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Interregional Seminar for the
Industrial Processing of Rice

SUMMARY

RICE STARCH AND RICE STARCH DERIVATIVES [1/]

by

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1. This paper briefly reviews the present status of knowledge in the area of rice starch and rice starch derivaties. The characterics, properties, uses, and methods of preparation are described. Several problems in marketing and production are discussed and possible solutions suggested.

2. The characteristics of rice starch are described, discriminating between Common and waxy varieties. The characteristics defining the quality of a particular rice starch or rice starch derivative depend on the particulare use to be made of them in the paper, textile, adhesive, food or other industries. They are therefore varied, and are described when dealing with the different uses of rice starch and rice starch derivatives.

3. A few of the characteristics of rice starch are highly peculiar but others are entirely comparable to those of other starches. All of them are analysed in order to establish a scientific and technical basis for comparing the competitive position of rice starch in each particular starch

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market. It can be said that rice starch is, in most of its properties, very similar to that of corn and sorghum. This holds for both, the common and the waxy varieties.

4. Starches of different origin provide a wide variety of choice for individual applications, but they are insufficient to cover the very many and specific needs of modern technology. Consequently, the starch industry has developed procedures to alter the characteristics of the natural starches to meet the requirements for special uses. The derivatives of greatest importance in the market are the cationic starches hydroxyethyl starches, oxidized starch, and various cross-linked starches. The cost advantage held by corn starch has dominated the market, and besides this only a few starches of other sources, such as potato or sorghum, have been used for derivatization processes. Rice starch derivatives, with perhaps some minor exception, are not manufactured on an industrial scale although procedures for their preparation have been patented. The information on this subject is scanty. Nevertheless, as it could be expected, the available data do not reveal a particular behaviour of rice starch in derivatization processes. On the other hand, the general properties of rice starch derivatives do not appear to be essentially different from those of other comparable starches which certainly have a great diversity of industrial applications and an important market.

5. The uses of rice starch and rice starch derivatives are described, paying special attention to the important sectors of paper, textiles, and foods. The requirements for each particular use of rice starch and rice starch derivatives are described briefly. Particular attention is paid to waxy rice starch as thickening agent for food uses. Its freeze-thaw stability make it specially suitable for refrigerated and frozen foods. Only some starch derivatives are comparable to it in this respect. This is an interesting advantage as the price of starch derivatives ranges generally about twice that of the raw original starch.

6. From the viewpoint of properties, applications, manufacture and suitability for derivatization, rice starch has commercial possibilities similar to those of corn starch. The mandatory factor determining the competitive position of rice starch and rice starch derivatives in the market is the price of the rice starch. This is about twice the price of corn starch. It is largely, if not mainly, due to the price of the original cereal; rice is much more expensive than corn. It appears therefore that rice starch has no possibilities to compete with corn or other starches if the price of rice does not decline substantially. A more complete and rationalised utilization of the rice grain, with higher returns in the rice and rice starch processing plante is also needed; in this sense, rice offers unique advantages over other cereals, which are discussed below.

7. The manufacture of rice starch and rice starch derivatives is briefly discussed. Commercial methods for the isolation of starch involve the following steps: a) steeping, b) grinding, c) removal of fiber, d) separation of starch and protein, and d) drying. Usual conditions are: steeping in aqueous alkaline solution (0.3-0.5 % NaOH), at room temperature, with recirculation, for about 24 hrs. or longer (one process uses only two hours), wet milling, removal of fiber by sieve bends or centrifugation, separation of starch and protein by centrifugals and/or hydrocyclones and drying by conventional methods (the use of a flash drier has some advantages). Reference to the treatment of waste water in the rice starch plant is made.

8. The latest methods for the manufacture of the main rice starch derivatives are reviewed. The existing information is scarce and it generally must be obtained from the patent literature. Prior to establishing a plant for the commercial production of rice starch derivatives, studies should be undertaken on a pilot plant scale directed to determine the particular conditions of treatment andthe suitability on the different rice varieties.

9. The successful development of improved rice varieties has opened a new area of problems. Although at present the Asian region as a whole has not reached the desired situation, in some regions the expanding output has created surpluses. This situation may be a common one in the next future. An important alternative to the solution of the problem, if surplus becomes actually generalised, is to expand the domestic and export market for rice. In this connection, improvement of equipment and technology is a necessary step. In this context, it is very likely that a change in quality standards of both the local and export market will occur. The demand for high quality rice is expected to increase; that of rice for specific uses also. Consequently, new and more profitable alternatives are expected to be needed to expand the market for rice, particularly for medium and low quality rice. Rice starch processing industry can have an important role in this respect. There are, however, several aspects to be taken into consideration, besides the price of the rice, commented above. First, sufficient quantities of rice have to be produced to meet the domestic food needs. Second, the nutritional value of rice must be used to feed rice-eating people adequately. Not only enough quantity but also good quality rice are needed in the diet to solve scarcity and malnutrition. Industry processing of rice to beneficiate starch does not allow to recover the nutrients of the kernel, in their whole value, for human food. This is regrettable when well balanced rations are needed. On the other hand, these nutrients, along with other accompanying non-starch constituents, are largely responsible for the difficulties arising during the starch isolation process.

10. Recent knowledge on the distribution of chemical constituents within the rice kernel has shown new approaches for the utilisation of the grain. The brown rice kernel may be fractionated by abrasive milling in three portions of quite different composition. The outermost one, as it is well known, is rich in proteins and vitamins, but also in fiber and unstable fats. Its value as cattle feed is recognized, particularly after adequate

destabilisation. The underlying fraction is rich in proteins and vitamins but more stable than the previous one; its fiber content also is much lower. It is a highly nutritional food, particularly suitable for children, and it should not be wasted, particularly in developing countries where rice is the stapple food. Finally the third fraction or residual nucleus is practically stable and contains only about 5 per cent protein; its fiber, fat, and ash contents are generally lower than 0.1 per cent. This latter fraction certainly is an excellent starting material for the commercial isolation of rice starch. A plant for the integral utilization of rice based on these principles is suggested. The advantages it involves and the many possible rice products to be obtained, besides rice starch and rice starch derivatives, are described. The simplified flow diagrams of the rice starch and rice starch derivatization plants are given, indicating the equipment they are composed of.

11. The profitability of the plant for integral utilization of rice is discussed. It is highly dependent on the raw material price. Therefore, when assessing the economics of the plant, two different alternatives are considered. In the first one (Alternative A) the price of rice is the present price. In the second one (Alternative B) the price of rice is the maximum price allowing competitive prices of all the manufactured products. A summary economic statement, giving investment, operating costs, revenue and profits is presented for plants with capacities of 25.000 and 50.000 tons paddy/year.

12. The suggested plant for integral utilization of rice appears to be actually feasible. However, a pre-investment study, including pilot plant work and marketing, is necessary to evaluate accurately the factors influencing the economics of the plant and appropriately select the optimum operating terms.

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RICE STARCH AND RICE STARCH DERIVATIVES [1]

by

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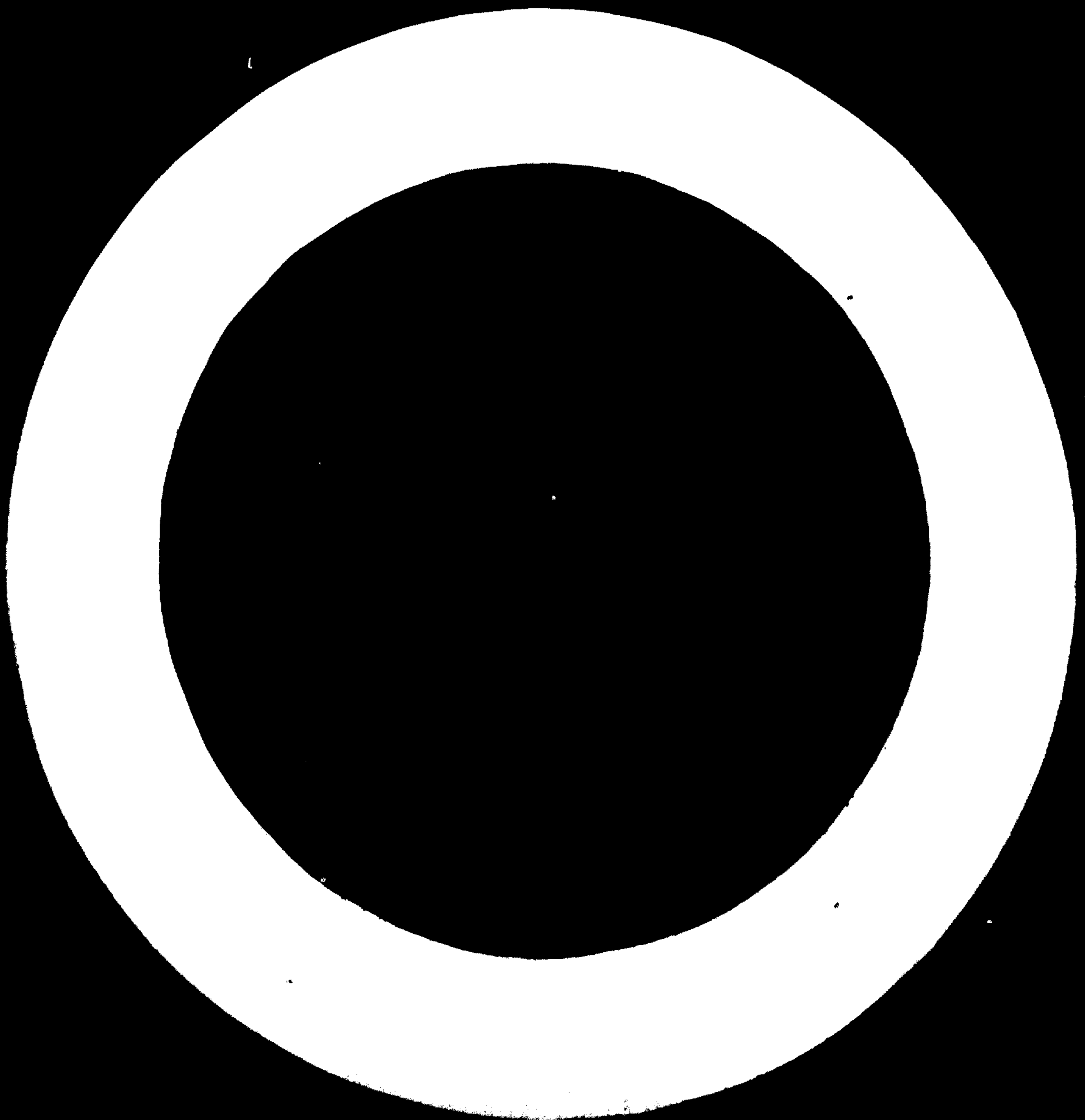

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I. QUALITY DEFINITION OF RICE STARCH AND RICE STARCH DERIVATIVES.

1. Rice starch is obtained from the seed of "Oryza sativa" as a dry, white, lustrous, free flowing powder. It is composed of polygonal in shape, usually 5-sided, granules with a centric hilum. Naturally occurring compound grains are sometimes detected, they have an angular outline and contain individual granules separated by stroma. In addition, rice starch granules aggregated into clusters are frequently found in commercially available samples, generally due to inappropriate processing. Causes of aggregation are surface gelatinization of granules during the drying process or alkaline gelatinization during the steeping and separating stages. The presence of clumps may impair the properties of starch for specific uses -such as a dry dusting powder. Clumps may give non - homogeneous pastes. In some cases, association of granules may be accepted, although as an indication of a desirable incipient gelatinisation.

2. Rice varieties are divided into two main classes: ordinary or common (the rices of world commerce) and waxy. The starches they contain differ

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markedly in their composition, properties and uses, and they are dealt with separately from this time forth.

3. Common rice starch. Rice starch granules have the smallest size of ordinary starches. Their particle size distribution comprises a continuous range of sizes from less than 0.5 μ to 13 μ (1). Starch samples of Indica and Japonica non - waxy rice varieties have been found to have somewhat different average sizes, they ranging from 3.9 to 5.7 μ and from 3.8 to 4.3 μ ., respectively (2). Rice starch granules have the highest surface area of common starches (about 8,000 $cm^2/g.$), and their specific gravity ranges from 1.4435 to 1.646 (3).

4. The pH of commercial rice starch frequently is slightly alkaline due to uncomplete removal of the steeping liquor. As reported by Schoch (4), it is not objectionable for most of its uses. In the starching of fabrics, an alkaline pH is desirable as it favours dispersion of starch granules in water and decreases the tendency of starch to settle. In cosmetics, when rice starch is used as a face powder, the low alkalinity may help to counteract the acidity of skin. However, in some cases, such as enzymic conversion of starch, alkalinity should be neutralised.

5. Rice starch granules (non-waxy) show moderately restricted swelling and solubility when heated in water. Reported values are, respectively, 16.3 and 21.6 % at 85°C (5) and 19.0 and 18.0 % at 92°C (6). The gelatinisation and pasting characteristics of rice starch are dependent upon rice variety. The gelatinisation temperature ranges from 55° to 78°C (3). Due to the low birefringence of the rice starch granules, use of the B.E.P.T. (birefringence end point temperature) technique is not always reliable for this purpose. The amylogram reveals a moderate peak viscosity, a moderate stability on cooking, and a pronounced tendency to retrograde for the non - waxy rice starch (4). (see Fig. 1), which forms tender opaque gels.

6. Amylose content of rice starch varies greatly with variety, usual ranges being 11-37 % for the non-waxy type, although wider limits have been reported (3). Corresponding iodine binding capacities are 2.08-6.99 %.

7. Rice starch, as other starches in commerce, contains water and minor amounts of non-starch constituents. The water content is dependent upon the temperature and relative moisture of surrounding atmosphere. Schierbaum (7) determined the hygroscopic equilibria of rice starch at 20°C for different relative humidity levels; obtained data for adsorption and desorption cycles are shown in Table I. The non-starch constituents of commercial rice starch, frequently called "contaminants", are protein, mineral matter, fiber and fat. The level of "contaminants" is dependent on the efficiency of the starch isolation process. In commercial practice, the maximum contaminant levels use to be about: 0.5 % protein, 0.1 % fat, 0.5 % ash, and traces of raw fiber. The range of variation of values reported in the literature including laboratory and commercial starch are given in Table II.

