CHAPTER III

RESULTS

1 Preliminary Investigation

Comparisons of tabletting properties of spray dried starch aggregates prepared from various native starches which were commercially available in Thailand and their crosslinked (Table 7) found that crosslinked rice flour exhibibited the most satisfactory compression characteristics. The compressiblity of 6 hour-crosslinked rice flour was highest reaching 7.5 kiloponds(kp.),and gave the shortest disintegration time, only 1 min.10 sec.(at the compressional force of 1,000 lb.), while the flowability was fairly good(Angle of Repose below 35^{o}) (Lieberman & Lachman, 1981). The glutinous rice starch exhibited similar compressibility to rice starch. However, the spray drying of glutinous rice starch slurry was more difficult to obtain starch aggregates than of rice starch because of its stickiness, requiring longer time and higher power consumption. Tapioca, corn, and mung bean starch gave unsatisfactory compreessibility. Therefore, rice starch was chosen for further studies.

Spray-drying conditions were investigated in preparing starch aggregates using native rice starch without pretreatment. The following conditions: concentration of starch dispersion, inlet drying air temperature, feed rate and atomizing pressure were varied at various levels, then physical and tabletting properties were evaluated.

2. Effects of Spray-drying Conditions on the Properties of Spray-dried Starch Aggregates

2.1 Effects of Concentrations on Physical and Tabletting Properties of Spray-dried Starch Aggregates

When concentration of rice starch dispersion was increased from 30 to 40 and 50 % W/W, the mean diameter of starch aggregates (determined through scanning elec tron microscopy, Herman et al.,1989) increased from 40 to 60 and 89 µm respectively (Table 8 and Fig.19-20). The bulk, tapped density and % compressibility varied very slightly at different concentrations. Nonetheless, the angles of repose decreased from 39.0 to 34.7 and 31.96 for 30 % , 40 % and 50 % concentration respectively. The flow rates showed clearly that only 50 % concentration gave satisfactory result at 15.62 g./sec., while starch aggregates prepared from 30 % and 40 % concentration could not be

Table 8 Effects of Concentration of Starch Slurry on Physical Properties of Starch Aggregates. (F.R. 12.96 g/min, Temp. 130 °C, P. 1.5 bar)

CONC.[1] [% W/W]	MEAN DIA.[2] [um]	% M.C.[3]	B.D.[4] [g/ml]	T.D.[5] [g/ml]	% COM.[6]	A.O.R.[7] [o]	Fl.R.[8] [g/sec]
30	40	9.3	0.58[0.002]	0.71[0.003]	18.31[1.67]	39.00[0.63]	0
40	60	10.0	0.57[0.001]	0.70[0.004]	18.57[2.10]	34.70[1.16]	0
50	89	10.7	0.54[0.002]	0.65[0.002]	17.42[1.07]	31.96[1.10]	15.62[1.37]

1 = Concentration
2 = Mean Diameter(determined by S.E.M.)
3 = % Moisture Content
4 = Bulk Density
5 = True Density
6 = % Compressibility
7 = Angle of Repose
8 = Flow Rate

Standard Deviations in parentheses

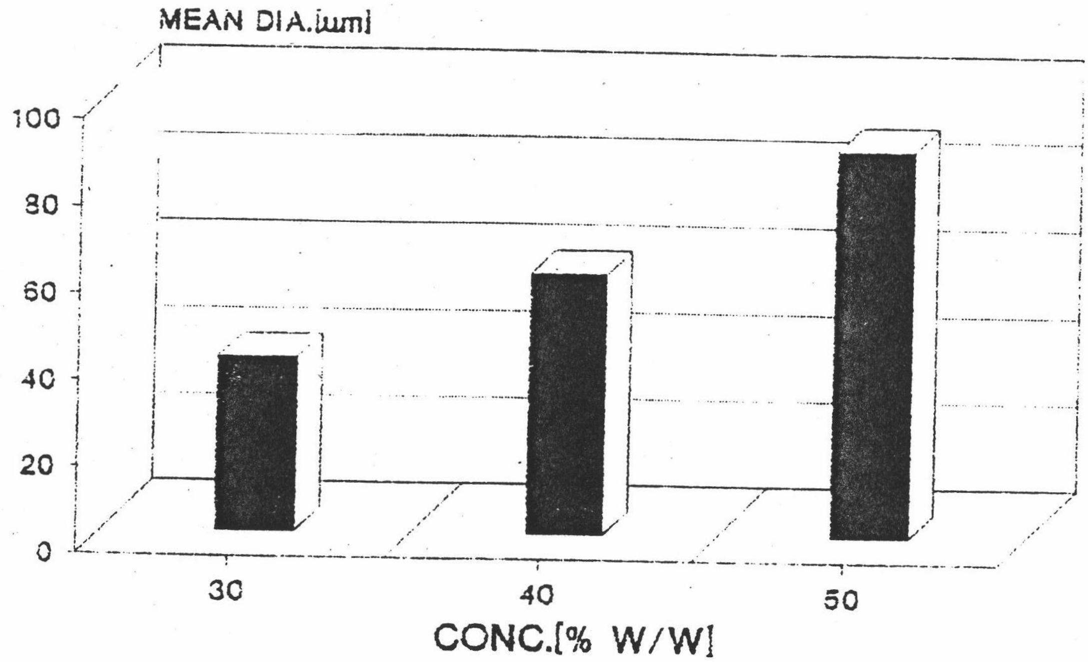


Figure 19 Effects of Concentrations of Starch Slurry on Mean Diameters of Starch Aggregates.......

