Note

Considerations on Degree of Heat treatment of Frozen boiled red beans

Yukari IKEHARA, Satoru UJIHARA, Norita WATANAB

*Osaka Customs Labolatory
4—10—3, Chikko, Minato—ku, Osaka—shi 552 JAPAN

The degree of heat treatment of red beans has been determined by the measurement of the ratio of gelatinization.

In general, measurments of natural polymers like starches are hard to stabilize.

Materialized useful and stable methods are mesurements of catalaze activity(to observe inactivity of enzyme), X—ray diffractive patterns(to examine the differences of crystalline structure of starch granule), and moisture ratio(to measure water absorbent in starch granules).

These methods were useful and stable for determination of the degree of heat treatment of red beans

1 Introduction

The boiled red beans after heat treatment have been frozen in export countries and exported to Japan for home consumption.

According to the International Convention on the Harmonized Commodity Description and Coding System(HS), they are classified in HS Item No. 0713.32, in other words Import Quota Items, in case of undergoing moderate heat treatment designed mainly to ensure better preservation by inactivating the enzymes and eliminating part of the moisture ; on the other hand, they are classified in HS Item No. 2004.90, statistical code No.219, in other words Automatic Approval Items as prepared vegetables in case of such treatment should affect the internal character of the cotyledon.

Thus, they are differently treated not only by HS but also by import system. Then, they are usually treated by the method of hydrolysis with the enzymes[1]. But in general, natural polymers have bad reproducibility even in the same samples, for example, there occurs the range of fluctuation in measurement of the same sample, so it is hard to gain stable results. And, in case of the measurement of the ratio of gelatinization of starch, it takes long time, so it is necessary to search for useful and stable methods.

Then, we examined the degree of heat treatment of red beans by the mesurements of “catalaze activity" (in order to observe inactivity of enzyme), “ X—Ray diffractive patterns” (in order to examine the differences of crystalline structure of starch granule), and“moisture ratio" (in order to measure water absorbent in starch granules)

2　Experiments

2．1　Samples

Red beans made in China soaking for20 hours were heated with excessive water and taken out on occasion to make various degree of gelatinization of starch and put them into nylon bags after removing water and then preserved in the freezer at−30℃.

After thawing, removing skin of red beans and outside water, they were used for the following experiments.

Further, each sample was measured the ratio of the gelatinization by the method of hydrolysis with the enzymes.

2．2　Equipment

X−ray diffraction equipment : Rigaku Inc.

Drying oven(normal atmospheric pressure) : Ikedarika Inc.

2．3　Catalaze activity

Mashed samples were put into test tubes with 3 %−hydrogen peroxide solution.

2．4　Measurement of crystalline structure of starch granule by the method of X−ray diffraction

Mashed samples were spread on the sample glass plates, and measured at the condition of $2\theta = 30° \sim 4°$ by X−ray diffraction before drying.

The condition of the X−ray diffraction was shown as follows.

X−ray, Cukα ; filter, Ni; kV／mA, 40／25 ; div ergence slit, 1°; receiving slit, 0.15mm ; chart speed, 0.5m／min

2．5　Measurment of moisture ratio

After thawing, removing skin of red beans, mashed by a glass mortar, and measured precisely about 2g in the weighing bottle which was dried beforehand, then dried at the temperature of 105℃ ±1℃ in the drying oven.

3　Results

3．1　Catalaze activity

Catalaze activity, was examined by3%−hydrogen peroxide solution. The relationship between catalaze activity and the ratio of gelatinization was shown in Table 1.

“＋＋＋”means violently bubbling, “＋＋”means medial bubbling, “＋”means slightly bubbling five minutes after putting red beans into 3%−hydrogen peroxide solution.

Gelatinized sample about 60 % had a little activity after putting into test tubes with 3%−hydrogen peroxide solution, but the samples over70 ～80% didn't have activity after leaving them as they were. It is estimated that the samples over 70% don't have activity.

Table 1　Relationship between the ratio of gelatinization and catalaze activity

The ratio of gelatinization(%)	Catalaze activity
9．0	＋＋＋
15．3	＋＋
59．7	＋
75．6	——
90．9	——

3．2　Measurement of the crystalline structure of starch granule by the method of the X−ray diffraction

It is known for long that crystalline structure gradually changes in proportion to gelatinization of starch. The degrees of gelatinization were appreciated by the disintegration of crystalline substance[2].

Though a transformation of noncrystalline substance is not related to X−ray diffractive patterns, actually noncrystalline substance gelatinizes with the abvance of the gelatinization of crystalline substance.

The relation between the advance of the gelatini−

zation and the transition of crystalline structure was shown in Fig.1.