8. Protein content is used in practice as a criteria of purity of starch; it indicates the extent to which the individual granules have been separated from the proteinaceus matrix. High protein levels may affect the properties of starch, such as increase the turbidity of its pastes. Fat content also depends greatly upon the isolation procedure; rice germ and rice bran are rich in fat and can easily contaminate starch. At the relatively low moisture level of dry starch, high fat contents develop undesirable flavors. Differences in fat content have also been attributed to the nature of starch, on the basis of the results found in samples from Japonica and Indica varieties, the fat content of which ranged from 0.4 to 0.8 % in the former and from 0.1 to 0.3 % in the latter (8). The amount of ash is of lesser importance as a guide to quality.

9. Other characteristics of common rice starch are described in Chapter 2.

10. Waxy rice starch. It contains practically only amylopectin. Amylose contents ranging from 0 to less than 1 % are generally found, although higher figures have been reported (3). Differences between the waxy and the non-waxy starches are largely, if not mainly, due to the amylopectin content. The granules of the two kinds of starches are alike in size, shape, total surface area, and specific gravity (3) and show the same birefringence and X-ray diagram (9). Starch granules from waxy rice swell more freely in hot water than non-waxy; according to Leach (6) their swelling power and solubility at 95°C are 56 and 13 %. Their gelatinization temperature range is 60°-75.5°C (3) somewhat narrower than that of common rice starch, although of similar level. Their pasting characteristics are, however, markedly different. Waxy rice starch exhibits through the amylogram, high pasting peak, extensive loss of viscosity during cooking, and very little tendency to retrograde (see Fig. 2). It forms clear pastes, stringy and cohesive, as typical in other amylopectin starches. Its most outstanding characteristics is, undoubtedly, the great stability of its pastes toward prolonged cold storage and toward freezing and thawing. Schoch (4) reported that aqueous 5 % pastes of waxy rice starch show no synerisis until after 20 freeze-thaw cycles, whereas other waxy starches such as maize and sorghum are stable for only three. This property makes waxy rice starch specially useful in the food industry (see Chapter 4).

11. Rice starch derivatives. Natural rice starch, as starches of other sources, may be processed into a series of derivatives exhibiting a great diversity of characteristics, with which a wide variety of industrial and food uses can be covered. A starch derivative is defined as "a chemically modified starch in which the chemical structure of some of the glucose units has been altered" (21). This definition includes esters, ethers, oxidised starches, graft-copolymers and cross-linked starches. It does not comprise the acid-modified starches, which represent "per se" a field of great interest. Rice starch derivatives are characterised by the

nature of their chemical modification, degree of modification, degree of polymerization and physical form-granular or pregelatinized. Nevertheless, the properties and specific applications of rice starch derivatives are not dependent only upon these characteristics. Since rice starch is a natural polymer, it is subjected to varietal and production variations, which may affect the results of derivatization. Therefore rice starch derivatives are better characterized if their solubility, water absorption properties, behaviour on cooking and on subsequent cooling, and appearance and texture of pastes are properly described.

12. On the other hand, the characteristics defining the quality of a particular rice starch or rice starch derivative depend on the particular use to be made of it in the paper, textile, adhesive or food industries. Due to it, these quality requirements for rice starches will be better described in Chapter 4.

2. A QUALITATIVE COMPARISON OF RICE STARCH WITH OTHER COMPARABLE STARCHES.

13. Natural starches differ quite appreciably in their characteristics and properties and have consequently various advantages for individual applications. However, starches from different origins are used indiscriminately not only when their individual characteristics are identical but also when, these being somewhat different, the mandatory properties determining their uses result to be equivalent.

14. Rice starch has some highly peculiar characteristics. But it has some others which are entirely comparable to other starches. It is convenient to analyse all of them, in order to establish a scientific and technical basis for comparing the competitive position of rice starch in each particular starch market. Because of the noticeable differences between common and waxy starches, it is advisable to do the present comparative study discriminating both groups.

15. Common starches. As mentioned above, rice starch has the smallest granules of any of the common commercial starches (Table III). Out of these corn and sorghum are the more alike in size to it. There are, however, great differences in the total surface area among the three starches, as indicated by a rough ratio of 2.5:1:1. These differences are of importance in relation to some industrial applications (see Chapter 4). Differences in specific gravity are small, corn granules being the most heavy of the three starches and sorghum granules the least. As shown by the data given in Table III, commercial starches differ in their water vapor sorptive capacity. The differences among the cereal starches are small, rice, corn and wheat having the lowest sorptive capacities (at 92 % relative humidity).

16. The gelatinisation temperature of rice starch is high as compared with other common commercial starches (Table IV). Only that of sorghum is comparable. That of corn is somewhat lower. The gelatinisation temperature range of rice starch also is larger than that of corn or sorghum, undoubtedly because rice starch is markedly afected by variety whereas corn and sorghum are not. The heat of gelatinisation of starch in water increases in the order of increasing granule size and decreasing gelatinisation temperature (11). Consequently rice starch has a low value (5.7 cal./glucose unit (3)) as compared with other starches. Once more maize and sorghum are more similar to it than other common starches.

17. When an aqueous suspension of starch is heated to progressively higher temperatures, the granules imbibe water, swell and liberate a certain amount of solids. Each species of starch granules behaves somewhat differently. Rice starch swells rather slowly; the outline of its granules remains relatively visible and distinct even when cooked to high temperatures. Its swelling pattern is shown in Fig. 3 as compared with other common starches. It can be seen that corn and sorghum exhibit patterns entirely similar to that of rice, while other starches - the tuber starches - behave quite differently, swelling very much freely.

The amount of solids passing to the cooking water increases proportionally to the increase in volume; rice, corn and sorghum show again similar values (Fig. 4).

18. The behaviour of starch during pasting, cooking and cooling is of the greatest interest as it generally determines in a major part the uses of starch. Typical amylograms of rice and other common starches are given in Fig. 1. It can easily be observed that, with only minor exceptions, rice, corn and sorghum starches exhibit fairly similar behaviour. The peak viscosity irrespective of the temperature at which the pasting peak is attained, is moderate and practically the same for the three starches. The same happens with the ease of cooking, as indicated by the relationship of the viscosity at 95ºC to the peak viscosity, as well as with the stability on cooking given by the viscosity after 1 hour at 95ºC. The latter property is of special interest in relation with pressure and jet cooking, a usual practice in modern technology. The three starches have also a pronounced tendency to retrograde when cooled to 50ºC. Finally, the stability of the cooked paste toward shearing, desirable when the paste is to be agitated, stirred or pumped during processing, is fairly good in the three cases. Other starches, particularly tuber starches, exhibit quite different behaviour.

19. Transparency and clarity of pastes, gel strength, and freeze-thaw stability are other important properties of starches. Production of fruit jams, gum confections, and precooked frozen foods are examples of uses requiring appropiate selection of these properties. Aqueous starch suspensions are opaque, but they become more translucent as temperature increases. The various raw starches give characteristically different transparency/temperature curves. Rice and corn pastes have poor light transmission as compared with others, such as potato, tapioca or sweet potato (16). Generally, light reflectance is of greater interest than light transmission, because it is related to visual estimation of paste clarity whereas the latter is not. Rice, corn and sorghum form

opaque pastes whereas potato and other tuber starch give pastes of higher clarity.

20. Starch polymers, particularly amylose have a pronounced tendency to associate by hydrogen bonding and, at high concentrations, form gels. The gel strength is dependent on the extent of cooking the starch undergo during gel preparation, and on the starch itself. Osman and Mootse (18) investigated the effects of both variables on pastes of rice and other starches having similar maximum viscosity and found that cereal starches give stronger gels than tuber starches. They also found that gel strenght increases with cooking time and in the order rice, sorghum, corn and wheat, but with prolonged cooking a reversal of trends occurs, it appearing earlier for rice and wheat than for corn and sorghum (Table V).

21. Storage, particularly cold storage, and freezing result in increased tendency of starch molecules to associate; the starch losses its water-holding capacity with separation of watery liquid. Common (non-waxy) starches -rice, corn and sorghum included- are extremely susceptible to cold storage and freezing. Data of Hanson et al (19) given in Table VI show the separation of liquid upon thawing frozen sauces thickened with various starches after 1-2 months storage at -12°C. It will be noticed that about one half of the water content is released when thawing at 25°C. Retention of water is improved when thawing is at 100°C.

22. Finally, other properties such as the susceptibility of starch to alpha- and beta-amylolysis and the thermal decomposition, may be of interest in relation with some industrial applications. Leach and Schoch (13) investigated the solubilization of various granular starches with bacterial alpha-amylase and found that potato and arrowroot were the least attacked, tapioca the most susceptible, corn and sorghum (49.5 and 50.2 % solubilised respectively) were near to tapioca, and rice (32.6 %) was moderately resistant (Table VII). However, alpha-amylolysis of cooked

starches minimizes the differences as shown by the data of Otani and Takahashi (20) given in Table VIII. Please disregard absolute values which are dependent on experimental conditions and are not comparable to those given in the previous table. The important consideration is that rice and corn starches, when cooked, are attacked quite comparably by alpha-amylases. The limits of beta-amylolysis of autoclaved samples of rice and maize starches also have been reported to be practically identical (58.7 and 59.1 %, respectively, Table VII).

23. Cerniani (49) reported data on the thermal decomposition of various natural starches. Rice and corn starches (with 12.63 % and 11.10 % M.C. respectively) underwent sharp losses in water content at 170°C whereas potato starch did it gradually, showing defined losses at 160°C. The three starches developed browning with heating, but potato did it faster and to a greater intensity. Maximum dextrin yields were 83.26 % for corn starch, at 170°C, and 77.34 % for rice starch at 180°C.

24. Waxy starches. The characteristics and properties of waxy rice starch as compared with those of other waxy cereal starches are given in Tables II to VI and Figs. 2 and 5. The examination of these data reveals that, with the exception of the freeze-thaw stability, rice, sorghum and corn have fairly similar properties. The swelling power also is somewhat different. Rice starch sorbs water more rapidly than sorghum starch (Fig. 5). The gelatinisation temperature of the three starches is similar, although the range of variation is larger for rice starch (Table IV). As reported by Schoch (4), the three cited starches show a similar behaviour in the Brabender amylograph, with a high maximum viscosity, extensive loss of viscosity during cooking, and reduced retrogradation tendency (Fig. 2). Also, the pastes are clear, stringy and cohesive. In contrast, waxy rice starch has much greater freeze-thaw stability than waxy corn, waxy sorghum, and other starches (4)(18)(19)(48)(Table VI). This property confers to rice some advantages over other starches both of the common and the waxy varieties and makes it especially suitable for certain food uses.

3. DESCRIPTION OF RICE STARCH DERIVATIVES.

25. Starches of different origin provide a wide variety of choice for individual applications, but they are insufficient to cover the very many and specific needs of modern technology. Consequently, the starch industry has developed procedures to alter the characteristics of the natural starches to meet the requirements of special end uses. Quite a large number of modified starches and starch derivatives have been prepared, but only a comparative few have found general use. On the other hand, rice starch derivatives, with perhaps only some minor exception, are not manufactured on an industrial scale. The cost advantage held by corn starch (see Chapter 5) has dominate the market and besides this only a few starches of other sources, such as potato or sorghum, have been used as starting raw materials for modification or derivatisation processes. Consequently, open information on rice starch derivatives is meager. Procedures have been patented in which rice starch may be used. These are mentioned later on in Chapter 6. But this information covers a limited area. That the general properties of rice starch derivatives are not expected to be essentially different from those of the corresponding corn or sorghum derivatives, is indicated by the following facts: a) the three natural starches are alike in many of their properties, b) derivatisation causes specific modifications in the chemical nature of starch and consequently brings about specific qualitative changes in its properties, the extent of which can be controlled by adjusting processing conditions, and c) the scanty information on rice starch derivatives does not reveal a particular behaviour of rice starch in derivatisation processes. Accordingly, in the present Chapter, rice starch derivatives are described from a general viewpoint, with the prime purpose to show up the great diversity of "new" properties, suitable for "new" uses, that rice starch may get under adequate processing.

A. ETHERS

26. Cationic starches. They are prepared etherifying starch hydroxyls with adequate tertiary amines and converting the free base form of the tertiary amino ether into the cationic tertiary ammonium salt. These starch derivatives have lower gelatinization temperature and somewhat higher hot paste viscosity than the parent starch. Their cooked pastes remain fluid and relatively clear when held at room temperature. The positive charge taken in solution by the amino group makes this derivative substantive to negatively charged woodpulp fiber and accounts, as it will be seen later on, for its use in paper making. The so-called "onium" ethers of starch also are of interest. They contain quaternary ammonium, quaternary phosphonium, or tertiary sulfonium radicals, which carry a formal positive charge over the entire pH range, and become cationic polyelectrolytes in water (17).

27 Hydroxyalkyl ethers of starch. They are prepared by reaction of alkaline starch with lower alkylene oxides. Hydroxyethyl starch and hydroxypropyl starch, this to a lesser extent, are commercially important. At low degree of substitution (D.S.), they present reduced gelatinization temperature, and increased swelling and dispersion on cooking; their pastes are of greater clarity and increased cohesiveness, lowered tendency to retrograde and improved film-forming and adhesive qualities; ether linkages are resistant to acids, alkalis and mild oxidizing agents, a property which is advantageously used by the industry for further processing the starch derivative without modifying the substituent groups. Hydroxyethyl and hydroxypropyl starches are non-ionic, and hydrophilic. By increasing the hydroxyalkylation, a range in products with increasing degrees of water solubility can be obtained. Higher-substituted derivatives form translucent, colorless sols in cold water which do not retrograde, have good freeze-thaw stability, and resist biological spoilage. They also form films of good clarity, flexibility and smoothness (22).