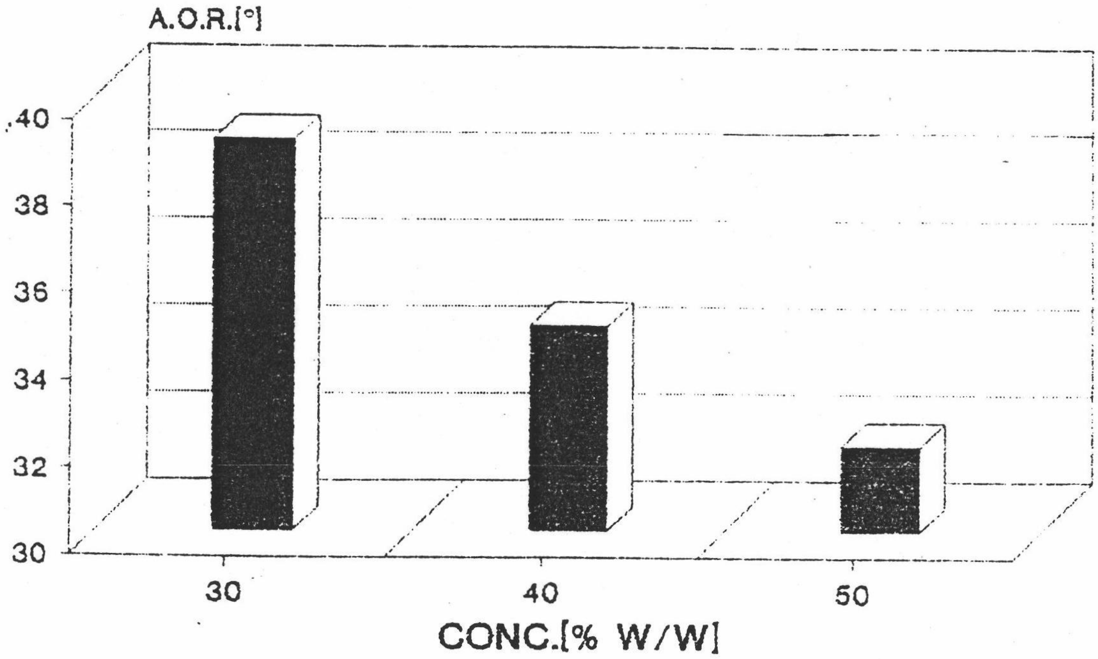


Figure 20 Effects of Concentrations of Starch Slurry on Angles of Repose of Starch Aggregates....

determined under the condition tested.

When the powders of starch aggregates prepared at various concentrations described above were com pressed into tablets at three different pressures, 1000 ; 1500 and 2000 lb. respectively, the results were presented in Table 9 and Fig.21-22. Starch aggregates prepared from 30 and 40 % starch dispersion could not be compressed into tablets at any pressure because of insufficient compressibility. 50% concentration gave a better result, friability values were lower than 0.68 % at all compressional pressures. Disintregation time values were also short, only 3 min. at 1,000 lb. and 4 min. at 2,000 lb. Nonetheless, the hardness values were rather low, with minimum at 3.8 kp (1,000 lb.), and maximum at 6.0 kp.(2,000 lb.)

2.2 Effects of Inlet Air Temperatures on Physical and Tabletting Properties of Spray-dried Starch Aggregates

When varying inlet air temperatures, only two temperature levels (130 and 135 °C) were successful in spray-drying process of starch slurry. If the temperature was below 130 °C, the products contained too much moisture. If it was over 135 °C, the gel was

Table 9 Effects of Concentration of Starch Slurry on Tabletting Properties of Starch Aggregates. (F.R. 12.96 g/min, Temp. 130 °C, P. 1.5 bar)

CONC. [% W/W]	COM.F.[1] [lb]	AV. WT.[2] [mg]	THICKNESS [mm]	FRIABILITY [%]	D.T.[3] [min]	HARDNESS [kp]
30	1000	*	*	*	*	*
30	1500	*	*	*	*	*
30	2000	*	*	*	*	*
40	1000	*	*	*	*	*
40	1500	*	*	*	*	*
40	2000	*	*	*	*	*
50	1000	301.9[1.48]	4.17[0.04]	0.68	3.0[0.38]	3.8[0.53]
50	1500	301.3[1.40]	3.95[0.04]	0.16	3.5[0.45]	4.9[0.69]
50	2000	300.7[5.38]	3.89[0.03]	0.54	4.0[0.42]	6.0[0.48]