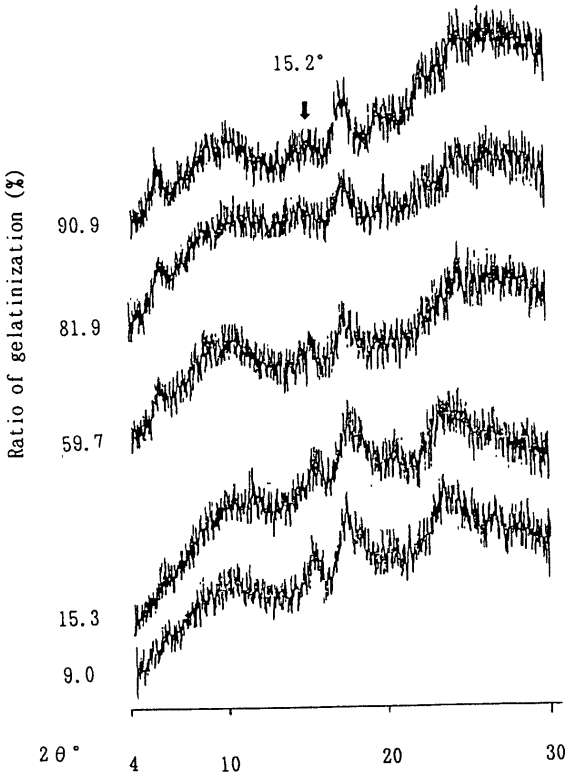

Fig.1 X—ray diffractive patterns of raw red beans and boiled red beans

As for raw red beans(the ratio of the gelatinization 9%), distinct diffraction line was shown. But with the advance of gelatinization, diffraction lines gradually broaden, especially at 2θ 15.2°(3b).

3．3 Measurement of moisture ratio of red beans

The process of gelatinization of starch is the Phenomenon, which micelle structure becomes loose for the sake of heat and takes in much water to reticulated structure, and occured dispersion to water[3].

The Progress of gelatinization is to absorb water and the moisture ratio is going up.

Then the relationships among the ratio of gelatinization, moisture ratio and the results of the catalaze activity was shown in Table2.

Table2 Relationship between three methods

Heating Temp. and time	Moisture ratio(%)	Ratio of gelatinization(%)	Catalaze activity
Raw	53.5	9.0	+++
60℃ 15min.	55.7	15.3	++
70℃ 15min.	56.9	34.8	+
80℃ 15min.	57.9	59.7	+
80℃ 30min.	59.7	84.4	—
90℃ 15min.	59.9	75.6	—
100℃ 15min.	61.3	81.9	—
100℃ 30min.	64.2	90.9	—

Samples 70～80% of the ratio of gelatinization or over 60% of moisture ratio are considered to miss catalaze activity.

The reason why moisture ratio doesn't go up owing to soking for a long time in water is that Fig. 2.

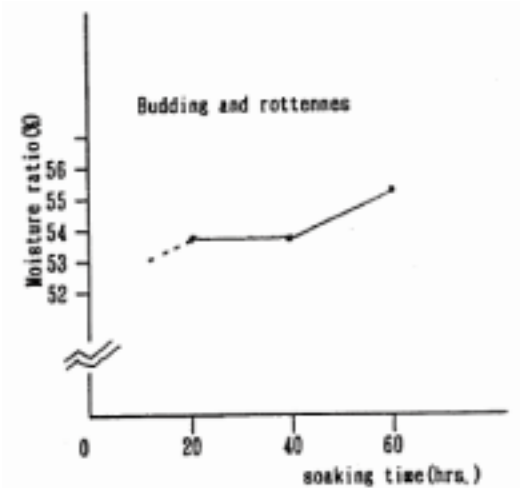

Fig. 2 Relationship between soaking time and moisture ratio

Budding and rottenness began, after reaching the balance of moisture ratio, and then moisture ratio was going up.

Starch granules, which are destroyed hydrogen

bond, irreversibly swell and gelatinize, on the other hand, which are not destroyed hydrogen bond, reversively hydrate and dehydrate that is to say contraction and swelling.

The relation between moisture ratio and the ratio of gelatinization (Table 2) draws S—shaped curve (Fig. 3).

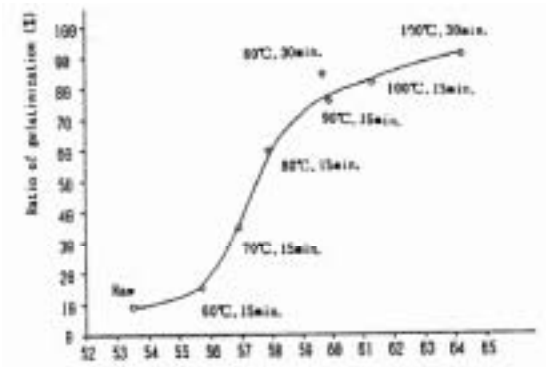

Fig. 3　Relationship between moisture ratio and ratio of gelatinization

Over 56% of moisture ratio and over 60℃ of the heat temperature, the ratio of gelatinization suddenly went up.

This means that the gelling point originates in 60～70℃[4)]

The degree of gelatinization and moisture ratio were theoretically proved to be of intimate relation.

By means of measuring moisture ratio repeated five times with raw red beans the reproducivility was observed. The results are shown in Table 3.

Table 3 Results of repeatability

Test No.	Moisture raitio (%)
1	53. 3
2	53. 5
3	53. 9
4	53. 9
5	53. 5
Average	53. 6
Standard deviation	0. 2683

4　Conclusion

As for index of the degree of heat treatment of the red beans, it is more precise to use plural indices for judging because of difficulty of measuring reproducibility to the same samples due to natural polymers.

Mesurements of catalaze activity, X — ray diffractive patterns and moisture ratio produced good results as useful and stable methods. It is proved to be highly precise measurement and timesaving especially for the moisture ratio.

References

1）Analytical methods for reference of The Central Customs Laboratory, No.24
2）Hizukuri, S., “Shokuhinkogyo”, 1(the last volume), p89～(1969)
3）Hizukuri, S., et al. “Denpunkagaku Handbook”: Asakura—Shoten, P25～(1977)
4）Hizukuri, S., et al.“Denpunkagaku Handbook”: Asakura—Shoten, P36～(1977)