28. Other starch ethers. Besides cationic and hydroxyalkyl ethers of starch alkyl, cyanoalkyl, carboxyalkyl and allyl ethers, among others, merit to be cited. It appears that, at present, none of them has gained wide commercial acceptance. The alkyl ethers, of which o-methylstarch is the most widely studied, have limited commercial interest. The alkyl ethers have centered the interest in the past, but its potential market fell to other products before they gained importance (23). Carboxyalkyl and cyanoalkyl starch ethers are now at the market and they deserve a short comment. The most common carboxyalkyl ether is sodium o-carboxymethyl starch, prepared by reaction of starch with sodium chloroacetate or other suitable agent. Low D.S. granular derivatives can be prepared which are not cold water soluble, but at D.S. higher than 0.1, water soluble products are obtained. The viscosity of carboxymethylstarch is very high, but it decreases significantly by the addition of electrolytes (21). Ultra centrifugal sedimentation patterns of carboxymethylated waxy and non-waxy rice starches have been reported (24). Ingestion of carboxylmethyl ethers of starch has been reported to cause gastric disturbances in humans and toxic effects in rats (21).

29. Reaction of starch with acrylonitrile in alkaline media form cyanoethyl ethers. With limited amounts of acrylonitrile and long reaction times granular products which gelatinise in water at pH 10-11 may be obtained whereas with excess acrylonitrile and short reaction times, water-insoluble products are prepared. A granular 0.05 D.S. cyanoethylstarch has been reported to be resistant to fungal growth and to withstand steam sterilisation without caking, by which its use as a base for surgical dusting powder has been recomended (21).

30. B. Esters

Starch acetates. One of the most common esters of starch is the acetate which can be prepared by acetylation with acetic anhydride either in alkaline aqueous solution for low degrees of substitution or in pyridine for higher degrees. The granules of a low D.S. starch acetate do not differ appreciably under the microscope from the parent starch. Staining with anionic or cationic dyes will neither show any difference. The solubility of starch acetates is dependent upon the D.S. and the D.P. Undegraded starch acetates are soluble in relatively few solvents, which include only those of a polar nature. Degradation increases water solubility. Starch acetates with acetyl contents up to 15 % have been reported to be soluble in hot water (50°-100°C); products with higher acetyl content (40 % or more) are insoluble in water but soluble in various organic solvents. Acetylation lowers the gelatinization temperature and increases the hot peak viscosity, dispersibility by cooking and sol clarity. Acetilation also minimises the tendency of starch to retrograde. Cloudiness and syneresis occurring in aqueous dispersions even of waxy starches can thus be eliminated. This is one of the properties of commercial importance of starch acetates. As low D.S. levels are sufficient for it, starch acetates in commerce are generally less than 0.2 D.S. (5 % acetyl). Much of the work on high D.S. starch acetates has been directed to find a substitute for cellulose acetate. Films of greater clarity, higher gloss, more flexibility, larger elongation before rupture, less cracking tendency, and easier solubility in water than the parent starch have been prepared (25). It has also been proved that both starch fractions produce clear, transparent, lustrous films, although only amylose give films of high tensile strenght and good extensibility. Similarly, starch acetates give moulded products which are clear, transparent and brittle, whereas amylose acetates may be moulded into strong and tough plastics (16). Therefore, highly substituted starch and amylopectin acetates are of low commercial interest; in contrast, highly substituted amylose acetates could be of high interest provided a low cost raw amylose would be available (25).

31. Inorganic esters of starch. The phosphate derivatives are the most important of this group; xanthates and sulfates are of lesser importance.

The xanthates are the S-metal salts of the O-esters of thiolthiocarbonic acid. Cereal xanthates have been developed using a process involving starch or flour, carbon disulfide and sodium hydroxyde. These cereal pulps can be oxidized to the xanthide and combined with wood pulp to enhance both dry and wet strength of paper and paper products. However, up to now, starch xanthates have not achieved commercial importance.(26). On the other hand, sulfate esters of starch appear to be available at the market. They form highly hydrophilic sols of excellent stability toward cold storage and freezing. However although there is some indication that starch sulfates are nontoxic, their use in food is not permitted. Starch sulfates possess anticoagulant and antilipemic activities, as well as some antipepsin activity. Information concerning this and other properties of starch and amylose sulfates has been compiled by Roberts (21).

32. Starch phosphates may be classified into two groups: the simple ester, formed by the reaction of the phosphate with a hydroxyl grouping on the starch molecule, and the di- and polyesters, formed by crosslinking between two starch molecules through a phosphoric group. According to the degree of phosphation, cold water swelling (0.07 D.S.) or cold water soluble starch monoesters (0.4-1.0 D.S.) can be prepared. The monoesters form long, cohesive pastes of higher viscosity, greater clarity and lower tendency to retrograde than those of the parent starch; these pastes have remarkable stability toward prolonged cold storage and toward freezing and thawing. Alkali metals decreases the viscosity of the pastes and soluble salts of polyvalent metals precipitate the starch from solution (27).

33. Cross-bonded distarch phosphate esters have different characteristics and properties. These are better described in the next section, as they are a particular class of cross-bonded starches.

C. CROSS-BONDED STARCHES

34. In general, cross-bonded or cross-linked starches are formed when starch reacts with polyfunctional compounds with more than one group capable of reaction. Cross-linking may be intermolecular and intramolecular in type. In the former case a marked increase in the average molecular weight results (28). Cross-linking in the granular starches reduces swelling and causes a higher resistance of the granule structure to disruption. This -and not the higher molecular weight- is the reason for the higher paste viscosity of cross-linked starches. The amount of cross-bonding has profound effects on water swelling, solubility, gelatinisation temperature and viscosity, At low degrees of cross-bonding, high viscosity pastes are obtained. As cross-linking increases, paste viscosity increases, reaches a peak and then decreases. At higher degrees of cross-bonding gelatinization in boiling water can be prevented. Extremely low degrees of cross-linking cause remarkable changes. As low as one cross-linking per 104 D-glucose units may bring about a marked increase in paste viscosity of granular (corn) starch (29); the cross-linked granules swell but do not rupture easily on cooking, forming a paste of increased viscosity. As low as one cross-link per 250 D-glucose units may prevent swelling of (maize) starch in boiling water. Cross-linking also increases stability to shearing action and resistance of starch to acid hydrolysis. Appropriate cross-linking result in cross-bonded starches which have remarkable stabilities to long and high pressure jet cooking at low pH (30), Cross-linking also reduces the tendency of starch pastes to retrogradation.

35. Amylopectin starch pastes have several disadvantages limiting their use in the food industry. These are partly its low stability to shearing action, but mainly its cohesive stringy nature. These disadvantages are easily overcome by chemical cross-bonding, one cross-link per several hundred glucose units being sufficient. Cross-linking also improves stability towards acids, but does not impair other desirable properties of waxy starches.

D. OXIDIZED STARCHES

36. Dialdehyde starch. Periodic acid oxidation of starch produces dialdehyde starch. The periodate ion reacts with the 2,3-glycol group of the D-glucose unit, cleavi g the C_2-C_3 bond and f rming two carbon,l groups. Part of these groups are free but other appear to be in hemiacetal linkage with primary alcohol groups and in hemialdal linkage by reaction with water (31). Dialdehyde starch is a fine powder which still retains some of the microscopical characteristics of the parent starch. However, it is not birefringent neither gives color reaction with iodine, and has few of the physical and chemical properties of the original product. Dialdehyde starch forms condensation products with proteins which undergo hardening and become resistant to putrefaction. The tanning and adhesive industry make use of it. Dialdehyde starch also reacts with polyalcohols forming acetal groups. This property is used to impart wet and dry strength to paper.

37. Hypochlorite-oxidised starches. Normally they are prepared suspending the starch in water and treating it with alkaline sodium hypochlorite. The commercially available product is a granular powder, extremely white if precautions have been taken during drying, as it is highly sensitive to heat. The microscopic appearance of the granules is little altered although some fissures and fragmentation can be detected. The birefringence, as well as other characteristics of the untreated granule such as the x-ray diffraction pattern are retained. However the alkaline hypochlorite oxidation brings about changes in the chemical nature of starch. Some carboxyl and carbonyl groups are formed and some rupture of the glucopyranose ring occurs; simultaneously a number of glycoside linkages are broken. The extent of changes is dependent upon reaction conditions, the pH being an operative factor. Hypochlorite-oxidised starches have lower gelatinisation temperature, hot paste viscosity and tendency to retrograde than the parent starch. On cooling, their pastes are of greater fluidity

and clarity than those of the untreated starch. They form clear, soft gels. Oxidized starch films are of a tough and horny character in comparison with the extremely brittle films of unoxidized starch.

4. DESCRIPTION OF THE DIFFERENT USES FOR RICE STARCH AND RICE STARCH DERIVATIVES.

Paper industry

38. The use of starch and starch derivatives in the paper industry is a subject covered by Nissen (32) in a recent work. An attempt is made here to briefly describe the most important uses and the starch products utilised. There are four main areas of application of starch in paper making. These are: wet end, size press, calender stack and coating. The application of starch at the wet end of the paper machine is intended to improve the strength and appearance of the paper. Nissen (32) defined the ideal wet end adhesive as that giving maximum strength and appearance improvement with maximum starch retention and minimum cost along with no deleterious side-effects. Potato, tapioca, sorghum and corn starches have been used but oxidized corn, and particularly cationic corn and potato, and dialdehyde corn starches are preferred because the improvement they bring, respectively, in dry and wet strength. Pregelatinized starches have been gaining acceptance. No single starch is equally suitable for all grades of paper. For the coarse grades - kraft wrapping and bag papers for instance - cationic corn is suitable. For fine grades - ledger papers for instance - lightly cooked native pearl starches are used. For high density sheets, oxidized starches are highly effective, acting also to increase the effectiveness of rosin size.

39. The main purpose of size press application of starch is to improve

writing and printing characteristics. For surface sizing applications enzyme-converted, corn and to lesser extent tapioca, potato and wheat starches and oxidized and hydroxyethyl derivatives are used. The mill equipment and the properties desired determine normally the type of starch to be used. Requirements range about 2-12 % solids, 50°-70°C, and 10-50 cps (Brookfield, No. 1 spindle, 20 rpm)(32).

40. In the calender stack a starch film is applied to improve surface characteristics. The type of starch to be applied varies with the fiber furnish, machine conditions and end use of the sheet. Thus, for heavy weight papers and linear board, starch that sets up rapidly is required whereas for cylinder boards, a low-viscosity starch with good film forming ability is desirable (32).

41. Adhesive requirements for paper coating have been described also by Nissen (32). Out of them high adhesive strength, stable viscosity and no side-effects on paper merit to be cited. Nevertheless, adhesive requirements are dependent on coating machinery and individual procedures. Starches used are varied: hydroxyethylated or oxidised products are used in brush coating, enzyme converted pearl corn starch in role coating, oxidized or enzyme-converted corn starch in air knife coating, and oxidised, hydroxyethylated, and enzyme-converted corn starches for trailing blade colors.

42. Rice starch derivatives having high water resistance, prepared by reacting starch with methylolated ureidopyrimidones, have been claimed to be useful in paper sizing (33). Also, polyacrolein derivatives of rice starch, useful as water-resistance adhesives in the manufacture of laminated fiber board and corrugated cardboard, have been patented (35). A survey of the literature on starch adhesives with applications for the paper industry has been reported recently (34).

Textiles

43. Starch and starch derivatives are used in sizing, finishing and printing. The largest consumption of starch is in sizing. Yarns are sized to improve their strength and abrasion resistance; also to reduce the fuzz of the yarn by cementing the surface fibers. Starch solutions used in sizing as well as the films they form must meet special requirements. These have been described by Compton and Martin (36). An important requisite for size solutions is to be of low cost, since large amounts are used. This is one reason for unmodified corn starch to be preferred over acid - modified or oxidized starches. Preparation of size solutions of constant quality must be easy, as it is carried out at the mill and mechanization of processing requieres uniform viscosity and solids content. In the slashing operation foaming problems may arise causing nonuniform size deposition. Slightly acidic pH of sizing solutions minimizes foaming, therefore buffered starch (pH 5.5. to 6.5) has some advantages. Pollution of streams by starch waste from sizing has become a problem in some cases and starch ethers with lower B.O.D., or other materials have been introduced. Out of the general properties of size films required for satisfactory weaving performance, the good adhesion between film and fiber appears to be the most important. The film also must be hard to resist abrasion but soft enough to flex and stretch as the yarn is processed. Size films must be easy to be removed by enzymes or acids during wet processing; due to it modified starches are more adequate than natural starches. Finally, it is also desirable that films be resistant to heat to prevent overdrying damage. In addition to the cited requirements, the preference for a type of starch is greatly based on cost and habitual practices as shown by the fact that in the U.S.A., corn starch is the most extensively used starch in slashing whereas in Europe potato starch is. Undoubtedly, rice starch is likewise suitable - cost aside.

44. Different rice starch products have found application in textiles. Some instances are: rice starch phosphates in the manufacture of wrinkle-free, fine-hand textiles from natural and regenerated cellulosic fibers (37); rice starches reacted with methylolated ureidopyrimidones, in sizing (33); rice starch polymers, prepared with polyacrylate or polymethacrylate, in finishing, and rice starch derivatives, obtained using acrolein, in stifenning textiles (35).

45. Natural rice starch has been traditionally used in laundry (4). The advent of synthetic fibers has decreased substantially this market. Recently a patent has been issued covering the preparation of a laundry starch composition which prevents sticking on the iron and is prepared by reacting poly (ethylen oxide) and rice starch (38).

Foods

46. Requirements for a food starch are varied and depend on the particular use for starch. They are described below. However, from a sanitation point of view both rice starch and rice starch derivatives must meet certain general requirements when intended to be used as foods and as ingredients in packaging materials for foods. The F.D.A., of U.S.A. has set standards in this respect (39). In the particular case of canning, the National Canners Association has also set standards for thermophille counts (40).