* Conc. 30 & 40 % cannot be compressed into tablets

1 = Compressional Force

2 = Average Weight

3 = Disintegration Time

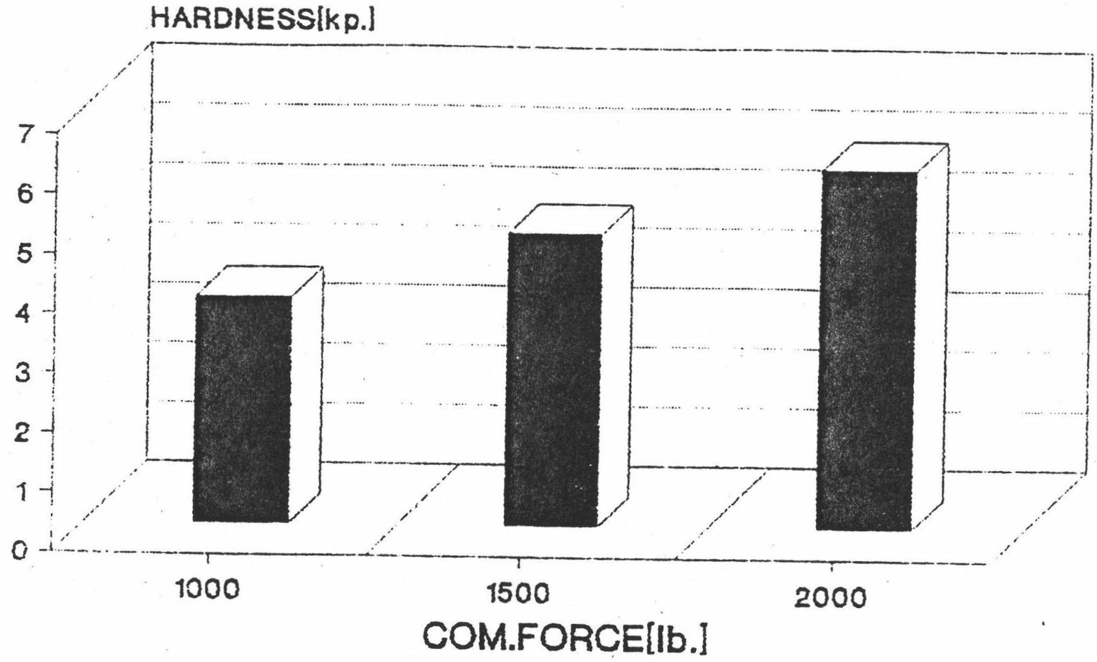


Figure 21 Pressure-Hardness Profile of tablets prepared from Starch Aggregates spray-dried at 50 % w/w conc.

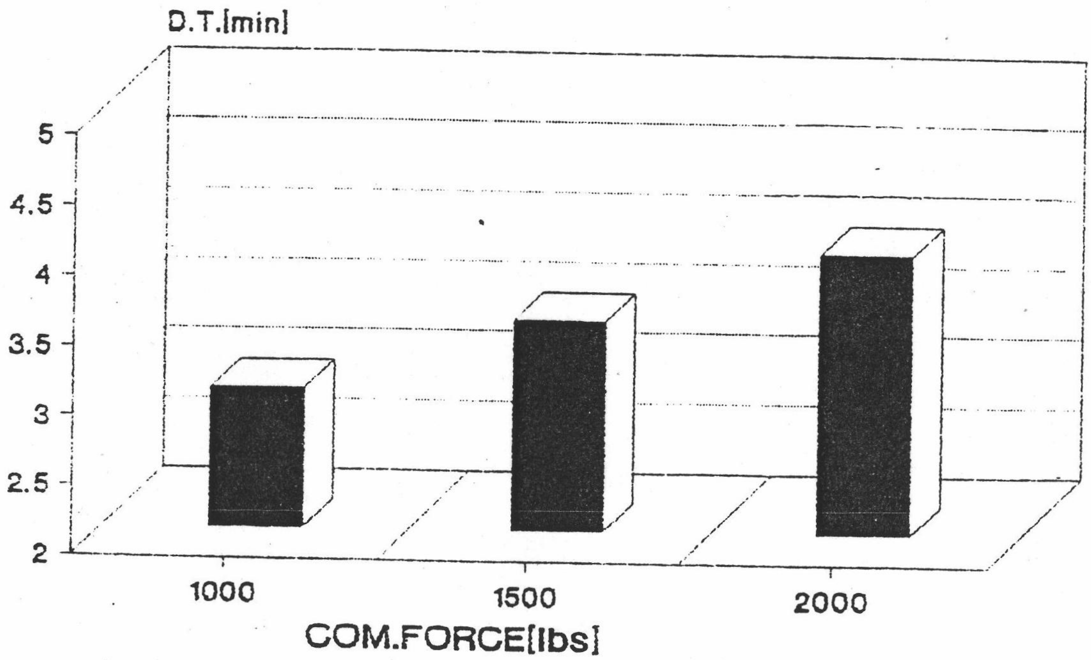


Figure 22 Pressure-Disintegration Time Profile of Tablets prepared from Starch Aggregates spray-dried at 50 % w/w conc.

developed in the atomizer and it could not be sprayed out.

The mean weight diameters of starch aggregates dried at 130 and 135 °C were 102 and 105 um. respectively (Table 10 and Fig.23-24, Size distribution data in Table 25-26[Appendix]). Moisture contents were 10.7 and 8.6 % respectively. Bulk and tapped density of starch aggregates at the two temperatures were not much different. The other properties, i.e. compressibility, angle of repose and flow rate were also similar.

When comparing the tabletting properties of starch aggregates produced at 130 and 135 °C and compressed at 1,000 lb., the friability values were 0.68 and 1.29 % respectively (Table 11 and Fig. 25-26). Hardness values were 3.8 and 3.0 kp. respectively, indicating poor com pressibility. Disintegration time values were 3:00 and 1:35 min. respectively, showing rapid disintegration. At 1,500 and 2,000 lb., the results proceeded in the same fashion except the friability values were all with in 1% limit. Disintegration time increased slightly to the maximum of 3:30 and 2:00 min. at 1,500 lb., 4:00 and 2:25 min. at 2,000 lb. for inlet air temperature of 130 and 135 °C respectively. Hardness of all tablets decreased with increasing inlet air temperature at

Table 10 Effects of Temperature on Physical Properties of Starch Aggregates.
(Conc. 50 % W/W, F.R. 12.96 g/min, P. 1.5 bar)

