The heat treatment is generally performed by using an autoclave at 121 °C with a combination of gradual cooling for the production of amylase-RS of amylose starch containing high enough. The treatment temperatures used vary, which is 110°C (Berry, 1986), 121°C ((BJöRCK and NYMAN, 1987); Sievert and Pomeranz 1989; Sievert and Wursch 1993), 127 °C (Berry, 1986),134°C ((Berry, 1986);(BJöRCK and NYMAN, 1987); Sievert and Pomeranz 1989), or 148°C (Sievert and Pomeranz 1989) for the processing time of 30-60 minutes.

Parboiling is one of the preheating phases of starch before treatment further processing. Marsono (Marsono and Topping, 1999)and Topping result of research (1999) shows, the content can be enhanced through the RS rice parboiling process. RS can also be improved through the process of cooling and freezing.

Roasting can increase the RS, according to Wasteland *et al.* (1989), bread making process produce soft part (crumb) on the inside and the hard part (crust) on the outside with RS different. The content of the highest RS obtained in the process of development and RS lows in the combustion stage for 35 minutes. Roasting process optimized to obtain high RS ie at low temperatures with a longer processing time(Liljeberg, Åkerberg and Björck, 1996). Extrusion, the processing of starch with temperature treatment (90, 100, 120, 140, or 160°C), moisture content (20%, 25%, 30%, 35%, or 40%), and engine speed presses (60, 80, or 100 rpm) can produce RS3. combination treatment by way of storage at 4 ° C for 24 hours before drying can increase the levels RS3(Faraj, Vasanthan and Hoover, 2004).For process optimization, complex amylose-fat can increase the extrusion product from corn starch. Microwave irradiation can affect the structure of starch, which is initially insoluble turned into soluble. But quantitatively, it does not affect RS levels (Emanuele Marconi, * *et al.*, 2000)

Chemical Modification

RS production process, in addition to physical processes, can also be done through chemical modification, such as hydroxypropil starch, starch adipic, asetylat starch, and starch fosforilat. Other modifications are cross linked starch, starch esterification, hydroxipropilat starch, cationic starch, starch anionic, nonionic starch, starch zwitterions, and starch succinate (Wurzburg 1989).

RS simple production process can be done by acid treatment. Acid treatment with starch ratio of HCl 160: 1 at 90 ° C for one hour can produce the RS 49.50% (Tester et al. 2004). Starch can pyrodextrin reduce the ability of enzymes that hydrolyze starch through the mechanism glycosidic bond resulting in lower digestibility and maltoolygosacaride amylase enzyme in the small intestine. RS production process can also be done through modification of HCl 1% (w / w) at 25 ° C for approximately 78 hours producing RS 35%. Chemical modification by a combination of heat treatment can RS produces up to 63.20%. Currently, pyrodextrin process widely used in the production of RS compared the cross linking process modifications(Laurentin *et al.*, 2004).

Chemical modification can also be done using acid treatment chloride 0.15% (dry basis) and orthophosphoric or sulfuric acid 0.17% (Wurzburg 1989). Commercially, the combination of the use of chemicals and the heating can be done by adding acid and stirring. Acid starch can be dried further by using a spray dryer (spray drier) for hydrolysis and transglycosilation stages.

Modifications cross linking can be achieved by enzymatic or addition of chemicals (Haynes *et al.*, 2000). Chemicals used between trimetaphosphate others, namely sodium, phosphorus oxychloride, or a mixture of acetic acid anhydride and adipic acid. Cross linking formed by the addition sulfonate group and phosphate will increase the hydroxyl group so resistant to attack amylolytic that occurs in starch molecule (Hamilton and Paschall 1967). Distarch phosphate containing 0.40 to 0.50% phosphorus can SDS produce and RS4(Woo *et al.*1999). Chemical modification can produce SDS starch RS4 13-69% and 18-87%. Distarch phosphate is one RS from corn starch having a high amylose content and is used as a food additive (E1413) in the European Union.

Biochemical Process

RS biochemical production processes carried out by adding the enzyme or microbes producing enzymes.The basic principle of the use of enzymes for the production of RS is changing the structure starch thus obtained which contains amylose starch. The process can be done by changing the structure of amylopectin with glucanotransferase to straighten the chain, or change the fagots to be straight like structure amylose. The amylose fragments can be crystallized for use as a hospital. The enzyme functions to break the chain so that it becomes shorter. The less chain length, durability starch digestibility will increase. Modified corn starch with glucanotransferase contains at least 35% degree of polymerization 35 (DP35).

Enzymatic reactions can be obtained through the process as well as the reaction amitotic degradation using an acid. One example of the degradation of starch is maltodextrin by way of a partial degradation of α-amylase. The main stages include the enzymatic reaction conditioning starch, the addition of enzymes, enzyme inactivation, and drying. Some enzymes that can be used is isoamilase and pullulanase. Other processes that is by forming maltodextrins (DE <10, especially DE <5) are dissolved in water, setting the optimal pH for the enzyme, the addition of the enzyme, mixing and incubation, enzyme inactivation, mixing, drying spray dryer, and grinding the starch to a certain size.