47. Baked goods. Starch has a diversity of uses in baking. It can be utilised as a carrier in baking powders, as an ingredient in pie fillings, icings, craker and cookie doughs, cakes and biscuits, and in operating procedures. In baking powders, starch acts as an inert dispersing agent protecting active ingredients (usually bicarbonate and acid) from moisture, thus avoiding weakening of gasing power. Rice starch has been reported to be well suited for this purpose (41). The starch used in pie fillings manufacture must meet several requirements, such as high viscosity, glossy appearance and stability toward high temperature, acids, shearing,

and storage. These have been described by Hamilton and Paschall (27). Unmodified starches do not meet all of them. The waxy starches although have some advantages, breakdown easily. Cross-bonded waxy starch phosphates have been reported to give good results (27). Waxy rice starch phosphate appears to be adequate for this purpose. Common rice starch is sensitive to direct heat and is not generally used in the preparation of fruit fillings; it is however used in the preparation of soft-filled pies (42). Stabilizers of various types are used in icings, with the purpose to absorb water by forming a gel and help to avoid the crystallization of sugar or surface stickiness in humid weather. Vegetable gums and corn starches are used; rice starch, particularly the waxy type, would probably be more suitable. Biscuits, cakes and the like require low protein content (≃ 7 %) flours to develop proper texture and eating qualities. From 5 to 15 per cent of the flour weight of corn and other starches is used to prevent the development of doughy textures (43). Dafaert (44) carried out a baking experiment with rice starch and noted that the "bread" from ordinary rice was hard and compact whereas that from waxy rice had risen beautifully, with a volume 4 times larger, and was extremely porous. More recently, Rotsch (45) reported that use of rice starch increases bread volume and improves crumb texture. On the other hand, the batter-mix process (46) opens new possibilities to rice flour and rice starch in bread making.

48. Canned foods. Most of the uses of starch in canned foods are based on the utilization of the properties of its pastes to thicken and/or modify the texture of foods. In the canning industry starches are used primarily in specialty type foods (condensed soups, bottled sauces, baby foods and specialty dinner products). The selection of the starch for a given application is complex. It depends on the texture and reology desired, the conditions of use, aging properties and taste requirements. Processing conditions are also considered. Good resistance to high temperature, stability toward shearing action and no tendency to retrograde are

properties generally required. The demand for these has been met partially by amylopectin starches. Unfortunately they have fragile granules, and the viscosity of their pastes falls on prolonged stirring or heating. In condensed soups, requiring extra-water to final preparation, this is unacceptable. This limits the use of waxy rice starch in spite of the excellent properties it has as thickener (18)(19)(48). A further inconveniencesis the cohesive stringy nature of the gel, which makes it unacceptable in certain food products. All these disadvantages have, however, been overcome in the cross-bonded starch phosphates without interfering with the desirable aspects of these starches. The extent of cross-bonding must be designed for specific uses. For example, more cross-bonding is required when food processing involves pressure-cooking than when it does not. Jet cooking requires even higher cross-bonding. In neutral or mildly acidic foods a starch of lower cross-linking is used than in acidic foods. Cross-linked waxy starch is particularly suitable as a thickener in Chinese foods because of the clarity, slime, and low gel tendencies of its pastes. It is also widely used in canned foods where a sauce is a component, such as spaghetti in tomato sauce. Another application is found in bottled sauces such as tomato ketchup. With cross-bonded acetylated starches, baby foods and fruit and cream pie fillings have good keeping quality under a wide range of temperature conditions. In the waxy cereal starches -corn and sorghum- this type of derivatisation is extensively used; waxy rice starch is equally adequate, but no commercial use appears to have been made of it. A recent patent (47) refers the uses of acylated cross-linked rice starch.

49. Frozen foods. Common cereal starches do not withstand freezing and thawing, which cause gel firming, opacity, grainy texture and liberation of water. Waxy corn and sorghum starches, being better, are not satisfactory because only resist a few freeze-thaw cycles. In contrast, waxy rice starch gives excellent results (18)(19)(48). It has been on the

market in Europe. Although waxy rice starch is affected by acids, the pH normally found in practice does not damage it. As reported by [illegible] (50) some objections, have however been reported on the effects of waxy rice starch on flavor. On the other hand, it is interesting to note that waxy rice flour has been proved to have better freeze-thaw stability than purified waxy rice starch (4). Because the cost advantage of the flour, this is a point to take into consideration. In fact, waxy rice flour has been commercially available in U.S.A. However the importance of waxy rice as a thickener has decreased with the advent of more suitable starch derivatives such as those containing phosphate, acetyl or propionyl groups in combination with cross-linking.

<u>Other food uses</u>. Many other food uses have been envisaged for starch, and it is more than likely that many of them hold for rice starch in natural or modified form, however this field has not been adequately explored. Starch finds one of its important applications in the manufacture of salad dressing. Starches give dressing the correct body, in addition to stabilizing the emulsions; they must withstand the attrition of the homogenizers and resist acids. Starch phosphates, cross-bonded starch or mixtures of cross-bonded and waxy starches give good results. Another area is in meat processing where starch serves as a binder and stabiliser. A recent patent (51) use rice starch as an hydrophylic adjuvant in the preparation of sausage casing materials. In candy making starch has several applications. Acid hydrolysed (corn) starch is the most commonly used but high amylose (corn) starch is showing promise in the manufacture of gum confections. Redried starch is used in molding; also, it is added to confectioners sugar to keep it from lumping. The combination of large surface area and strong affinity for moisture of starch granules, along with good edibility and low cost, determine largely the use of starch as moulds and moisture adsorbing agents, diluents, bulking agents and fluidifying agents. With the exception of price, rice starch has all of these properties.

Miscellaneous uses

51. The following are instances of the practically unlimited uses of rice starch and rice starch derivatives, of which only a few have been explored: explosives (11), flocculant for coal washing plants (52), dry lubricant for bobbinet machines (53), graft polymers (54)(55), oil well drilling (56), photographic film (specially purified rice starch for photographic uses is on the market in Europe), cigarette filter (57), and modified carbohydrate materials for use as tobacco substitutes for smoking (58). The most important and traditional use today is in cosmetics.

5. MARKETABILITY OF RICE STARCH AND RICE STARCH DERIVATIVES IN COMPETITION WITH OTHER COMPARABLE STARCHES

52. In the foregoing chapters, information has been presented showing that natural rice starches have a few peculiar properties which make them particularly appropriated for some specific uses-such as cosmetics and specialty foods. These account for a certainly limited market. It has also been discussed that natural rice starches have some general properties entirely comparable with those of corn and sorghum, which make rice suitable - or at least, expected to be suitable - for most of the same uses. This is especially true for the derivatives, the properties of which can easily be varied within a wide range controlling the extent and conditions of the derivatisation process. On the other hand, it will be seen later on (Chapter 6) that the manufacture of rice starch and rice starch derivatives present similar aspects to that of corn as it concerns with investment and production costs. Therefore, the mandatory factor determining the competitive position of rice starch and rice starch derivatives in the market is the price of the raw rice starch. In Table IX the approximate price of rice starch is given compared with corn and

other starches. Rice starch is about twice the price of corn. The reason is the cost of the original cereal as it is shown in Table X. The prices of rice in last years were abnormal because of production problems in Asia. But even considering normal years, rice is much more expensive.

53. It appears therefore that rice starch has no possibilities to compete with corn or other starches, provided the price of rice is not comparable with that of corn. An essential first step is the reduction the price of the starting raw material for rice starch manufacture. This means the need for an actually lowered cost of rice, but also a more complete utilization of the rice grain with higher returns in the rice processing plant. These aspects are discussed in Chapter 8.

6. MANUFACTURE OF RICE STARCH AND RICE STARCH DERIVATIVES

A. RICE STARCH

54. Commercial methods for the isolation of starch involve the following essential steps: a) steeping, b) grinding, c) removal of fiber, d) separation of starch and protein, and e) drying. A preliminary cleaning step to remove undesirable impurities from the raw rice to be used should be included. In the first step, rice -generally brokens- is soaked in an aqueous caustic soda solution to solubilise the protein and facilitate the liberation of the starch granules. Different operating conditions are used. The strength of the caustic solution is between 0.3 % and 0.5 % sodium hydroxide. The temperature ranges from room temperature (56) to 50°C (59). The total steeping time is usually 24 hours. The alkaline liquor is run off after a first steeping period and replaced by fresh solution; this operation can be repeated. In contrast, Zhusman (60) reports a steeping period of only 2 hours, with continuous circulation of the alkaline liquor through the rice mass, which can be stirred simultaneously. The steeping liquors run off are sent to the protein

recovery section. The softened rice kernels are then conveyed to the mills where they are ground with a small quantity of fresh soda solution. Another alternative is to wash the kernels with water prior to grinding (59)(60). Grinding is performed in suitable revolving disc or pin mills. After grinding, the starch slurry is further diluted with soda solution or water for removal of pulp. Separation of starch from the fibrous material is achieved by the use of shakers, reels static screens or centrifuges. Sedimentation of starch at pH about 10 is slow and, according to Zhusman (60), it can be accelerated by addition of sulfurous acid to the starch slurry leaving the mill. Saturated lime water has also being suggested (59) for diluting the starch slurry to assist in flocculating the fibrous material for retention on the screens.

55. According to Hogan (59), the process used in the U.S.A. prior to discontinuance in 1943, operated with broken rice which was steeped with water containing sulfur dioxide for 72 hours at 49°C. After steeping, the rice was ground in a Buhr mill, and passed through reels and over shaking screens to remove hulls and fibers; the starch slurry was made alkaline with sodium hydroxide and centrifugated. As reported by Zhusman (60) the use of sulfurous acid involves a series of problems such as long duration of the steeping time, heating of the soaking water, corrosive effects on metal, and harmful conditions of the operation. Also, as reported by Akher et al. (61), who studied comparatively the alkali and the sulfurous acid procedures, the highest yields and greatest purity for the rice starch are given by the alkali extraction.

56. The starch is separated from protein on a continuous centrifugal and finally purified and concentrated through hydrocyclones or further continuous centrifugals; then, the starch is dewatered and dried. The sequence of operations is varied and depends on the equipment facilities and the efficiency of same. A brief description of this part of the process, giving equipment used, flow-sheet, and composition of products

and by-products can be found in the paper of Zhusman (60).

57. "Crystal" starch, a commercial form of rice starch, is prepared from centrifuge cake which is pressed into cubes, wrapped in paper, dried, and the resulting blocks broken into dust-free lumps. Another alternative is to press commercial starch into dense boards and break them up.

58. The isolation of starch has also been accomplished - on a non commercial scale - by sonic vibration (62). By this action the non starch components are broken down, permiting operation with less than 50 per cent of the water usually necessary. Rice starch yields ranging from 54 to 64 % have been reported.

59. In a recent paper by Syfried (63) a review is given on the amount, concentration, and treatment of waste water in rice starch plant.

B. RICE STARCH DERIVATIVES

ETHERS

Cationic starches. Paschall (17) reviewed recently the production methods of cationic starches. According to this author, the preparation of tertiary aminoalkyl ethers is attained by treating an alkaline suspension of starch with a tertiary amine containing a beta-halogenated alkyl, a 2,3-epoxypropyl, or a 3-chloro-2-hydroxypropyl radical. Low D.S. granular ethers can be prepared commercially using an epoxyamine or halalkyl tertiary amine. At the completion of the reaction, the starch slurry is filtered, and the product washed and dried. In the preparation of high D.S., cold-water soluble, granular derivatives, the swelling of the starch granules should be inhibited using appropiate agents. By the action of a quaternary ammonium salt containing a 2,3-epoxypropyl or a 3-chloro-2-hydroxypropyl radical, on an alkaline slurry of starch quaternary ammonium alkyl ethers can be produced. These derivatives may also be obtained by quaternizing tertiary aminoalkylstarches with alkylating agents. The preparation of cationic starches containing primary and secondary amine groups generally present more problems than that of the tertiary amino and quaternary ammonium ethers.

61. Hydroxyalkyl ethers. Hydroxyethylstarch is prepared by the reaction between starch and ethylene oxide in the presence of aqueous alkali. Neutral alkali metal salts are used as swelling inhibitors (64)(65). Ethylene oxide is dissolved in the suspension. Temperatures usually not exceeding 50 °C are used. The commercial preparation of derivatives of D.S. lower than 0.1 is readily performed but that of higher D.S. presents filterability problems (22). The presence of a very small amount of sodium ethylene diamine tetracetate is claimed (66) to increase the efficiency of the utilisation of ethylene oxyde and prevents formation of dark coloured colloidal material during the reaction. A procedure of stabilisation against discoloration appliable to rice starch ethers has been patented (67). Hydroxyalkylstarch can also be produced by reacting dry starch containing alkali or a latent alkaline catalyst with ethylene or propylene oxide gas, as reported by Paschall (22) who reviewed the preparation methods of hydroxyalkyl ethers. Rankin et al. (68)(69) and Zusuki et al. (70) have reported on the influence of processing conditions on the properties of hydroxyethylated starches. Patents have been granted recently covering hydroxyalkylation procedures of starch but those specifically concerned with rice starch are meager. Mima and Yokoyama (71) prepared hydroxyethyl starch by treating gellated rice starch with pyridoxine and ethylene chlorhydrin.