Temp. [c]	M.Wt.Dia. [um]	% M.C.	B.D. [g/ml]	T.D. [g/ml]	% COM.	A.Q.R. [o]	Fl.R. [g/sec]
130	102	10.7	0.54[0.002]	0.66[0.003]	18.18[1.65]	31.96[1.31]	15.62[1.37]
135	105	8.6	0.52[0.001]	0.67[0.004]	22.39[1.89]	32.85[1.52]	16.94[1.57]

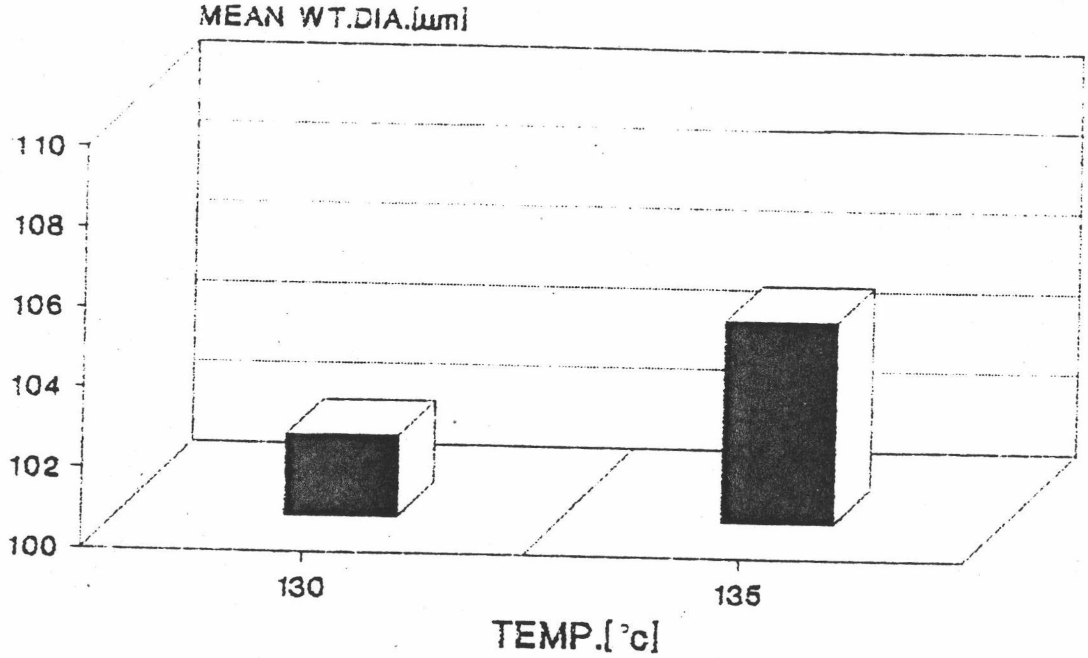


Figure 23 Effects of Temperatures on Mean Wt. Diameters of Starch Aggregates.

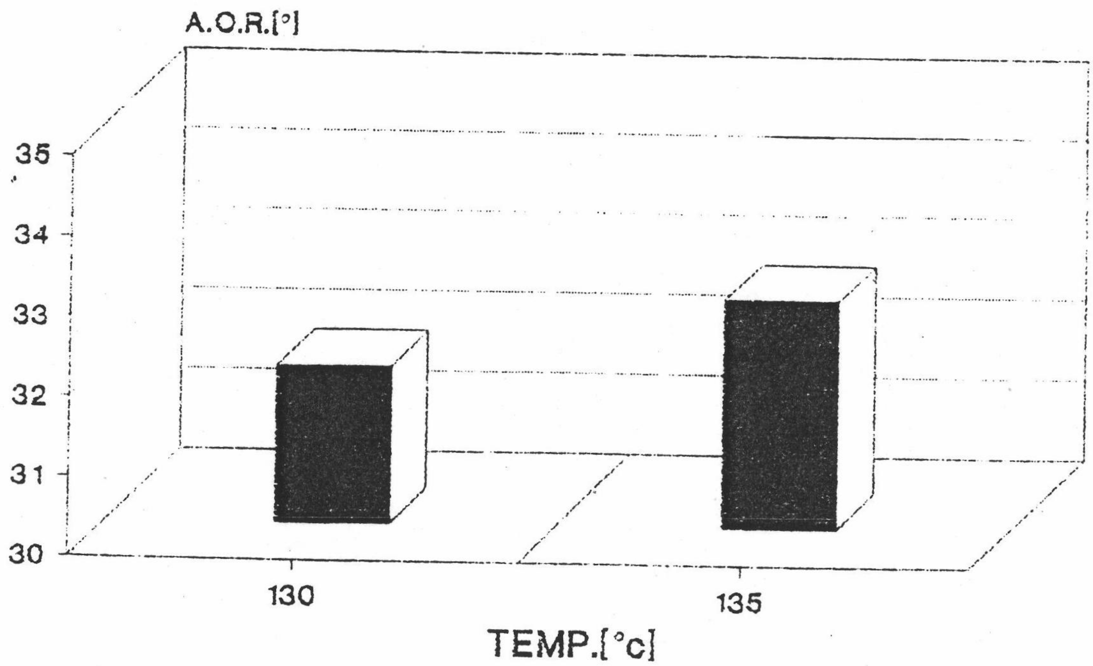


Figure 24 Effects of Temperatures on Angles of Repose of Starch Aggregates.

