Changes of Starch during Microwave Treatment of Rice

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Abstract

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The properties of rice after microwave irradiation were evaluated by means of amylograph and enzymic determination of the total and the damaged starch. The content of the total starch was not affected by the immediate energy output used for irradiation but that of the damaged starch increased with microwave energy absorbed and the temperature of treatment, mainly at the moisture of 30% and the temperature of 100°C. The results of damaged starch determination are in accordance with the amylographic readings of changes at maximum viscosity. Amylographic characteristics suggest minimal changes resulting in MW treatment of rice at moisture below 23%.

Keywords: rice; starch; amylograph; microwave

Rice (*Oryza sativa* L.), a major cereal crop, is the staple food source for half of the world population. Rice is an excellent source of energy, in the form of starch, and it gives the benefit of providing proteins with a higher nutritional quality than those of other cereal grains (Moldenhauer *et al*. 1998). At present, many possible applications of microwave (MW) energy in the food industry are known. MW drying was demonstrated to be an alternative means for the rice drying (Wadsworth & Koltun 1986). Major components and the enzymic system of rice can be influenced during MW treatment. Since starch comprises approximately 90% of the dry matter of the rice endosperm, the research on rice cooking behaviour has focused on this fraction. Wadsworth and Koltun (1986) used two long-grain cultivars and one medium-grain cultivar of rice for drying under vacuum by means of MW energy to determine the effects on the physicochemical properties and eating characteristics. Amylographic characteristics were used to obtain more information on the influence of the starch fraction of rice on its cooking behaviour. No significant differences were found in both maximum viscosity and setback viscosity between the air-dried controls and MW dried rice. Marsono and Topping (1993) reported the effect of MW treatment on the contents of total and enzyme resistant starch in white and brown rice (three Australian cultivars – Calrose, Doongara and Waxy). The starch content was maintained or increased by cooking in a MW oven except with cv. Waxy. The increase was consistent with starch gelatinisation and therefore, with greater susceptibility to enzymic attack. Cooked rice had a higher content of resistant starch than the corresponding raw product, possibly because of the production of retrograded starch. It can be concluded that although the content of the resistant starch in rice increased by the techniques known to increase the resistant starch in other foods (heating, cooking, cooling and freezing), the impact was not as great. Zheng *et al*. (1996) treated two japanase cultivars of rice (700 W, 3 min, 500 g batches) with MW and determined physicochemical properties, cooking quality and enzyme activities. It was found that both cultivars of rice had debranching enzymes, and that α-amylase activities were significantly lower than those of the untreated controls. Cooking qualities, such as water absorption capacity, pH, and iodine blue value of cooking water, β-amy-

lase activity and insoluble amylase content, were slightly lower in the treated than in the untreated rice. However, physicochemical properties such as gelatinisation temperature, maximum viscosity, ultimate viscosity, breakdown value, gel value, and soluble amylase content were slightly higher in the treated rice. Total starch and total amylose contents were not significantly different in the treated rice and the controls.

The purpose of this investigation was to determine the effect of MW treatment on the changes of the total and the damaged starch, and on the amylographic characteristics of milled rice.

MATERIAL AND METHODS

Moistening of rice. Samples of white and short-grain rice (*Oryza sativa* var. *indica*), were used. Samples differing in the moisture contents (ca 23% and 30%) were prepared by soaking in water. The starch granules of rice must absorb water and swell, and then they must be heated rapidly to ensure complete gelatinisation, i.e. the conversion of hydrogen bonding between starch micelles to hydrogen bonding with water. Figure 1 shows the course of rice soaking. The excess water was drained off on filter paper and the samples of rice were dried for 20 min on air at ambient temperature (Kaasová *et al*. 2000).

Parameters of microwave oven and measurement of absorbed power. Domestic MW oven Whirlpool MT 243/UKM 347 (Norrköpping, Sweden), frequency 2450 MHz, pulsed variable MW rated power output from 90 to 1000 W by a timer, inner cavity volume 25.4 l, without sample rotation during measurement. MW oven was preheated before each measurement by heating 2 l of water for 5 min. The absorbed power according to BSEN 60705 test (International Standard BSEN 60705, 1995) was determined every day. The load of water in this test is (350 +/– 5) g, the initial water temperature is (10 +/– 2)°C. The mean value of absorbed power (n = 22) corresponding to the rated power output of 350 W was 298.42 W; standard deviation was 8.5 and variation coefficient (relative standard deviation) 2.85% (Skulinová *et al*. 2002).