ESTERS

62. Starch acetates. The preparation of starch acetates is covered by a

recent paper of Kruger and Rutenberg (25). Several chemicals have been used as acetylating agents, out of which acetic anhydride has generally been preferred. Rice starch acetates have been prepared using it (72) (73)(47). One of these patents covers the acetilation with acetic anhydride of an alkaline suspension of cross-linked rice starch subsequent to cross-linking with epychlorhydrin (47). The esterification can be carried out in alkaline solution, maintaining the conditions that favor acetylation over anhydride without appreciable hydrolysis of the starch acetate. The optimum acetylation pH is temperature dependent; at room temperature it is about 8. After completion of reaction, the starch slurry is acidified, filtered or centrifugated, washed and dried (74). Rice starch acetates have also been prepared by treating the starch with a mixture of acetic acid and acetic anhydride at 50°-75°C, in the presence of a catalyst (SO_4H_2, $ZnCl_2$, or $HClO_4$) and an organic liquid such as bencene, xylene or toluene, (72)(73). Acylation of starch by alkaline-catalysed transesterification with vinyl acetate has been used in the preparation of commercial starch acetates (25). The reaction which is carried out in alkaline pH requires the presence of water. The vinyl ester of acetic acid, has the property to form "in situ" during alkaline acylation the aldehyde corresponding to the acid. This fact can be used to introduce simultaneously cross-linking in the starch (47).

63. **Starch phosphates.** The starch-phosphate reaction has been carried out on a commercial scale by soaking the starch granules with the phosphate solution, separating the starch by filtration or centrifugation from excess solution, drying without gelatinizing the granules to a moisture content of less than 20 %, and then heating to reaction temperatures of about 120°-175°C (75). According to a recent patent (76) starch phosphates are prepared by spraying starch with the phosphate solution and then heating step-wise under vacuum.

64. The mechanism of the reactions giving simple esters or crosslinked phosphates is not well established; both classes of phosphates can occur together, and the reaction conditions determine the formation of one or the other. Generally, when simple phosphates are used, monoesters are formed under acid pH and crosslinked under more alkaline conditions. When complex phosphates are used, monoesters are formed under mildly alkaline pH and crosslinked under higher pH (77).

65. Methods have been developed to obtain starch phosphates giving pastes of increased viscosity (78)(75)(79). According to one patent (78) the starch phosphate mixture is preconditioned by heating it to 45°-90°C prior to dehydrating and final heating with this purpose. According to another (75) this can be attained by reacting starch granules and phosphate in a fluidised bed, passing through a stream of hot air or inert gas at 149°-190°C. As indicated by the authors, rice starch may be used.

CROSS-LINKED STARCHES

66. Mullinger (30) reviewed the preparation of cross-linked starch up to 1963. He listed numerous crosslinking agents, out of which phosphorous oxychloride, epychlorhydrin and trimetaphosphate have been widely used. Recent patents cover the use of paraformaldehyde in the presence of a controlled amount of mineral acid (80), and metaphosphate in the presence of cloroacetate in alkaline pH (81). A Belgian patent (47) describes the preparation of cross-linked rice starch. The procedure can be summarised as follows: Rice starch is suspended in a polar solvent and an alkaline catalyst is added. The cross-linking reaction is preferably carried out with acrolein phosphorous oxychloride or epychlorhydrin, at a pH usually ranging from 9 to 13. After completion, the reaction is stopped by lowering the pH with a strong mineral acid such as hydrochloric or sulfuric

acid. When acrolein is used, acidification is not enough to stop the reaction, and this is accomplished by adding sodium bisulfite. After subsequent dewatering and washing, the product is finally dried.

OXIDIZED STARCHES

67. Dialdehyde starch. Tegge (82) and more recently Mehltretter (31) reviewed the laboratory-scale and industrially-scale preparation of dialdehyde starch. Starch dialdehyde is now manufactured by treating starch with periodic acid, which is reduced to iodic acid during the reaction. Iodic acid can be reconverted to periodic acid by electrolysis and re-used to convert another batch of starch to the dialdehyde. This cycle forms the basis of a two-stage process developed by Pfeifer et al. (83). This process employs periodic acid prepared from crude iodine. An electrolytic cell is used to convert the iodine to iodic acid, then to periodic acid. The used oxidant solution from a previous run is electrolysed in the cell too to regenerate periodic acid to the desired level. The oxidant is pumped to the oxidation tank, temperature is adjusted, and starch to be oxidized is added. After the reaction is completed, the liquor containing iodic acid is removed and sent to the cell system for re-use. The starch slurry is filtered or centrifugated -the supernatant is returned to the cell- washed, and dried. The process can be continuous. More recent papers describe improved electrolytic cells (84)(85).

68. The paper of Pfeifer et al. (83) describes the production of dialdehyde starch on a pilot plant scale and reports the influence of factors such as temperature and pH of reaction, mole ratio of periodic acid to starch, and concentration of periodic acid. A recent paper of Fleche (86) is of interest in this connection as it deals with the conditions of reaction and determination of degree of oxidation of dialdehyde starch. Although as far as it known, no paper reporting the

adequacy of rice starch for this derivatization process has been reported, the experience with corn, sorghum and wheat starches suggests that rice is equally suitable.

69. <u>Hypochlorite oxidised starches</u>. They are prepared by treating a suspension of starch granules with a solution of an alkaline hypochlorite. After completion of the reaction, the suspension is neutralised with acid, and the starch is washed to remove salts and then dried. Hullinger (87) gives a detailed description of the procedure on a laboratory-scale basis, and Scallet and Sowell (88) describe briefly a typical commercial process. The degree of oxidation can be varied over a wide range by suitable modification in hypochlorite concentrations, reaction time, pH, and temperature. In a recent patent (89) flow sheets and graph relating the characteristics and properties of oxidised starches with reaction time and varying conditions are given. The alkaline hypochlorite oxidation of starch catalysed by multivalent salts, such as $MgCl_2$ or $CuSO_4$ is claimed to result in whiter oxidised starches of higher viscosity, transparency and dispersion in water, with less degradation (90)(91).

7. THE EFFECTS OF THE NEW HIGH-YIELDING VARIETIES OF RICE ON THE RICE STARCH PROCESSING INDUSTRY.

70. The widespread cultivation of high-yielding varieties has made self sufficiency a possibility in the most Asian countries in the 1970's. Although at present the Asian region as a whole has not reached the desired situation, it is well known that in some regions expanding output has created surpluses (92). This situation may be a common one in the near future. It is now generally accepted that the successful development of improved rice varieties has opened a new area of problems. A recent

paper by Barker (93) deals with this subject. As reported by this author, a major portion of the rice produced in Asia is consumed on the farm. It can not be expected that rice consumption increase parallels rice production increase. Furthermore, the bulk of the increased production should enter the market channel. But, the market capacity is limited. This is true for both the domestic and the export markets, The first will increase slowly; consumer benefits from abundant supplies will be distributed among other items or conveniences. Concerning the export market, it will be remembered that only about 2% of the world production is traded internationally and some countries approaching self-sufficiency are looking to this market as a source of export earnings.

71. A decline in price is expected to occur, this, by itself, will affect little to the competition in the trade. It however may affect the economy of the producer, who, on the other hand will not alter his plans of higher production because of a change in price.

72. Without any doubt, an important alternative to the solution of the problem is to expand the domestic and export market for rice. A stronger rice demand will support the actual expansion of production and will contribute to attain the ultimate objective of the new high-yielding varieties: to rise the life level in rice eating countries.

73. To expand the domestic and export market for rice, the improvement of drying, transportation, storage and milling facilities is a necessary step. The economics of handling and processing depends upon the techniques used. But the improvement in equipment and technology should not be based on the to-day's market requirements. It is very likely that a change in quality standards of both the local and export markets will occur, it probably being greater in the domestic trade. Such changes should be considered and solutions anticipated. The demand for high quality rice is expected to increase; that of rice for specific uses also. Consequently,

new and more profitable alternatives are expected to be needed for expanding the domestic and export market for rice, particularly for medium and low- quality rice. The latter can very well be essential for further increasing the rice production and improving handling and processing.

74. Rice starch processing industry can have a role in expanding the markets for rice. Positive reasons are: declining prices of rice, expected surpluses of low- and medium eating quality rice, higher benefits from more elaborated items, and source of foreign exchange. Along with positive reasons, there are negative ones. The most important, both from the economic and social points of view, is not to use the potential nutritive value of rice to feed rice-eating people adequately. As to eat enough rice or to have surpluses of it does not mean to solve the problem of malnutrition.

75. Common processing of grains to beneficiate starch does not appear to be a good means to save the nutritional elements of rice for human food . Plans have to be elaborated looking for a compensated solution to the problem directed to: 1) Beneficiate the nutritive potential of rice to supply food for humans, specially for children, and 2) Produce starch and starch derivatives but also non conventional products from rice to open and expand domestic and specially export markets. Some ideas related with these purposes are presented in the following chapter.

8. PLANT FOR THE INTEGRAL UTILIZATION OF RICE.

76. Should a plant for the production of rice starch and rice starch derivatives be an integrated part of a rice mill or a completely separate unit? Some considerations should be made before answering the question.

77. The commercial isolation of rice starch does not beneficiate the nutritive constituents of rice with their whole original value for human feeding. The gluten is segregated as a byproduct of limited value, despite it being (along with another nutrients) the most valuable part of the kernel. On the other hand, the presence of these nutritive constituents in rice is largely responsible for the difficulties arising during the starch isolation process.

78. Recent knowledge on the distribution of chemical constituents within the rice kernel (96) has shown new approaches for the utilization of the grain which may also be extended to the isolation of starch. Curves in Fig. 6 show the general distribution patterns of major constituents in rice. There are two main types of curves. One type, represented by starch, which shows a continuous increase in concentration toward the center of the kernel and a second type, including the rest of the constituents considered, which shows an inverse pattern. Two classes can be distinguished within the latter group of curves, One class showing an uninterrupted decline in concentration from the periphery to the center of the kernel - as the curves for ash and fiber content do - and the other increasing first up to a peak in outside layers and then decreasing consistently toward inner regions - fats and proteins show such a distribution.

79. The especial distribution of constituents in rice allows to fractionate the kernel of brown rice into three fractions with quite different composition and properties. The outermost fraction the bran which may account for about 5-7 % by kernel weight, is, as it is well known, rich in protein, vitamin, fat, fiber and ash (Fig. 6 zone A). Its high fiber content and the unstability of its fats make it inadequate for human feeding. When it is stabilized by appropriate methods, it is

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* Rice gluten (with about 80 % protein content) is sold in Europe at about 0.75[illegible] $ per kilo protein content (10[illegible]).

a valuable feed stuff. Recently, Deshikachar and Parpia (95) have reviewed the stabilisation of rice bran. In recent investigations carried out at the author's Institute, an improved process and machinery for the in-plant estabilisation of bran have been developed, and they are being introduced commercially.

80. The next kernel fraction -zone B in fig. 6- is of the greatest interest as it is a highly nutritional feed, very well appropriated for children. It contains high levels of nutrients, mainly proteins and vitamins, which should not be wasted particularly in developing countries where rice is the staple feed.

81. Finally, the inner portion of the kernel -zone C, Fig. 6- has an unusual composition, particularly interesting for rice starch production. The fat, fiber and ash contents are extremely low, generally less than 0.1 %; the protein content also is unusually low and the starch content amounts near 95 % (d.b.). Undoubtedly, this is an excellent starting material for the commercial isolation of rice starch.

82. The unusual composition of the inner fraction of the kernel makes it suitable for other uses. Thus, by simple grinding, a "special rice flour" is obtained which may be used in some cases as a substitute for rice starch or other cereal starches. Moreover, the cited inner fraction of the kernel can be readily converted into convenience rice products with new characteristics, by treatments essentially identical to those used in the preparation of rice starch derivatives. The changes in water absorption, cohesiveness, texture, stability toward high temperature and cool storage, etc., that such treatments can cause in both the residual rice kernel or its flour open new possibilities for the utilisation of rice, and new markets too.

83. Fig. 7 shows the flow-sheet diagram of a plant for integral utilisation

of rice, based on the possibilities commented above. Paddy is fed to rubber roll huskers, after a previous dry cleaning. The hulls may be used as a source of energy for the plant. Cargo rice is undermilled, removing the 5-7 per cent by kernel weight, and the bran is subsequently stabilised to be used as cattle food. Undermilled rice is conveyed to the whitening machines for deepmilling. A premium grade high protein flour can be produced using head rice. Brokens or mixtures of heads and brokens can be used to obtain ordinary high protein flour. About 10-15 per cent by weight of the undermilled kernel can be removed as rice flour. This should be converted into convenience rice products such as ready to eat extruded products, biscuits, milk-like products, precooked flour, etc. These should be intended for the domestic market, which should be adequately explored to determine its needs and possibilities in this respect. Deepmilled head rice and/or brokens can be sent to the starch plant. Alternatively, deepmilled head rice can be converted into convenience rice products as cited above, and brokens can be ground into "special rice flour".

84. It is thought that such a plant has more economic advantages and satisfy better the social needs in developing countries than a plant intended only for the production of rice starch and rice starch derivatives.

85. The plant for integral utilisation of rice's complex and its whole equipment and size needs depend largely on the capacities of several market sectors - rice, food stuff, protein rich foods, starch and starch derivatives. The country where the plant should to be located has to be taken into consideration too. These aspects of the problem deserve a separate study.

9. **POTENTIAL FUTURE DEVELOPMENTS.**

86. The field of application of starch and particularly of starch derivatives is practically unlimited. Economy is expanding the world over and demands for starch products satisfying special requirements for industrial applications are progressively increasing. This has been a powerful stimulus for research, and new derivatives for new uses are emerging constantly. The combination of derivatisation treatments is proving to be highly promising and the high amylose cereals have opened new interesting lines. The high D.S. derivatives are expected to play an important role when present processing difficulties be overcome. These areas have been approached only in relatively recent years and much remain to be done to attain the very many posibilities of utilisation that they offer.

87. In the rice starch industry, similar perspectives are expected. Moreover, the availability of common, waxy and high amylose, rices, along with the wide varietal differences within each group, make this cereal the source of the greatest diversity of natural starches and starch derivatives, which deserves to be adequately investigated and utilised.

88. As cited elsewhere (Chapter 8), the derivatisation of rice starch "in situ", i.e., in the rice kernel, is another area which also merits to be adequately explored.