Table 11 Effects of Temperature on Tabletting Properties of Starch Aggregates.
(Conc. 50 % W/W, F.R. 12.96 g/min, P. 1.5 bar)

TEMP. [°c]	COM.F. [lb]	AV.WT. [mg]	THICKNESS [mm]	FRIA. [%]	D.T. [min]	HARDNFSS [kp]
130	1000	301.9[1.48]	4.17[0.04]	0.68	3.0[0.38]	3.8[0.53]
130	1500	301.3[1.40]	3.95[0.04]	0.16	3.5[0.45]	4.9[0.69]
130	2000	300.7[5.38]	3.89[0.03]	0.54	4.0[0.42]	6.0[0.48]
135	1000	309.9[1.59]	4.30[0.03]	1.29	1.6[0.31]	3.0[0.53]
135	1500	308.9[1.43]	4.06[0.02]	0.97	2.0[0.28]	3.7[1.16]
135	2000	306.6[1.38]	4.04[0.03]	0.58	2.4[0.35]	3.1[0.30]

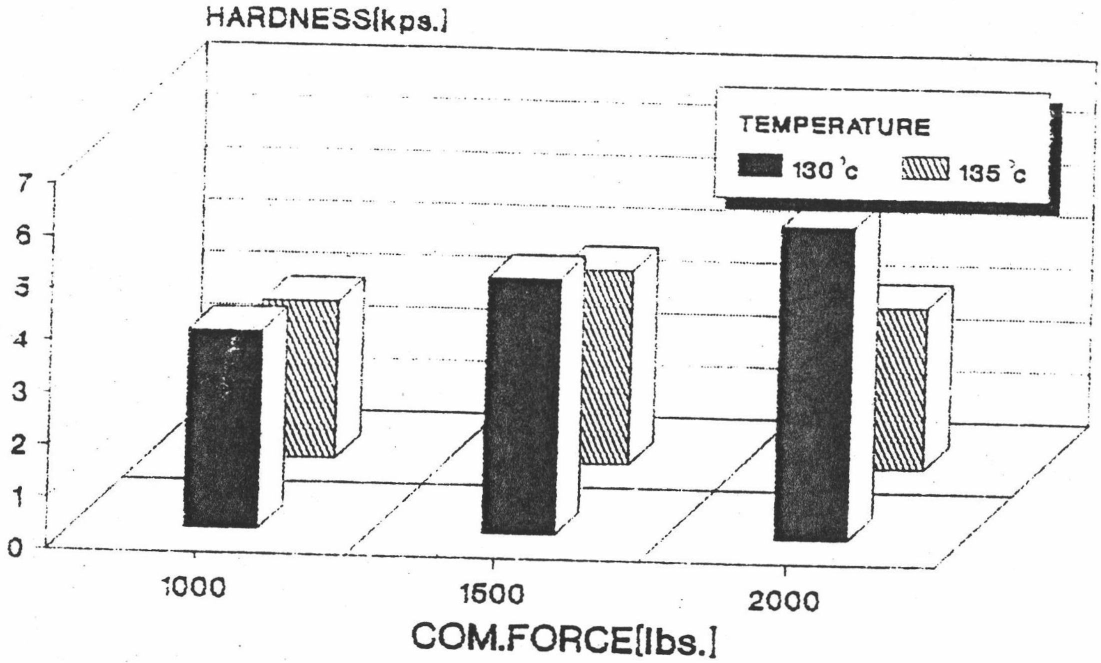


Figure 25 Effects of Temperatures on Hardness of Starch Aggregates Tablets spray-dried at 130 & 135 °C (at 1,000, 1,500 and 2,000 lbs.)............

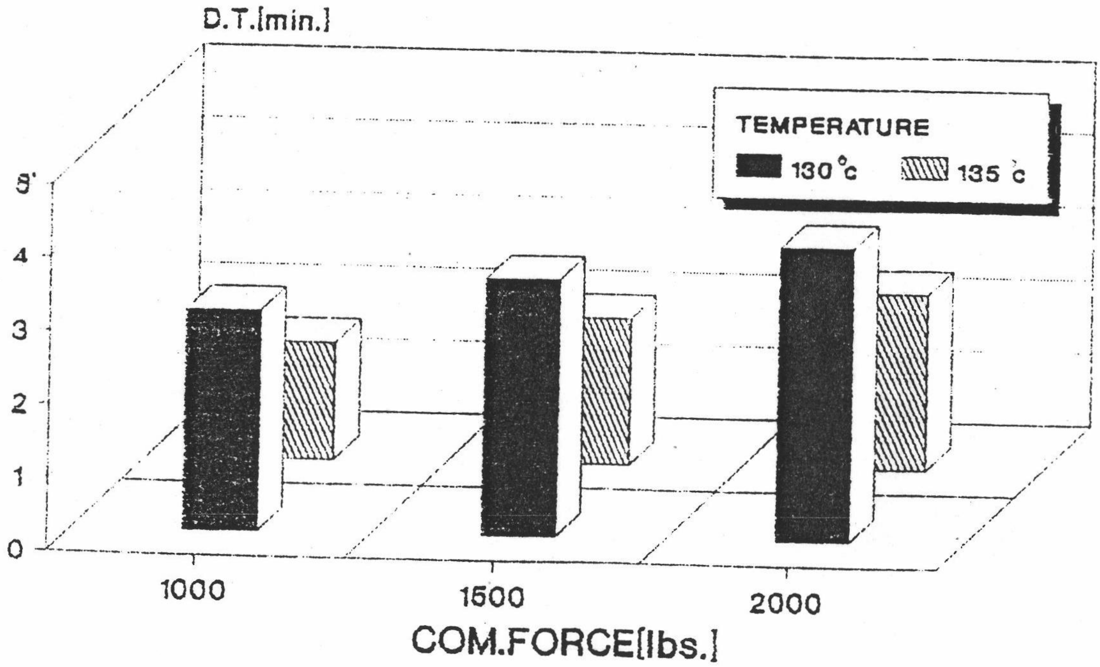


Figure 26 Effects of Temperatures on Disintegration Time of Starch Aggregates Tablets spray-dried at 130&135 °C(at 1,000, 1,500 and 2,000 lbs.)

all levels of compressional force.