Temperature measurement. The temperature of the treated samples was recorded using the NoEMI fiber-optic temperature system – table-top unit ReFlex, with 2 channels, Nortech Fibronic Inc., Canada. The temperature was measured with one probe, 50 mm on the right from the middle, in the location with the highest temperature. The detailed description of the experimental set up and the temperature measurement in MW treatment is given in our previous paper (Skulinová *et al*. 2002).

Microwave treatment of rice. A 200 g of rice sample was heated in MW oven; the rated power output was terminated when the desired end temperature of the heated sample was reached. The temperature of rice during microwave heating increased rapidly as a result of the exposure to MW energy, but the drying proceeded slowly during this time. MW power was switched off after the desired end temperature was reached and the sample of rice was then left for 1 min in the microwave cavity. The sample was then mixed and cooled to ambient air temperature in the vessel outside the MW oven (1 min) and returned to the MW oven. This cycle of heating and mixing with cooling was repeated five times until the temperature was the same in

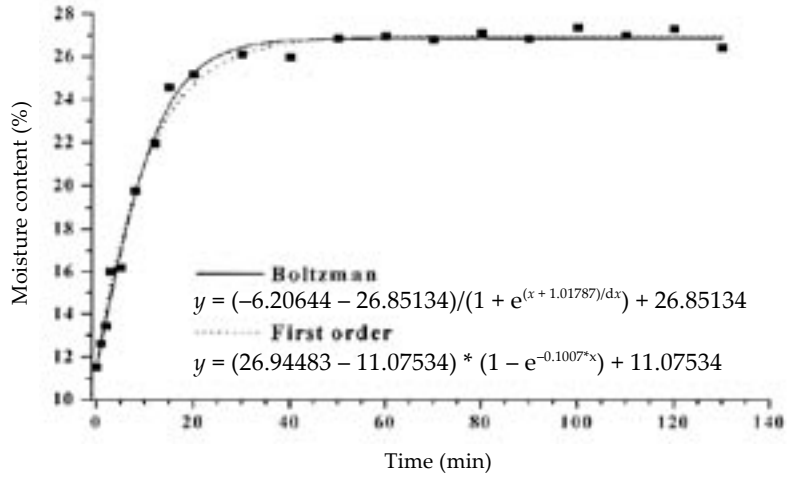

Figure 1. Course of rice soaking at temperature 25°C

every place of the sample. The next sample was treated in the MW oven after a break of 30 min. The power output was changed from 90 to 350 and 500 W; the end temperature of the heated rice was 60, 80, or 100°C; the moisture content of rice was 11, 23, or 30%. The absorbed MW energy E_{MW} (kJ) was calculated as the product of the absorbed MW power P_{MW} (kW) and the time of the MW treatment τ (s): $E_{MW} = P_{MW} . \tau$.

Determination of dry matter. Automatic drying electronic Precisa HA300 Moisture Balance (Precisa, Switzerland) was used for the determination of the dry matter content. The end temperature of drying can be set in the range of 40–250°C and the percentage of the dry matter content is automatically shown on the display.

Determination of total starch. The starch content was determined using the American Association of Cereal Chemists (AACC) Method No. 76-13 by means of the enzyme sets of Megazyme International Ireland Ltd. Starch hydrolysis proceeds in two phases. In phase I, starch is partially hydrolysed and totally solubilised by cooking of the sample in the presence of thermostable α-amylase. In phase II, the starch dextrins are quantitatively hydrolysed to glucose by amyloglucosidase (Megazyme 2000a). The sample of rice is milled to pass a 0.5-mm screen. Flour sample is weighed (~100 mg) into a glass tube (16 × 120 mm). All of the sample should drop to the bottom of the tube by means of tapping the tube. Then 0.2 ml aqueous ethanol (80% v/v) is added to aid dispersion, and the tube is stirred on a vortex mixer. Immediately 3 ml of thermostable α-amylase (300 Units) is added in MOPS buffer (sodium salt) (50mM, pH 7.0) and the tube is vigorously stirred on a vortex mixer. The tube is then incubated in boiling water bath for 6 min and stirred vigorously after 2 min and 4 min. Then it is placed in a bath at 50°C; sodium acetate buffer (4 ml, 200mM, pH 4.5) is added. The tube is stirred on a vortex mixer and incubated at 50°C for 30 min. The entire content of the test tube is transferred to a 100 ml volumetric flask. A wash bottle is used to rinse the tube contents thoroughly. The volume is adjusted with distilled water. An aliquot of this solution is centrifuged at 3000 rpm for 10 min. Duplicate aliquots of the diluted solution (0.1 ml) are transferred onto the bottoms of glass test tubes (16 × 100 mm). 3.0 ml of Glucose Determination Reagent (GOPOD) – glucose oxidase, peroxidase, 4-aminoantipyrine – is added to each tube (including glucose controls and reagent blanks) and the tubes are incubated at 50°C for 20 min. Glucose controls consist of 0.1 ml of glucose standard solution (1 mg/ml) and 3.0 ml GOPOD reagent. Reagent blank solution consists of 0.1 ml of water and 3.0 ml of GOPOD reagent. The absorbance at 510 nm is read for each sample and the glucose control against the reagent blank.