89. Efforts are being made to improve rice handling and processing in Asia and their results will have a favourable incidence in the rice starch industry, from both the technical and economical points of view. Wet fractionation, non sofisticated techniques are proving to be highly promising to achieve a more complete utilisation of rice milling by-products. Already identified are a series of fractions which might be designated

as high-fiber, low-protein fraction; low-protein, high starch fraction; and low-starch, high-protein fraction. These techniques may readily be introduced in the starch plant, thus increasing substantially the possibilities and the economies of the operation.

90. In summary, the rice starch industry, adequately reoriented, can afford an important contribution to the so called "industrial revolution" needed to complement the "green revolution".

10. EQUIPMENT AND ECONOMICS OF THE PLANT FOR INTEGRAL UTILIZATION OF RICE.

91. As described previously, the plant for the integral utilization of rice comprises: a) rice mill, b) starch plant, c) derivatization plant and d) other processing facilities for the stabilization of bran, and the manufacture of high protein rice foods.

92. The rice mill is a conventional milling unit. However, due to the fact that high yields of brokens are not a disadvantage and that there is no need for the milled products to be graded, the milling plant is a highly simplified one.

93. The starch plant is specially intended to process deepmilled rice[a]. The unusual composition of this product allows for further simplification of the plant - such as reduction in fiber separation facilities. Fig. 8 shows the flow diagram of the plant. It consists of: a) Silos (S-800) for reception of rice and scales (not drawn) for weighing of the input to the

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[a] To be transformed into an ordinary starch plant, additional equipment should be installed rather than substituted for.

plant. b) Steeping system composed of tanks (S-100), pumps (S-101) and heat exchangers (S-102); evaporators (E-100) are also included. c) Wet-milling facilities comprising mills (M-200 and M-500) and sieve-separators (M-100 and M-400). d) Gluten section composed of centrifugal separators (G-100, G-200 and G-300), rotary drum filter (G-500) and dryer (G-600). e) Starch section consisting of dewatering centrifuge (D-100) and drying units (flash dryer, D-300).

94. The starch derivatisation plant has been designed to fulfil requirements for several derivatisation processes. Only minor additions are needed to satisfy the special requirements of some derivatisation processes. The manufacture of starch dialdehyde is one instance; the electrolytic cell and evaporator for the periodic acid cycle would be necessary additional equipment. These have not been included here. As shown in Fig. 9 the plant is composed of: a) Reagents preparation and metering section (P-100, P-200 and P-300). b) Reactors battery consisting of tanks (P-400) equipped with agitators and heaters, and appropriated pumps, piping and valves to enable the system to operate batch-wise or continuously. c) Purification facilities comprising rotary drum filters (P-500 A) and washing tank (P-600). d) Dewatering and drying facilities comprising rotary drum filters (P-500 B) or dewatering centrifuge, and drying units - flash dryer, P-700, and rotary drum dryer, P-800.

95. The profitability of the plant for integral utilisation of rice is highly dependent on the raw material price, which makes up about 70 % of total processing costs. The present price of rice is not advantageous for starch production (see Chapter 5). Therefore, when assessing the economics of the plant, two different bases should be considered: A) To assume that the plant operates buying the rice at the present price. Then, the prices at which the manufactured products should be sold have to be calculated. B) To establish reasonably competitive prices for the manufactured products

and then, to determine the maximum price of the rice to operate with profitability.

96. When calculating the operating costs and the revenue to assess the economics of the plant in each case, the following assumptions have been made:

1) Products generating incomes. Products, and their production given as percent brown rice weight, are:

Stabilised bran	5.0 %
High protein rice foods . .	18.3 %
Rice starch	12.0 %
Rice gluten	2.6 %
Rice starch derivatives . .	62.0 %

2) Prices. Prices common to both alternatives (A and B) are: a) Stabilised bran, 57.1 US$/ton. b) Rice starch, 176 US$/ton (it is expected that rice starch will have to be sold at a price similar to that of corn starch). c) Rice gluten, 250 US$/ton. The average prices of high protein rice foods and rice starch derivatives are commented later on.

3) Operating costs. They comprise raw material, wages, overhead salaries, power, water, fuel oil, and other, as well as amortization of total investment within eight years.

97. Profitability of the plant. Table XI shows the investment, costs, revenue and profits of a plant for integral utilisation of rice operating under conditions established for alternatives A and B. Two production capacities have been considered in each case: 25.000 and 50.000 tons paddy/year.

98. Alternative A: At the fixed present price of rice (176 US$/ton cargo rice) good profitability (12 % profits on costs basis) is reached if the high protein rice foods are sold at an average price of 343 US$/ton and the starch derivatives at 324 US$/ton. The latter can be lowered to 299 US$/ton if the capacity of the plant is 50.000 ton paddy.

99. Alternative B: Assuming 285.7 US$/ton as an acceptable average price for high protein foods and rice starch derivatives, and the same profitability as before (12 % profits on cost basis), the price of the rice should be: 148.1 and 158.1 US$/ton cargo rice for the 25.000 and 50.000 tons paddy plants respectively.

100. It is thought that the suggested plant for integral utilization of rice is actually feasible. However, a pre-investment study, including pilot plant work and marketing, is necessary to evaluate more accurately the factors influencing the economic results, in order to appropriately select the terms for optimum operation of the plant.

ACKNOWLEDGEMENTS

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Many persons have contributed, either directly or indirectly, to gather the background information upon which the present paper has been written. To all of these people the author also is deeply indebted.

11. LIST OF TABLES

TABLE I

Hygroscopic equilibria at 20°C of rice starch.[a]

Relative humidity	Adsorption (%, wet basis)	Desorption (% wet basis)
20	5.1	5.9
35	7.9	9.2
45	9.4	10.5
60	12.7	14.0
79	15.2	16.1
90	24.6	24.8

(a) Data taken from (7).

TABLE II

Minor constituents of rice starch.[a]

Constituent	Rice starch	Waxy rice starch
Protein (%)(Nx5.95)	0.13 - 0.53	0.05 - 0.51
Fat (%)	0.45 - 0.87	0.10 - 0.12
Ash (%)	0.28 - 0.65	0.15 - 0.36

(a) Data taken from (11) (16).

6. 8. 73

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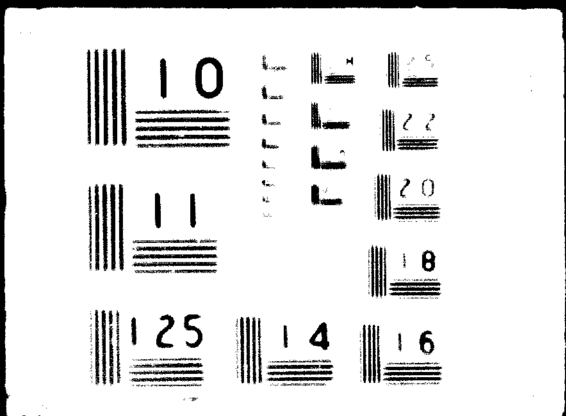


TABLE III

Physical characteristics of rice starch as compared with those of starches of other origins.

Starch	Size (μ)(a)		Surface area (cm^2/g) (b)	Sorptive capacity (92 % r.h.) (c)			Density (g/cc) (d)	X-ray pattern (e)
	Range	average		Minimum	Maximum	Average		
Normal:								
Rice	2-10	4.8	8,000	24.20	25.49	24.84	1.510	A
Arrowroot	-	-	-	26.62	27.42	27.15	1.510	C
Corn	5-25	15	3,077	24.34	24.82	24.55	1.517	A
Potato	15-100	-	853	31.62	32.99	32.30	1.511	B
Sago	-	-	-	26.16	26.68	26.46	1.494	-
Sorghum	6-24	15	-	-	-	-	1.500	-
Sweet potato	-	-	-	25.18	25.33	25.26	-	A
Tapioca	5-35	20	-	25.22	25.99	25.62	1.521	A+C
Wheat	-	-	1,907	24.34	24.43	24.38	1.542	A
Waxy:								
Rice	2-8	4.7	-	-	-	-	1.480-1.496	A
Maize	-	-	-	-	-	-	1.480	A
Sorghum	4-24	-	-	-	-	-	1.490	A

(a) Data taken from (3)(10)(14)(94); (b) id.,(3)(11); (c) id.,(12); (d) id.,(2)(13); (e) id.,(12)(16).

TABLE IV

Gelatinization temperature of rice starch as compared with starches of other origins.

Starch	Gelatinization temperature (°C)[a]
Normal:	
Rice	61-78
Corn	62-72
Potato	56-66
Sorghum	68.5-75
Tapioca	58.5-70
Wheat	52-63
Waxy:	
Rice	60-75.5
Maize	63-72
Sorghum	67.5-74

(a) Data taken from (2)(6).

TABLE V

Pasting characteristics of rice starch as compared with starches of other origins.[a]

Starch	Concentration of paste (%, d.b.)	pH of paste	Maximum viscosity of hot - paste (g.-cm.)	Initial rise in viscosity	One-half maximum viscosity	Maximum viscosity	Maximum viscosity +5 minutes	Maximum viscosity +20 minutes
Normal:								
Rice	5.49	6.2	101	0	15	31	71	30
Corn	4.90	5.6	113	10	19	52	121	14[illegible]
Potato	1.96	6.6	105	0	0	0	0	0
Sorghum	4.66	5.5	110	0	12	76	124	136
Tapioca	3.54	6.2	108	0	0	0	0	0
Wheat	6.44	6.2	105	41	123	345	520	440
Waxy:								
Rice	3.13	6.0	110	0	0	0	0	0
Corn	2.98	5.8	105	0	0	0	0	0
Sorghum	3.42	5.9	108	0	0	0	0	0

(a) Data taken from (18).

TABLE VI

Liquid separation on thawing sauces, thickened with various starches and flours (a) (b).

Thickening agent	Thickness of sauce (line spread)	Liquid separation (c)	
		25°C thaw(%)	100°C thaw(%)
Common starches:			
Rice (Colusa variety)	23	45-50	0-14
Corn (small granule)	24	46-61	21
Potato	23-24	50-65	-
Sago	24	50-56	4
Sorghum	22-23	49-63	13-19
Sweet potato	22	53	10
Tapioca	21-26	31-53	0
Waxy starches:			
Rice (Mochi Gome variety)	22	37	0
Rice	28	4-10	0
Corn (W M 42 Iowax 1)	21-22	17-55	0
Corn (Amioca, Clear Gel)	22-26	49-63	0
Corn (White)	25	48	0
Sorghum	25	45-59	0
Waxy cereal flours:			
Rice (Mochi Gome variety)	24	0-26	0
Corn (White)	25	38-50	0
Sorghum	28	51-59	0

(a) Data taken from (19).
(b) Frozen storage: 1-2 months at -12°C.
(c) Sauces thawed at 25°C reached a temperature of approximately 21°C; sauces thawed at 100°C reached a temperature of approximately 93°C.

TABLE VII

Susceptibility of various starches to alpha - and beta-amylase attack.

Starch	Starch solubilised by alpha-amylase(%)(a)(b)	Limits of hydrolysis by beta-amylase(%)(c)(d)
Rice	32.6	58.7
Corn	49.5	-
Maize	-	59.1
Potato	18.4	62.6
Sorghum	50.2	-
Tapioca	55.7	-
Wheat	48.5	65.4

(a) Data taken from (13)
(b) Bacterial alpha-amylase, 0.5 % enzyme, 24 hours' digestion at 50°C.
(c) Data taken from (11).
(d) Hydrolysis of autoclaved starch by barley beta-amylase.

TABLE VIII

Saccharification of cooked starch by Taka-amylase.[a]

Steam pressure Kg/cm²	Saccharification[b] rate (%)		
	Rice	Corn	Potato
2.1	21.0	27.8	18.5
2.8	33.8	28.3	18.9
3.5	32.9	32.9	22.9
4.2	34.8	37.5	25.6

(a) Data taken from (20)

(b) 0.5 hrs.

TABLE IX

Prices of various starches.[a]

Starch	USA	Sweden	France Export	France Import	Germany	Spain
Rice	0.22-0.26	0.41	0.48	0.3	0.5-0.55	0.28-0.31
Corn	0.17	0.11	0.09	0.13	-	0.17
Potato	0.17	0.1	-	-	-	0.20
Wheat	-	0.16	0.16	-	-	0.18-0.21

(a) U.S. Dollars / Kg.

TABLE X

Prices of rice and corn.[a]

Year	Brown rice[c]	Milled rice[c]	Broken rice[c]	Corn[b]
1965	0.123	0.135	0.094	0.057
1966	0.153	0.163	0.124	0.058
1967	0.217	0.220	0.156	0.056
1968	0.204	0.200	0.149	0.057
1969	0.176	0.181	0.112	0.066

(a) U.S. Dollars / Kg

(b) According to F.A.O. (101).

(c) " " (102).

TABLE XI

PROFITABILITY OF A PLANT FOR INTEGRAL UTILIZATION RICE

	PLANT I 25,000 Ton. paddy/year	PLANT II 50,000 Ton. paddy/year
	1,000 US$	
Investment	1,278	2,245
Alternative "A" (1)		
Costs	5,420	10,277
Revenue	6,070	11,510
Profits	650	1,233
Alternative "B" (2)		
Costs	4,782	9,564
Revenue	5,356	10,712
Profits	566	1,148

(1) Rice price: 176 US$/ton. cargo rice
High protein rice foods: 343 US$/ton
Rice starch derivatives: 324 US$/ton. Plant I; 299 US$/ton. PLANT II.

(2) Rice price: 148.1 US$/ton. cargo rice, Plant I; 158.7 US$/ton. cargo rice, Plant II.
High protein rice foods: 285.7 US$/ton.
Rice starch derivatives: 285.7 US$/ton.