2.3 Effects of Feed rates on Physical and Tabletting Properties of Spray-dried Starch Aggregates

Feed rates were varied in the range of 4.32, 12.96 and 21.60 g./min. Mean weight diameters of starch aggregates at these feed rates were 108, 102, and 106 µm., while moisture contents were 17.24, 10.70 and 9.61 % respectively (Table 12 and Fig. 27-28 , Size distribution data in table 25, 27-28). Bulk and tapped densities of the starch aggregates produced at different feed rates were nearly equal, varying from 0.52 to 0.54, and from 0.65 to 0.70 respectively. Angles of repose of 31 and 32 were obtained, and fast flow rates were obtained , reaching at 16.34 g./sec. From these results, it showed clearly that feed rate exhibited no effects on physical properties of starch aggregates.

The feed rate at 4.32 g./min gave high friability of tablet, exceeding 1.0 % limit for all three compressional forces. However, short disintegraion time values were attained, ranging between 3:30 min. and 4:15 min. and gave good hardness properties, vary ing between 4.2 and 7.7 kp. (Table 13 and Fig. 29-30)

Table 12 Effects of Feed Rates on Physical Properties of Starch Aggregates.
(Conc. 50 % W/W, Temp. 130 °C, P. 1.5 bar)

F.R. [g/min]	M.Wt.Dia. [μm]	% M.C.	B.D. [g/ml]	T.D. [g/ml]	% Com.	A.O.R. [°]	Fl.R. [g/sec]
4.32	108.00	17.24	0.52[0.002]	0.66[0.003]	22.22[1.83]	32.28[1.59]	16.34[1.48]
12.96	102.00	10.70	0.54[0.001]	0.65[0.004]	17.42[1.69]	31.96[1.68]	15.62[1.37]
21.60	106.00	9.61	0.52[0.002]	0.70[0.003]	25.80[1.92]	31.38[1.73]	16.13[1.56]

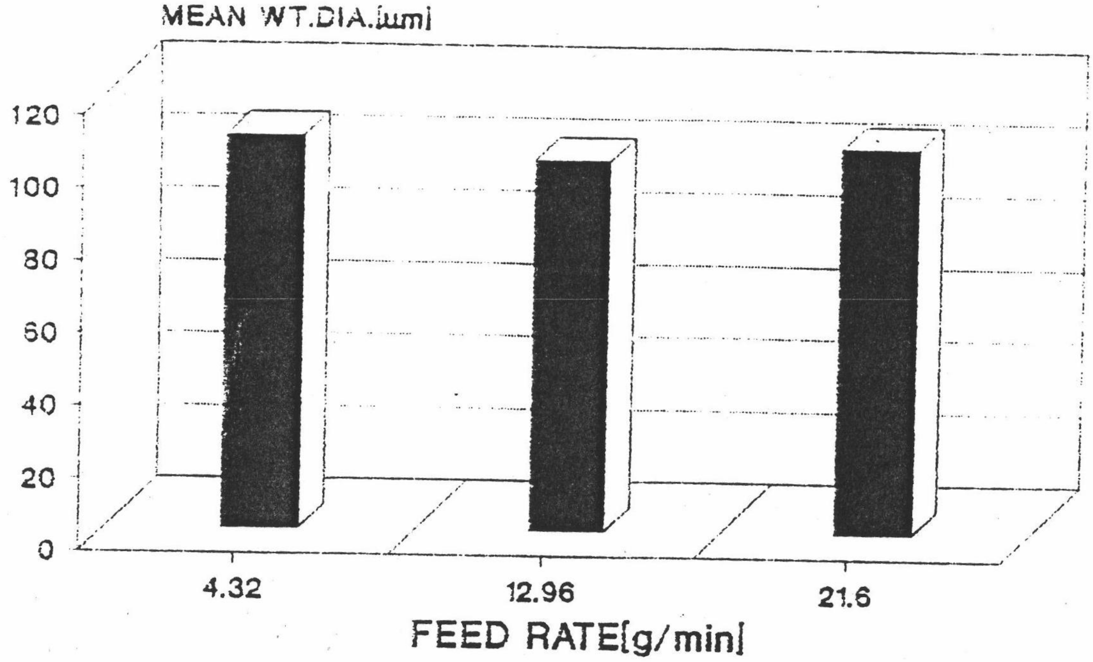


Figure 27 Effects of Feed Rates on Mean Wt. Diameters of Starch Aggregates prepared at Different Feed Rates...............................