Total starch content *TS* (%) is calculated according to the following expression:

$$TS = \Delta A \cdot F \cdot \frac{100}{w} \cdot \frac{162}{180} = \Delta A \cdot \frac{F}{w} \cdot 90$$

where: ΔA – absorbance (reaction) read against the reagent blank

F – conversion from absorbance to μg (F = 100 μg of glucose/absorbance for 100 μg of glucose)

w – the weight (mg) as "the basis" of the flour analysed

162/180 – adjustment of free glucose to anhydrous glucose (as it occurs in starch)

Determination of damaged starch. Damaged starch granules are hydrated and hydrolysed to maltosaccharides plus α-limit dextrins by a carefully controlled treatment with purified fungal α-amylase. The fungal α-amylase treatment is designed to give near complete solubilisation of the damaged granules with minimum breakdown of the undamaged granules. This reaction is terminated by the addition of dilute sulphuric acid; aliquots are treated with excess levels of purified amyloglucosidase to effectuate complete degradation of the starch-derived dextrins to glucose. The amount of glucose is specifically measured with a high purity glucose oxidase/peroxidase reagent mixture. The values determined are presented as weight percentage damaged starch in flour on an "as is" basis (Megazyme 2000b). Rice flour samples (100 ± 10 mg) are accurately weighed into thick-walled glass centrifuge tubes (12ml capacity). Before the addition of fungal α-amylase solution, the tubes plus the contents are pre-heated to 40°C for 2–5 min. Fungal α-amylase solution (50 U/ml) is pre-heated to 40°C (5–10 min) in a small glass beaker. To each tube is added 1.0 ml of pre-heated fungal α-amylase (50 U/ml); the tube is immediately stirred vigorously on a vortex mixer for 5 s and then incubated at 40°C for exactly 10 min (starting with the addition of the enzyme). 5.0 ml of dilute sulphuric acid (0.2% v/v) is added to terminate the reaction, and the tubes are centrifuged at 3000 rpm

(1000 g) for 5 min. Aliquots of the supernatant solution (0.1 ml) are carefully and accurately transferred onto the bottoms of two test tubes. To each tube amyloglucosidase solution (0.1 ml, 2 U) is added and the tubes are incubated at 40°C for 10 min. 4.0 ml of GOPOD reagent is added to each tube (including glucose standards and reagent blank tubes), and the tubes are incubated at 40°C for 20 min. The absorbance of each sample is measured at 510 nm.

Calculation of damaged starch *DS* (%):

$$DS = \Delta A \cdot F \cdot 60 \cdot \frac{0.1}{w} \cdot \frac{162}{180} = \Delta A \cdot \frac{F}{w} \cdot 5.4$$

where: the signification of the parameters is the same as given above, 60 – volume correction (0.1 ml taken from 6.0 ml)

Determination of viscous properties and starch gelatinisation by amylograph. The sample of rice was ground on laboratory mill Retsch ZM 1000 using 1500 rpm and a sieve with a circular hole of the diameter of 0.5 mm. Principally, amylographic determination is based on a rotational viscometric measurement. The changes in the starch gelatinisation during heating of the suspension are proportional to the changes of viscosity and are registered during the heating time. General conditions of the amylographic measurement are given in the International Association of Cereal Science and Technology (ICC) Standard No. 126/1. The shape of the amylographic curve registered is pre-determined by the starch properties that are, except for the preliminary starch damage, affected to a great part by the activity of amylolytic enzymes.