The production process can produce flour enzymatic RS 50%. Stages of the manufacturing process includes a substrate with a ratio of 1: 2, heating by autoclaving at 100 ° C, cooling, addition of the enzyme amylase, deactivation of the enzyme at a temperature of 100 ° C, washing, and drying (Pomeranz and Sievert 1990). Enzymatic modification can be performed optimally RS to yield ranged from 55-60% with a degree of polymerization 10-35 and a peak temperature of 115 ° C or the range 90-114 ° C.

Characteristics of Product

RS granules can be produced through a unique way by utilizing materials other extras like enzymes, dietary fiber, specific molecular weight distribution, the use of high temperatures, and the use of temperature gelatinization (Delta H) 36 Journal of Agricultural Research, 30 (1) 2011 high as an indication of perfection process. RS starch can be produced from amylose starch containing at least 40% by heat treatment. At certain moisture content, starch overhauled and digested at amorphous section (irregular) using the enzyme α-amylase or chemicals.

One of the characteristics of RS can be detected through molecular weight, and can categorize as a heat treated starch, highly resistant heat-treated starch, and highly resistant starch. RS granules generally have a total dietary fiber (TDF) 20-50%. RS characteristics compared to products other hydrocolloid presented in Table 2.

Table2. *Resistant starch digestibility characteristics in comparison to other hydrocolloid products with the oven method*

Hydrocolloid	Total dietary fiber (%)	SV95	SV95 water/oil	Water content	starch/lipid
Resistant starch digestibility cross-link (control)	68.1	2.8	3.0	6.4	10.6
K-carrageenan	75.8	2.8	3.0	6.8	11.0
K-Carrageenan / locust gum of beans, nuts (1: 1)	72.7	3.4	2.6	4.0	13.4
Xanthan / locust gum of nuts (1: 1)	58.1	20.0	4.0	0	16.0
Low methoxyl pectin levels	70.9	3.0	3.2	6.4	10.4
carboxymethyl cellulose	71.3	3.4	3.4	6.2	10.4
sodium alginate	88.6	6.6	5.2	4.8	10.0
1-Carrageenan	79.3	3.0	3.0	6.8	10.2
Tara gum	72.1	4.4	5.0	3.2	12.0
Hydroxypropyl methylcellulose (HPMC)	69.6	3.4	3.0	4.4	12.6

Source: *Woo et al. (2008)*

Functional Value of Resistant Starch

RS widely consumed because of its functional value. RS hydrolysis by the digestive enzymes generally requires a longer time so that the process becomes slower glucose production. It is further correlated with plasma glycemic response (Raben et al. 1994). Indirectly, the RS has a functional value to people with diabetes.

RS2 generally produce a lower energy than the flour. RS energy value ranging between 2-3 calories (8-12 kJ), while flour energy yield 4 calories (16 kJ), depending on the process of metabolism.

RS is also widely used as a source of fiber. The Institute of Medicine in United States requires a source of fiber intake of 38 g / day for men adult and 25 g / day for adult women. In other countries, the intake of fiber average food required 25-30 g / day.

RS contains a fair amount of amylose so as to have a good effect for the digestive tract and metabolism in the glycemic management process and energy. Broadly speaking, the RS has three systems associated with effects metabolic and functional value in the body, i.e. as a material for fortification fiber, lowering calories, and fat oxidation.

As a material for fiber fortification, RS can be obtained by eating Hospital food sources, such as bread, biscuits, confectionary, pasta, and cereals. In 2003, WHO declared that dietary fiber can lose weight and obesity. It is related to controlling hormone system to digest food and control hunger (WHO 2003; Slavin 2005)

As a material to reduce calories, RS can reduce energy faster compared with starch and other carbohydrate products. RS natural energy yield of 2-3 kcal / g (8-12 kJ / g), while the flour to produce energy 4 kcal / g (16 kJ / g) (Behall and Howe, 1996); Aust *et al*. 2001).

As the material for the oxidation of fat, so that the RS can burn fat lowering the amount of fat stored in the body. The results showed that eating RS from corn can increase fat oxidation. It is associated with the metabolism of carbohydrates and proteins in the body(Higgins *et al.*, 2004). Results of research from Younes *et al*. (1995) by using rats showed that RS has the ability to lower the fat content as shown in Figure 8.

Consuming RS also can lower blood sugar content. RS will energy release in the small intestine in the form of glucose which is then fermented in the large intestine. RS produces energy by a process that is slow enough to not immediately be absorbed in the form of glucose. RS lowers the glycemic effect and are sensitive to the hormone insulin so as to reduce the potential for type 2 diabetes.