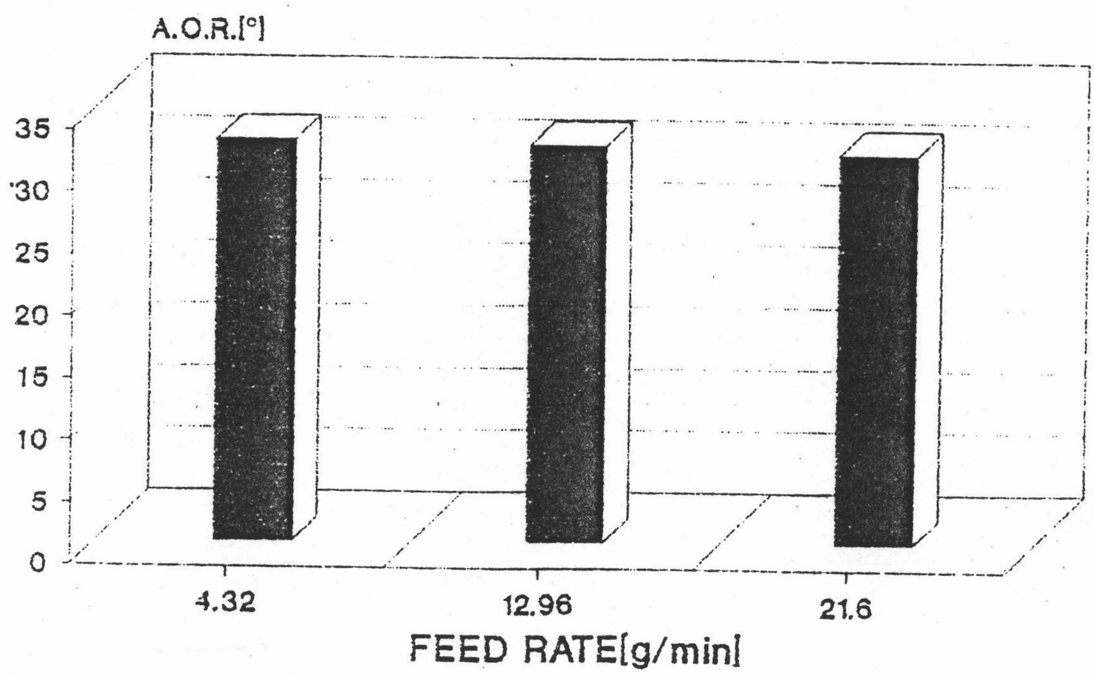


Figure 28 Effects of Feed Rates on Angles of Repose of Starch Aggregates prepared at Different Feed Feed Rates.................................

Table 13 Effects of Feed Rates on Tabletting Properties of Starch Aggregates.
(Conc. 50 % W/W, Temp. 130 °C, P. 1.5 bar)

F.R. [g/min]	Com.F. [lb]	Av.Wt. [mg]	THICKNESS [mm]	FRIA. [%]	D.T. [min]	HARDNESS [kp]
4.32	1000	306.3[1.71]	4.34[0.04]	1.12	3.50[0.46]	4.2[0.27]
4.32	1500	309.5[1.89]	4.11[0.03]	1.11	3.83[0.51]	6.6[0.41]
4.32	2000	308.8[1.64]	4.00[0.03]	1.11	4.25[0.42]	7.7[0.51]
12.96	1000	301.9[1.48]	4.17[0.04]	0.68	3.00[0.38]	3.8[0.53]
12.96	1500	301.3[1.40]	3.95[0.04]	0.16	3.50[0.45]	4.9[0.69]
12.96	2000	300.7[5.38]	3.89[0.02]	0.54	4.00[0.42]	6.0[0.48]
21.60	1000	310.3[1.65]	4.32[0.03]	1.11	1.10[0.35]	3.6[0.51]
21.60	1500	310.3[1.65]	4.16[0.04]	1.01	1.70[0.39]	4.6[0.61]
21.60	2000	309.0[1.67]	4.07[0.03]	0.74	2.00[0.34]	5.6[0.62]

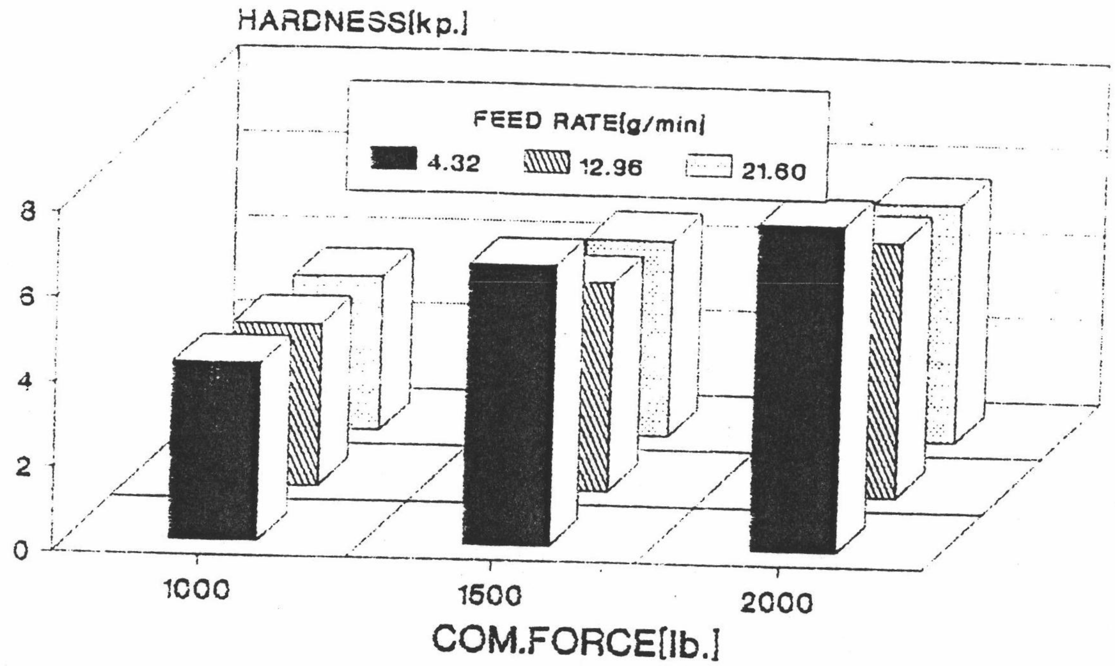


Figure 29 Effects of Feed Rates on Hardness of Starch Aggregates Tablets(at 1,000, 1,500 and 2,000 lbs.)....................................