α-Amylase activity is closely connected with the speed of the viscosity increase during standard heating up to 93°C and the total viscosity maximum on the curve. The lower α-amylase activity, the more rapid the viscosity increase (i.e. the slope of the linear part of curve) and the higher maximum value is reached (Figure 2). Moreover, maximum viscosity can also decrease as a result of a greater content of damaged starch. In general, flours with a high amylolytic activity as e.g. from sprouted grains, give a considerably lower curve than those from sound grains. In our case, it is necessary to consider the possibility of the starch damage caused by MW heating without any connection to the activity of amylases.

The evaluation of rice flour by means of amylograph is described in AACC Standard No. 61-01. Since rice starch gelatinises at especially high temperature, the maximum on the curve cannot be reached during the standard heating to 93°C. In the Standard, continuing heating is recommended until maximum is reached and viscosity starts to decrease. The results are expressed as a temperature 93°C plus the time in minutes to reach the maximum on the curve. In the same way as with general Standard method, the time to the first curve increase in minutes and the maximum viscosity on the curve in Amylographic units (AU) are also read from the curve. The repeatability of the amylographic determination is shown in Table 1 (Hubáčková 2001).

Water sorption capacity of cooked rice. The method according Hogan and Planck (1958) was used for the determination of the water sorption capacity. 5 g of rice were soaked in 50 ml distilled

Table 1. Determination of repeatability of amylographic characteristics

Number of measurement	Maximum amylograph viscosity (AU)	Time at which maximum viscosity is attained at temperature 93°C (min)	Temperature at a deflection of 100 AU (°C)
1	590	6.0	79.0
2	590	5.5	80.5
3	590	6.0	79.0
4	590	6.0	79.0
5	610	6.5	79.0
Average value	594	6.0	79.3
Standard deviation	8	0.32	0.60
Variation coefficient (%)	1.35	5.27	0.76

water at room temperature for 30 min in a stoppered test tube. Subsequently, the test tube was immersed in water bath at 70°C for 30 min. After the heat-treatment the grains were washed with distilled water until the combined cooking and washing water amounted to 90 ml. Further the cooked grains were washed with 10–20 ml methanol and spread on filter paper for 5 min to remove the surface moisture. The dry matter content was determined by drying at 100°C to constant weight on Precisa HA300 Moisture Balance (Precisa, Switzerland). The water sorption capacity values reported are equal to the percentage of the moisture content of the cooked and rinsed grains. They are expressed on a dry-weight basis and represent the average of duplicate determinations.

RESULTS AND DISCUSSION

An example of the amylogram of rice flour without MW radiation is shown in Figure 2. A lower amylographic maximum and a lower temperature of the start of gelatinisation were obtained with the MW-heated samples. Figure 3 illustrates the differences in maximum viscosity for MW-treated rice flour (condition of MW treatment of rice: moisture content of rice 30%, power output 350 W, end heating temperature 100°C). A probable starch damage can be presumed as a result of MW treatment or a higher temperature during heating (Hubáčková 2001).

When we compare the data read from the amylographic curves of all the samples, a certain tendency