RS naturally also can improve colon health associated with the process digestion. RS also affect the microbes contained in the channel digestion, particularly those associated with the fermentation process in the body. One result of microbial metabolism is butyrate which has anti-inflammatory and anticarcinogenic effects that may ultimately prevent cancer of the large intestine (Toscani et al. 1988).

Physiological Effects of Resistant Starch

Analytically, resistant starch is as insoluble fiber. However, physiologically resistant starch has physiological properties of soluble fiber. Some of the potential physiological effects of resistant starch are maintaining the health of the colon; as a prebiotic that helps maintain colon health; controlling the gilcemic and insulin response; gives a sense of satiety and lowers energy intake; and improve blood lipid profile. Like soluble fiber, resistant starch is a substrate for colonic microflora. Resistant starch is prebiotic which selectively increases the populations of beneficial colonic bacteria bifidobacteria and lactobacilli. Bifidobacteria and lactobacilli are the most beneficial colonic bacteria in humans as their host. Increasing the amount of bifidobacteria and lactobacilli in the gastrointestinal tract may suppress colorectal cancer by increasing the production rate of SCFA (especially acetate, propionate and butyrate), decreasing the pH of the intestinal environment, is proapotopsis and suppresses the growth of pathogens by increasing its competitiveness to the availability of nutrients, receptors and factors other growth. Resistant starch improves intestinal health with a laxative effect (laxative) that is lower than dietary fiber. Inside the colon, resistant starch fermentation increases fecal bulk and decreases the pH of the colon. Resistant starch also improves the health of the colon by increasing the speed of crypt cell production, or also decreasing colonic epithelial atrophy versus non fibrous foods. Also found indications that resistant starch may affect tumor genesis. SCFA fermentation of colloid microflora has a high proportion of butyric acid. The production of butyrate from resistant starch fermentation is twice higher when compared to wheat fiber and four times higher than pectin. Butyrate is used as energy by colonocyte and growth factor for healthy epithelial cells in the colon. Butyrates have been reported to be anti-carcinogenic. Three mechanisms believed to be involved in protection against the development and growth of cancer cells are initiation, differentiation and apoptosis. Several studies have shown that butyrate protects colon cells from DNA damage by inhibiting the growth and proliferation of tumor cells, increasing the differentiation (normalization) of tumor cells / cancer, producing phenotypes similar to normal adult cells, and enhancing apoptosis (program cell death) of colorectal cancer cells in humans. Resistant starch fermentation is reported to suppress the fermentation process of proteins and other nitrogenous components thereby suppressing the increase in the amount of ammonia that is carcinogenesis to the colonic epithelium (Govers et al 1999).

In addition, resistant starch fermentation also decreases the production of secondary bile acids. Bile acids are known to increase the risk of colorectal cancer. According to Bingham (1990), the conversion of primary bile acids into secondary bile acids is an early cause of colon cancer. The decrease in pH due to the production of SCFA leads to the inactivation of the 7α-dehydroxylase enzyme so that the conversion of primary bile acids into secondary bile is inhibited. In addition, a decrease in secondary bile acid concentration is also thought to be due to dilution factors due to increased stool volume. Resistant starch also has the ability to reduce the glycemic response and insulin response so that it can provide protection against diabetes. The addition of resistant starch in the product will slow down the digestive process. In contrast to normal, digested starch immediately after consumption, resistant starch metabolism lasts from 5 to 7 hours after consumption, reducing postprandial glycemia and insulin response and potentially extending the 'full' period. Because the resistant starch has a low glycemic index, its addition in the product to replace conventional starch will help lower the value of the product glycemic index. In order to effect a decrease in the glycemic index and insulin response, the amount of resistant starch is at least 14% of the total starch used in the formula. However, not all resistant starch exhibit hypoglycemic responses. 4 type resistant starches (acetylated potato starch) is reported not to lower blood glucose.

Studies in mice showed that the resistant starch affects fat metabolism: lower total lipids, total cholesterol, low density lipoprotein (LDL), high density lipoprotein (HDL), very low density lipoprotein (VLDL), intermediate density lipoprotein (IDL), triglycerides and triglycerides rich in lipoproteins. In some studies using test mice, the decrease of cholesterol and plasma triglycerides was demonstrated by rats fed with resistant starch rations (25% raw potatoes or peanut starch). The replacement of 5.4% of dietary carbohydrates with dietary resistant starch is also significantly reported to increase postprandial lipid oxidation so that in the long run it can decrease fat accumulation.

Conclusion

RS is a modified starch products are broadly divided into RS1, RS2, RS3 and RS4. RS can be produced from raw materials of starch-producing plants that are genetically having a high amylose contents.

RS has a functional value for fiber fortification, reducing calories, and oxidized fat. RS has significant potential to be developed as a functional food for health.

RS offers an exciting new potential as a food ingredient. It has been shown to possess physiological benefits similar to soluble fibers, and in addition to be used as a mechanism for sustained glucose release.

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