12. LIST OF FIGURES

Fig. 1

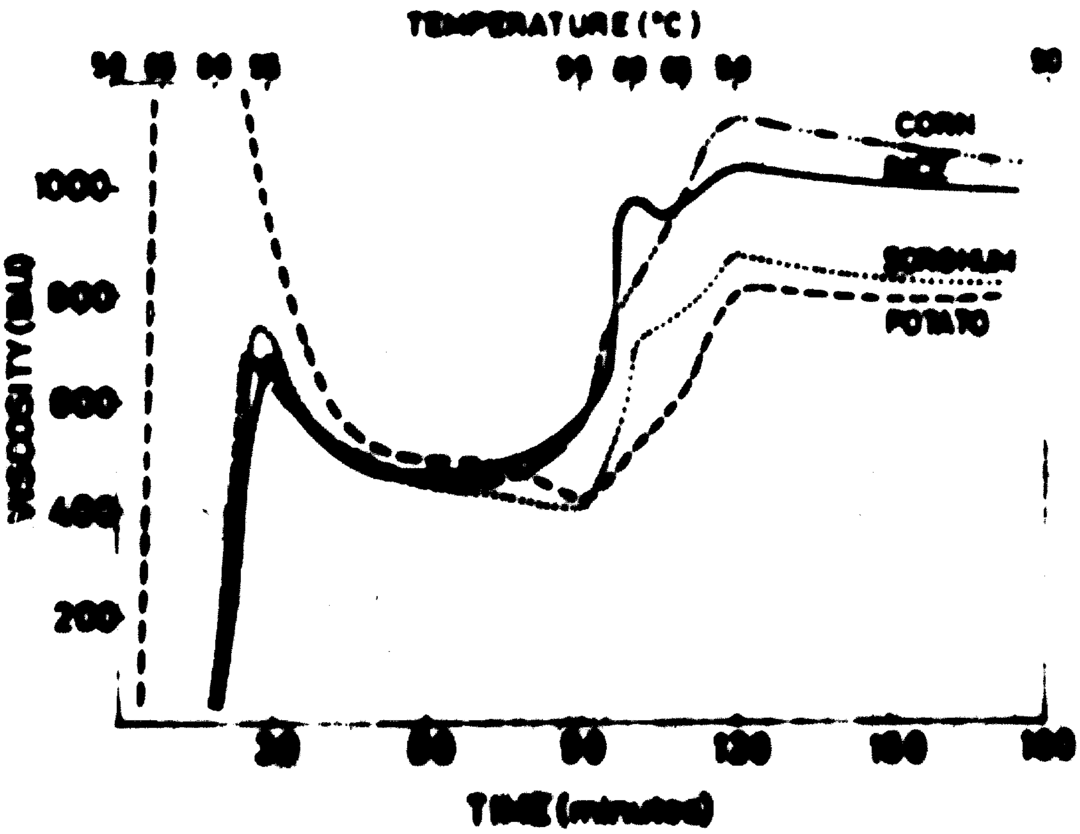

TEMPERATURE (°C)
CORN
RICE
SORGHUM
POTATO
1000
800
600
400
200
VISCOSITY (BU)
30
60
90
120
150
180
TIME (minutes)

Fig. 2

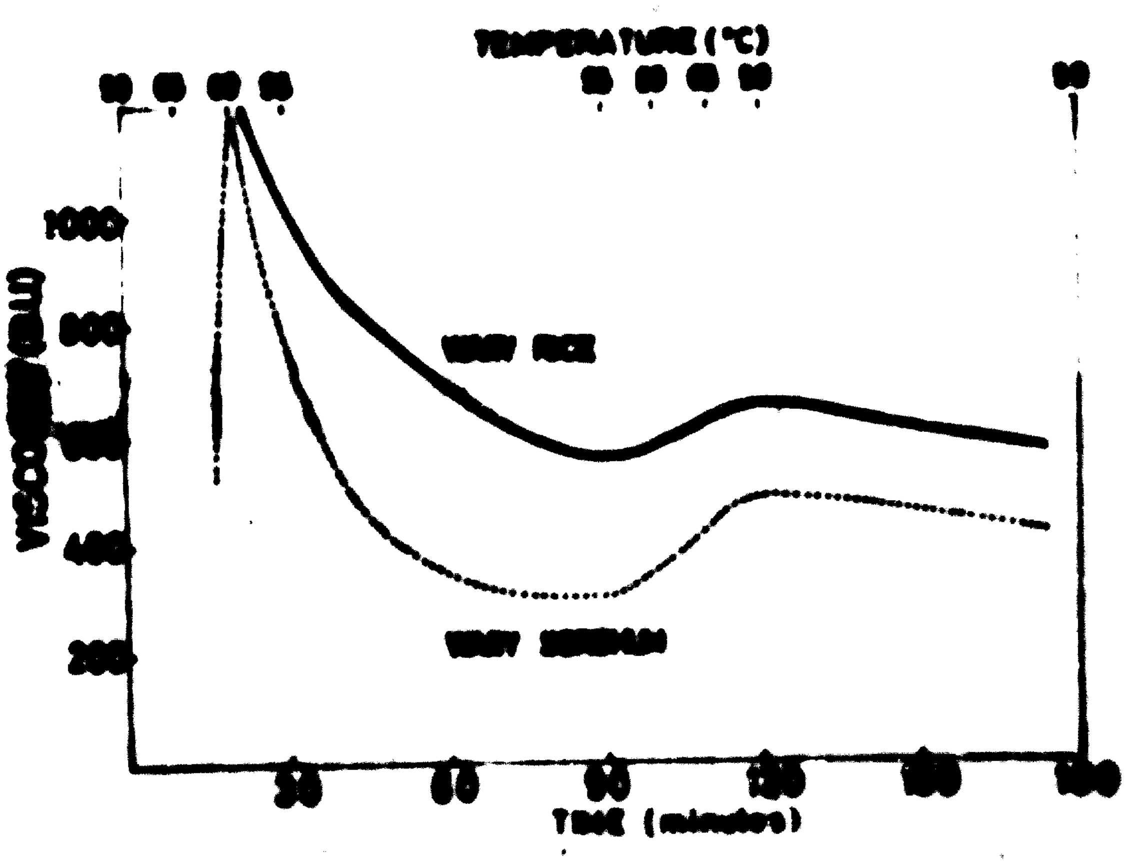

TEMPERATURE (°C)
1000
800
600
400
200
VISCOSITY (BU)
WAXY RICE
WAXY SORGHUM
30
60
90
120
150
180
TIME (minutes)

Fig. 4

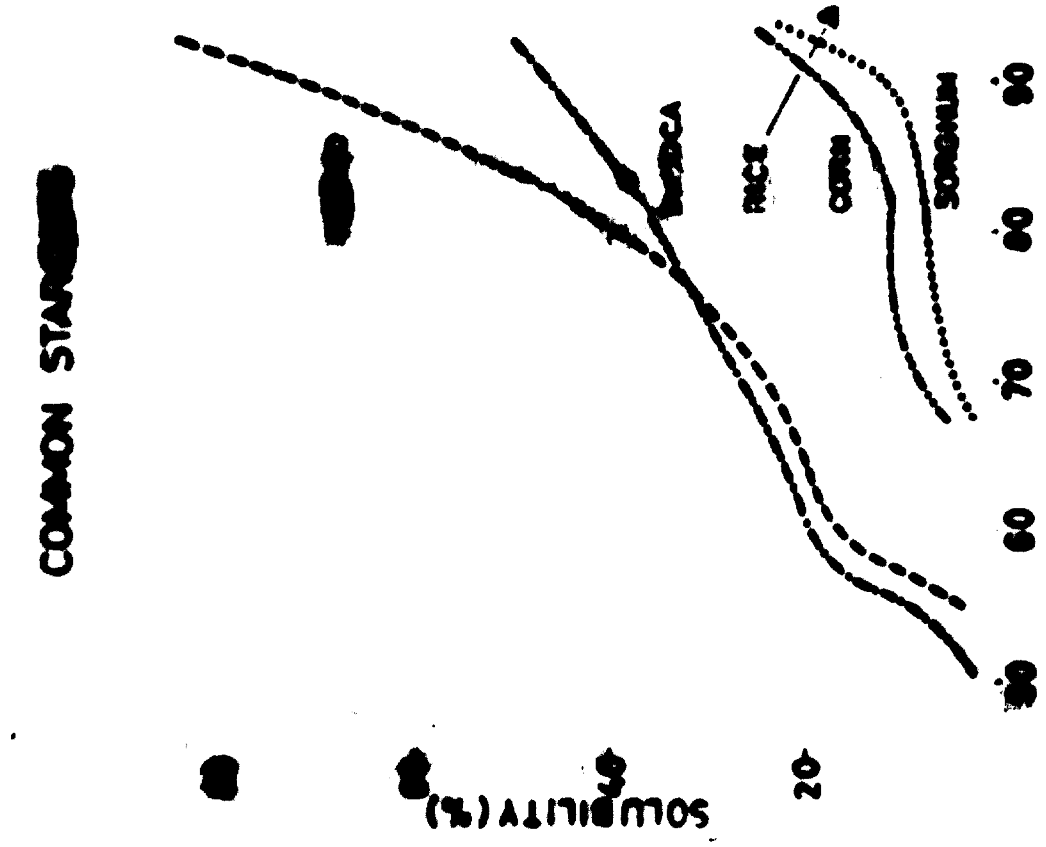

COMMON STARCHES
SOLUBILITY (%)
20
TAPIOCA
RICE
CORN
SORGHUM
50
60
70
80
90
TEMPERATURE (°C)

Fig. 3

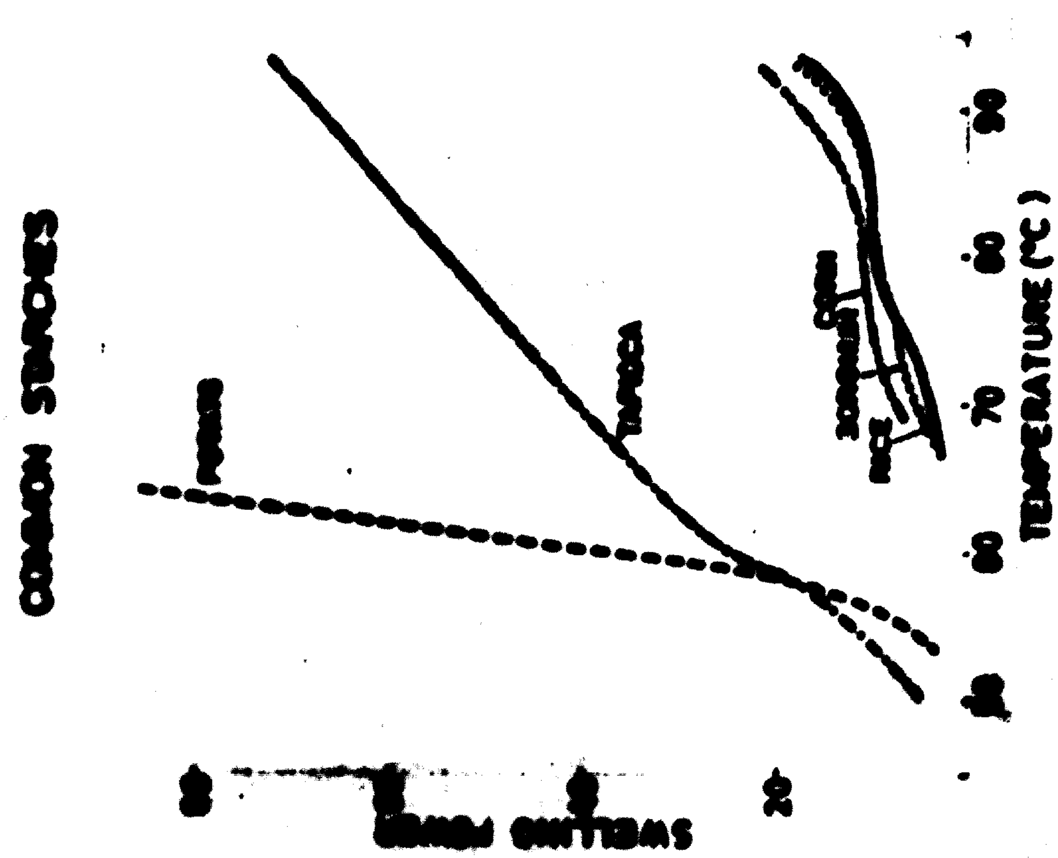

COMMON STARCHES
SWELLING POWER
20
TAPIOCA
CORN
SORGHUM
RICE
60
70
80
90
TEMPERATURE (°C)