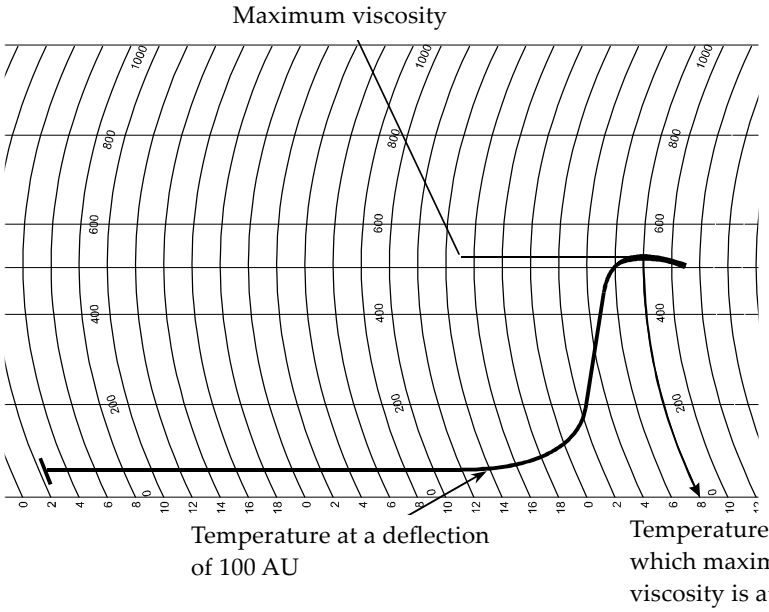

Figure 2. Amylogram of rice flour – sample without MW radiation

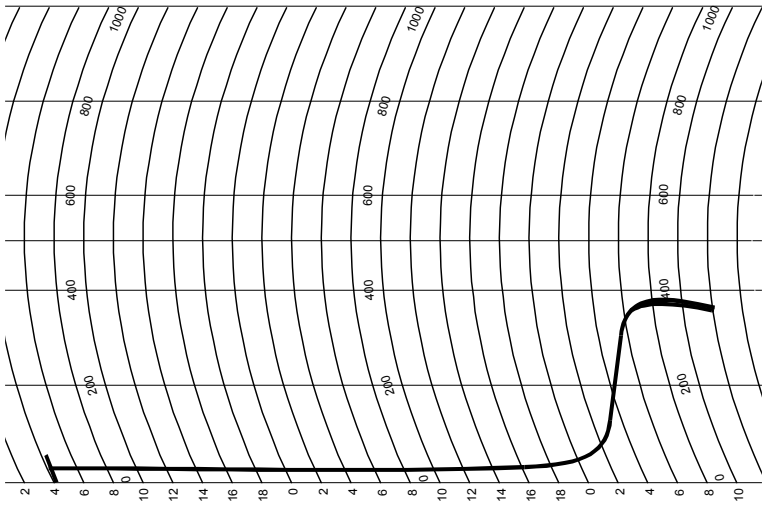

Figure 3. Amylogram of rice flour from MW treated sample (350 W, 100°C, moisture content 30%)