Fig. 5

WAXY STARCHES

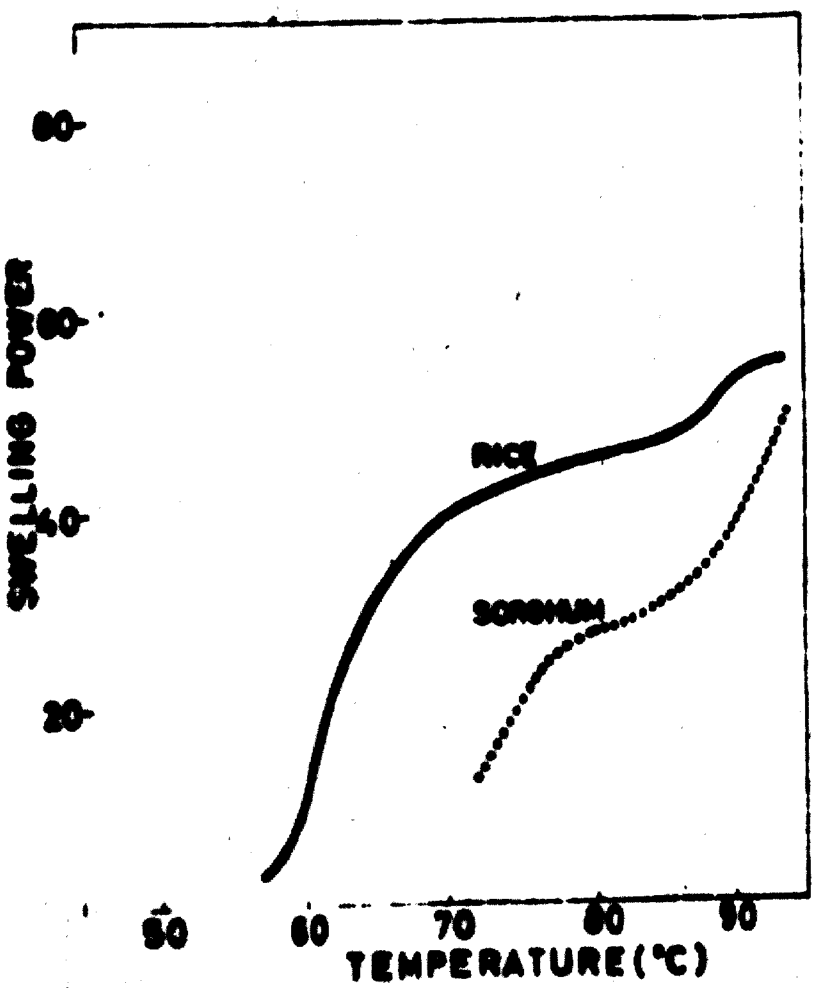


Fig. 6

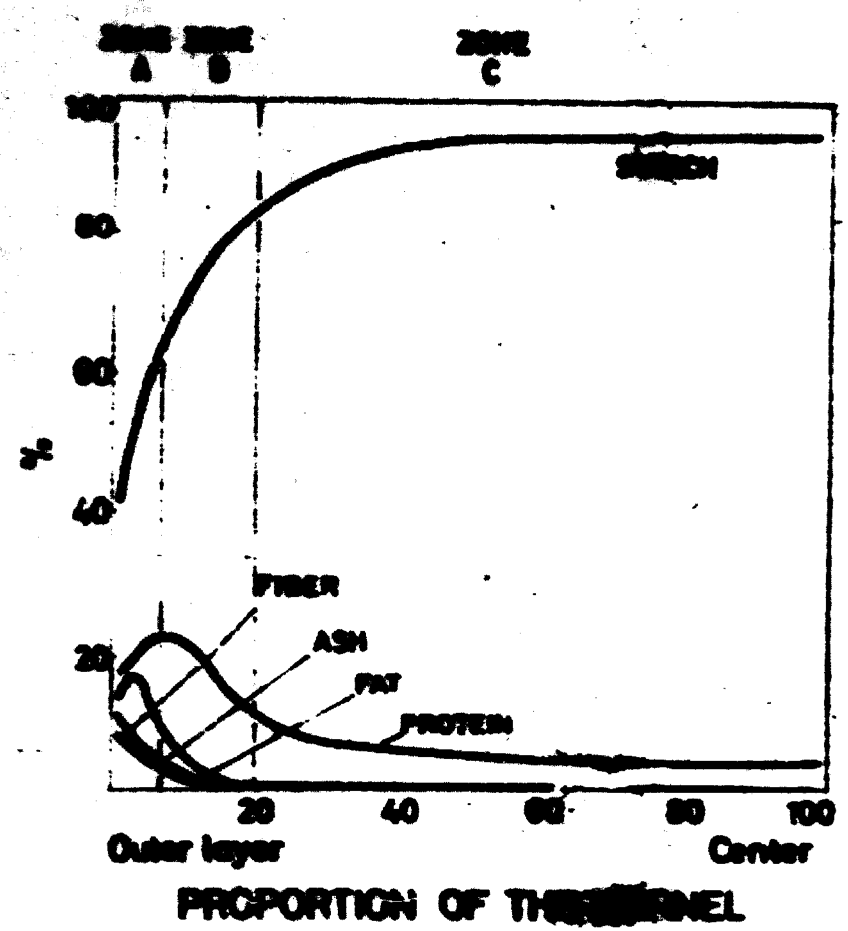
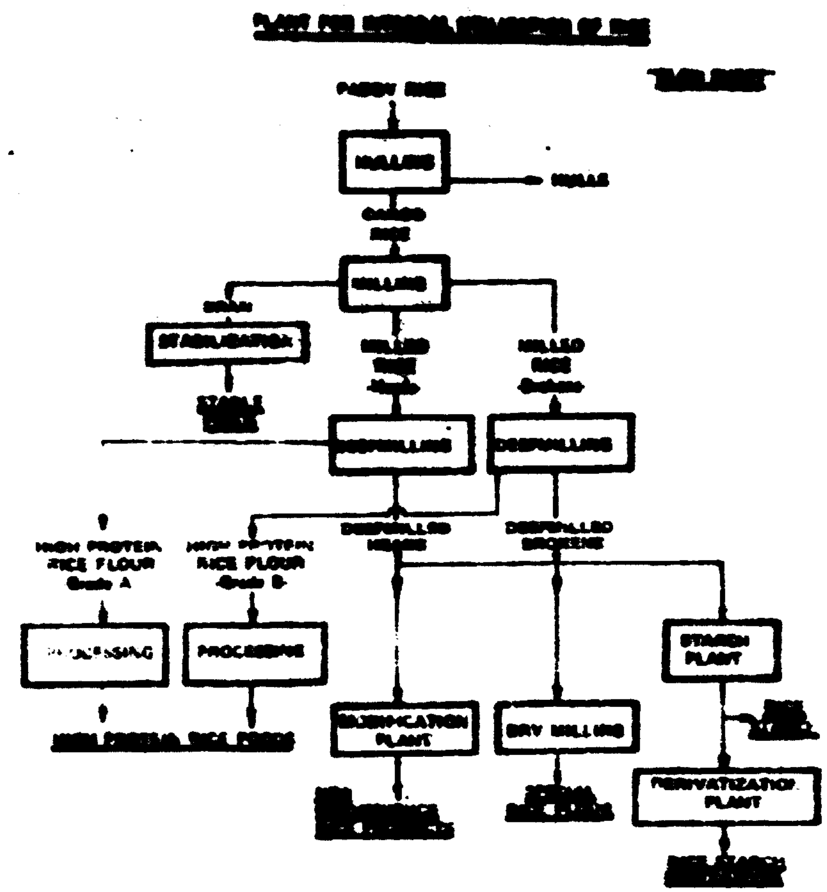

ZONE C
100
80
60
40
20
%
FIBER
ASH
FAT
PROTEIN
20
40
60
80
100
Outer layer
Center

Fig. 7


HIGH PROTEIN RICE FLOUR
PROCESSING
STARCH PLANT
DRY MILLING
DERIVATIZATION PLANT

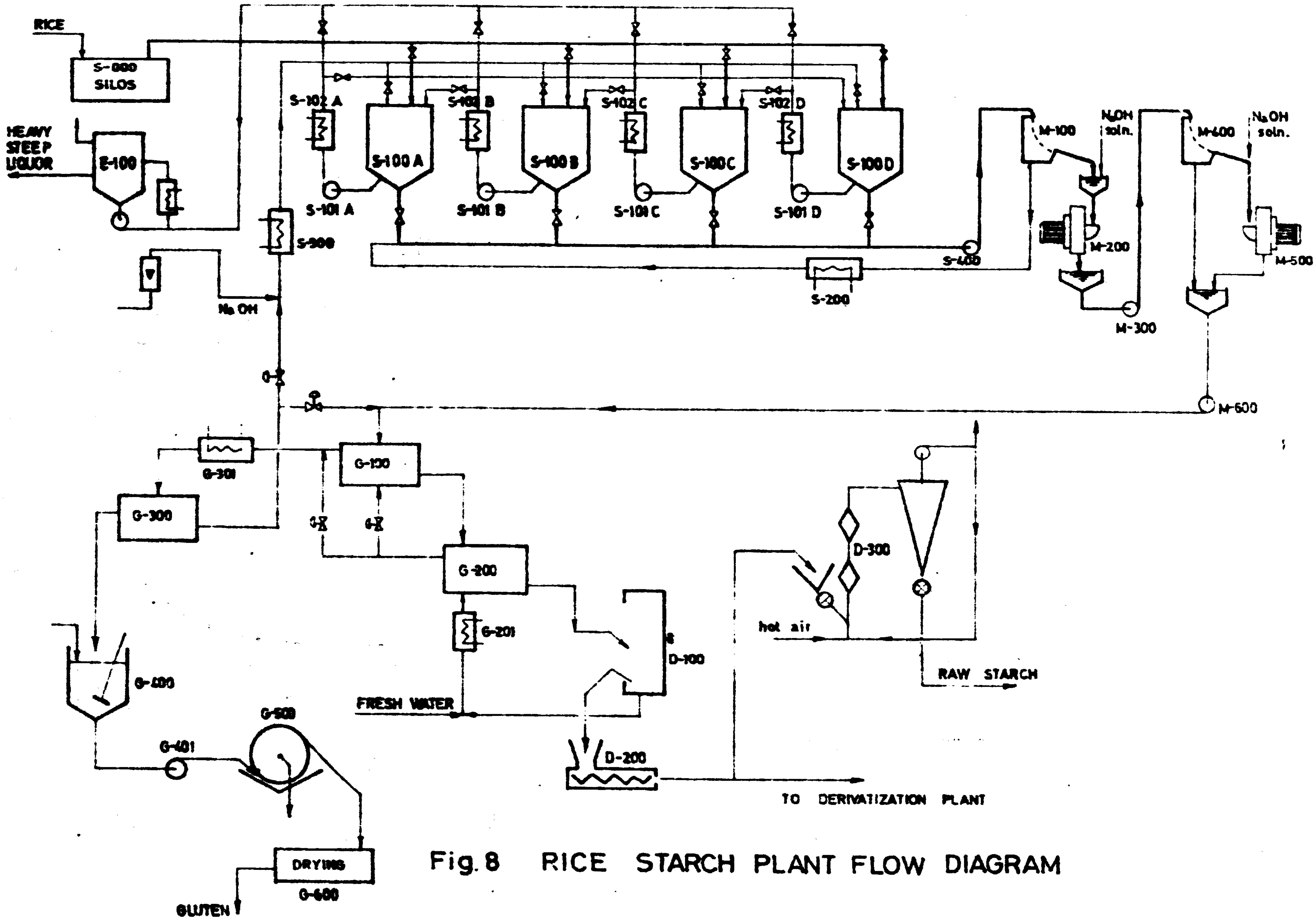


Fig. 8 RICE STARCH PLANT FLOW DIAGRAM

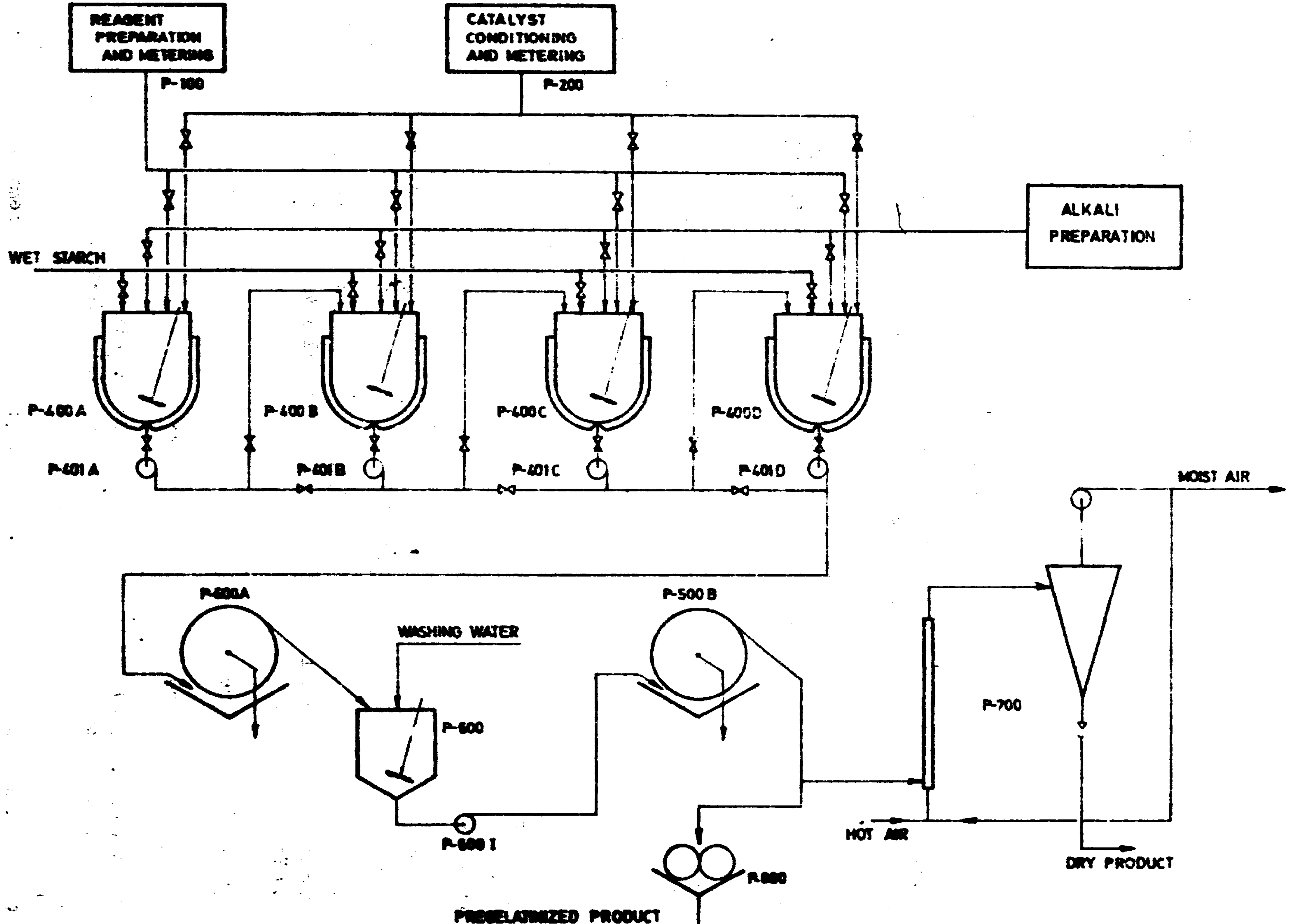


Fig. 9 DERIVATIZATION PLANT FLOW DIAGRAM

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