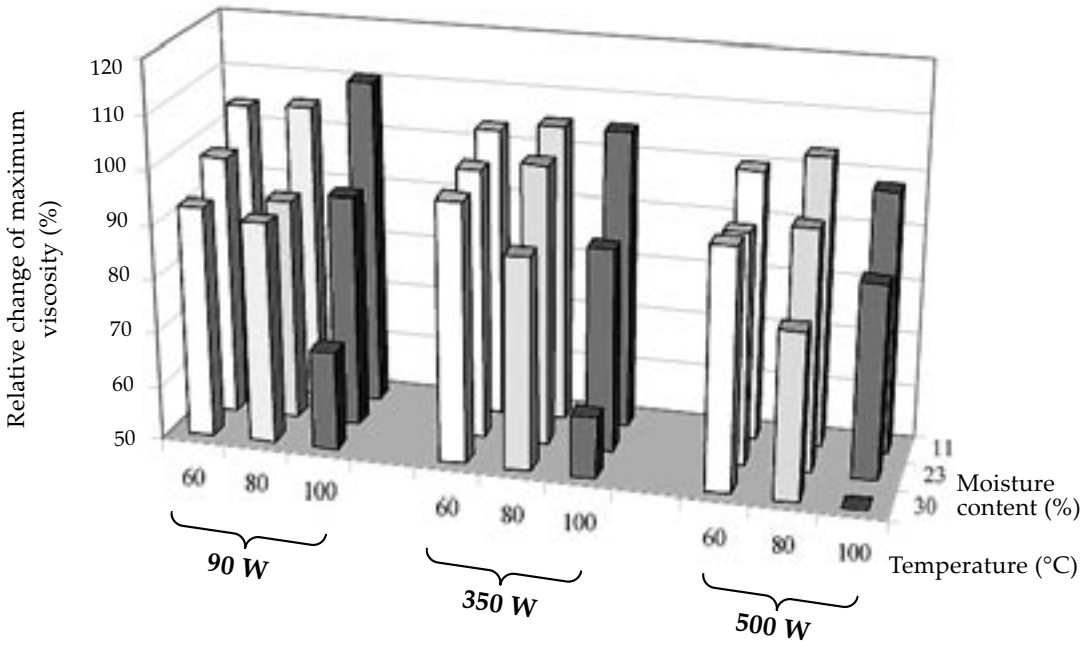

Figure 4. Evaluation of changes in maximum amylograph viscosity

can be seen in the changes that are affected by different moisture as well as by the irradiation output and maximum temperature of the respective sample. A complex diagram of all three effects on the changes of amylographic maximum is given in Figure 4. Relative changes are expressed in percentage of the basic value of the original non-irradiated sample that was chosen as 100%. In general, a very strong effect of increasing temperature of the sample is seen with samples of higher moisture. These changes are probably connected with the damage of starch grains due to higher temperatures. The tendency towards a decrease of viscosity is accented with a higher output used despite the fact that identical temperatures are reached. It can be concluded that MW heating of rice possessing higher moisture resulted in heat-damage to starch grains. In the sample of rice with moisture of 30% that was irradiated with the output 500 W up to 100°C no maximum was reached at all. Viscosity was increasing up to 93°C and then it continued to increase due to the evaporation of water from the starch gel for the next 90 min without any turn to a decrease.

The effect of the absorbed MW energy during heating is given completely in Figure 5 for all three output values used. Quite a distinctive decrease

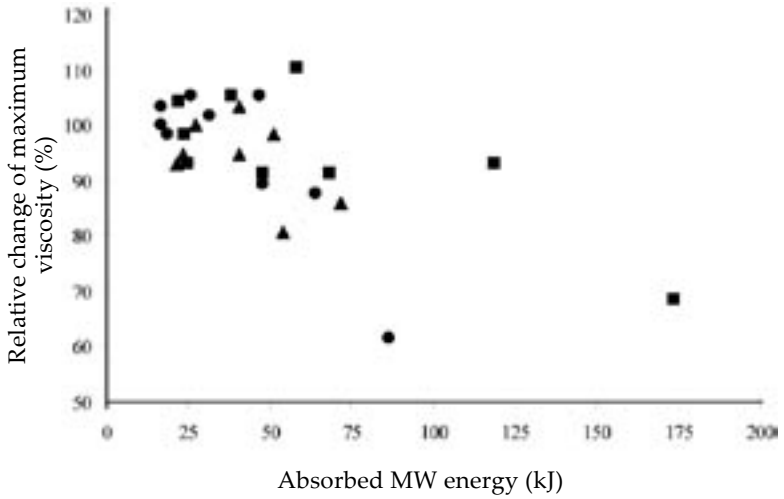

Figure 5. Relation between relative changes of maximum viscosity and absorbed MW energy

of the viscosity maximum is seen at higher total energy supplied, especially with the values above approx. 50 kJ. The effect on the decrease is accented with a higher output. The higher the output used, the quicker the viscosity decrease, and that already at lower values of absorbed MW energy. Again, a greater probability of starch damage is obvious at higher irradiation intensity and higher energy put into the rice in this way.

Table 2 summarises the results of the total and the damaged starch contents, water sorption capacity, and amylograph characteristics. It is obvious from

Table 2. Changes of amylograph viscosity, total and damaged starch contents, and water sorption capacity of rice during microwave treatment

MW power (kW)	Temperature (°C)	Time of MW radiation (s)	Absorbed MW energy (kJ)	Moisture content (%)	Amylograph viscosity (AU)	Total starch content (%)	Starch damage content (%)	Water sorption capacity (%)
90	60	326	25.00	29.95	530	86.97	4.85	56.81
90	60	312	23.93	22.39	560	85.71	4.33	46.33
90	60	284	21.78	12.20	595	85.66	4.52	46.37
90	80	888	68.11	29.68	520	87.13	5.82	56.08
90	80	622	47.71	22.24	520	86.69	4.97	35.68
90	80	500	38.35	11.65	600	85.92	4.71	52.02
90	100	2266	173.80	29.07	390	84.43	7.27	62.34
90	100	1550	118.89	23.20	530	87.28	4.88	53.82
90	100	758	58.14	12.05	630	86.71	4.47	53.40
350	60	62	18.74	29.61	560	86.51	5.25	49.15
350	60	56	16.93	22.37	570	86.50	4.55	44.89
350	60	56	16.93	11.37	590	85.39	4.70	45.31
350	80	158	47.76	29.77	510	87.10	6.42	46.16
350	80	104	31.44	22.84	580	84.95	4.63	43.35
350	80	86	26.00	12.15	600	85.86	4.63	48.11
350	100	286	86.46	29.32	350	86.92	9.19	54.66
350	100	212	64.09	21.03	500	86.98	5.37	49.67
350	100	154	46.55	11.71	600	86.53	4.31	51.87
500	60	50	23.56	29.71	540	87.01	5.43	51.84
500	60	46	21.67	23.20	530	87.48	4.97	53.63
500	60	58	27.32	12.20	570	87.68	4.37	54.63
500	80	114	53.71	29.70	460	86.73	5.89	52.72
500	80	86	40.51	22.07	540	85.80	4.48	58.15
500	80	86	40.51	11.41	590	85.28	4.59	52.37
500	100	232	109.30	29.85	–	86.79	9.84	56.27
500	100	152	71.61	21.77	490	86.91	5.17	51.08
500	100	108	50.88	12.08	560	86.46	4.14	51.15
–	–	–	–	11.98*	570*	87.20	5.57*	41.99*
Standard deviation					8.94	1.53	0.24	1.94
Variation coefficient (%)					1.51	1.75	4.39	4.62

*rice without MW treatment

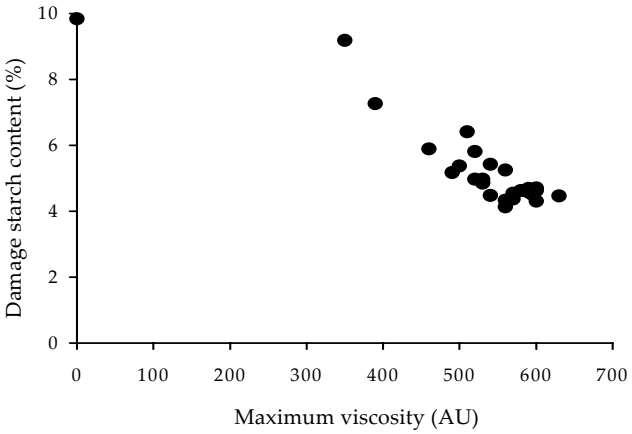

Figure 6. Relation between damaged starch content and maximum viscosity

these data that the content of the damaged starch in rice varies with the temperature, the power output, and the original moisture content of rice. The highest damage to starch was observed for the moisture of 30% and the temperature of 100°C. MW treatment does not affect the total content of starch in rice.

The decrease of the maximum amylographic viscosity was observed with increasing temperature of MW treatment and increasing power output at the moisture of 30%. A lower decrease occurred at the moisture of 23%, and minimal changes revealed dry samples at the moisture of 12%. The relation between the content of the damaged starch and the maximum amylograph viscosity is shown in Figure 6. It is obvious from this figure decrease that the content of damaged starch decreases with increasing amylograph height. Amylograph height decreases with increasing moisture content.

These results are in agreement with those of Halick and Kelly (1959). According to this paper, the amylographic viscosity curves were essentially identical for the control and the MW treated dry samples of rice; MW treatments did not materially affect the cooking and processing quality of the milled rice. The variability in water absorption in rice lots with similar cooking and processing characteristics is much greater than are the observed changes caused by the MW drying treatments. According to the sensory evaluation, it is not possible either to consistently detect differences in flavour or texture resulting from MW drying.

Conclusion

MW treatment does not affect the total content of starch in rice, however, the content of the damaged starch increases with microwave energy absorbed and the temperature of treatment, especially at the moisture of 30% and the temperature of 100°C. The results of the determination of the damaged starch are in accordance with the amylographic readings of changes in maximum viscosity. The amylographic characteristics suggest minimal changes resulting from MW treatment of rice at moisture below 23%.

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Souhrn

Pinkrová J., Hubáčková B., Kadlec P., Příhoda J., Bubník Z. (2003): **Změny škrobu v rýži během mikrovlnného ohřevu**. Czech J. Food Sci., **21**: 176–184.

Vlastnosti rýže po ozáření mikrovlnami byly zjišťovány u rýžové mouky na amylografu a enzymatickým stanovením celkového a poškozeného škrobu. Amylografickým rozborem bylo zjištěno, že se zvyšujícím se množstvím dodané energie se výška amylografického maxima snižuje, a lze tedy předpokládat, že dochází k poškozování škrobu. Obsah celkového škrobu se účinkem mikrovlnného ošetření prakticky nemění, zatímco obsah poškozeného škrobu se zvyšuje, zvláště při teplotě záhřevu na 100 °C a při vlhkosti rýže 30 %. Nárůst obsahu poškozeného škrobu je v souladu se zjištěnými amylografickými charakteristikami.

Klíčová slova: rýže; škrob; amylograf; mikrovlny

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