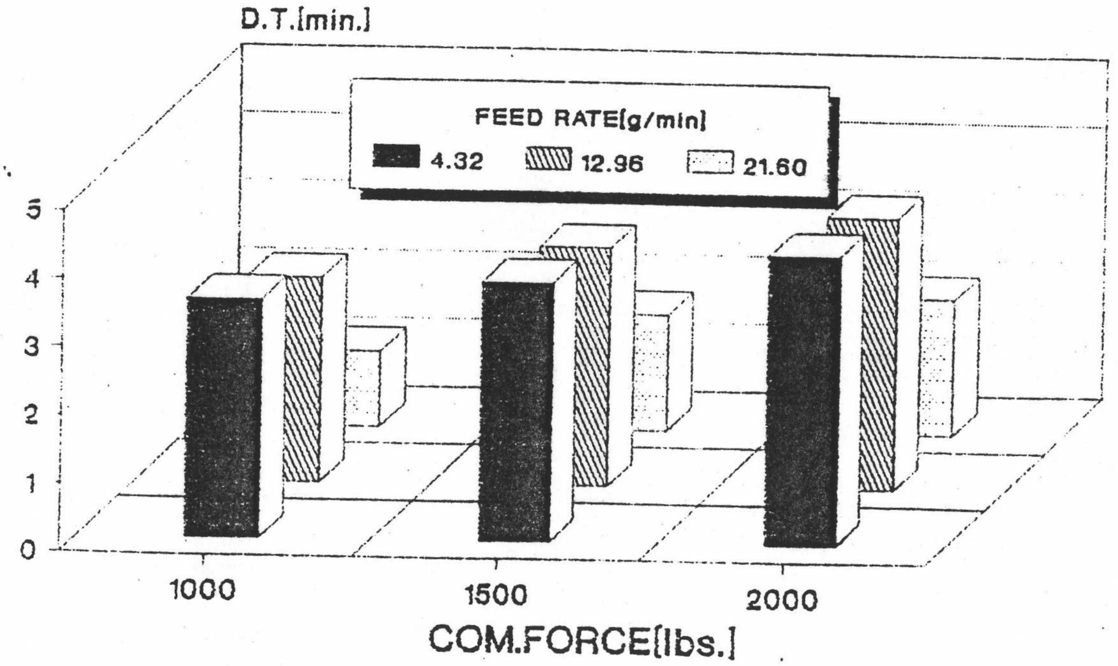


Figure 30. Effects of Feed Rates on Disintegration time of Starch Aggregates Tablets(at 1,000, 1,500 and 2,000 lbs.)..............................

When the feed rate was increased to 12.96 g./min., friability values were lower, and disintegration time became shorter, ranging from 3:00 to 4:00 min. as well as hardness values were lower, ranging from 3.8 to 6.0 kp. at all the three pressure levels employed.

At the maximum feed rate of 21.60 g./min., friability values were out of the limit,reaching 1.11 % at 1,000 lb. Disintegration time were shorter with the minimum at 1:05 min. (1,000 lb.), while hardness decreased slightly, with the highest value at 5.6 kp. (2,000 lb.)

2.4 <u>Effects of Atomizing Pressures on Physical and Tabletting Properties of Spray-dried Starch Aggregates</u>

The optimum atomizing pressure was found by experiment to be 1.5 bar(Table 14). This pressure yielded completely dry product. At 1.0 bar,the sizes of spray droplets were so large that they fell down to the bottom of the chamber as the wet mass. At 2.0 bar, the sizes were so small that they stuck to the wall of the chamber, forming an undried mass.

These results were due to the different droplet sizes produced by the atomizer. At low pressure, the droplet sizes of starch dispersion produced were large,

Table 14 Effects of Atomizing Pressures on Physical Properties of Starch Aggregates.
(Conc. 50 % W/W, Temp. 130 °C, F.R. 12.96 g/min)

P. [bar]	EFFECTS ON STARCH AGGREGATES
1.0	THEIR SIZES WERE SO LARGE THAT THEY FELL DOWN TO THE BOTTOM OF THE CHAMBER
1.5	SATISFACTORY PRODUCTS
2.0	THEIR SIZES WERE SO SMALL THAT THEY STUCK TO THE WALL OF THE CHAMBER

thus giving large starch aggregates.The large and heavy starch aggregates fell down to the bottom too quickly, allowing insufficient time for drying. In contrary, high pressure produced small droplet sizes, yield ing starch aggregates that were so small and light that they were blown too far, reaching and sticking to the wall of the chamber. Therefore the droplets form a moist layer, dry only at the surface.

Owing to the preceding results, concentration 50 % w/w, drying inlet air temperature 130 °C, feed rate 21.9 g/min, atomizing pressure 1.5 bar, which gave the most satisfactory tabletting properties, were selected to be the optimum spray-drying conditions for further studies.

3. Effects of Crosslinking Reaction on Physical and Tabletting Properties of Spray-dried Starch Aggregates

When rice flour was crosslinked and spray-dried at at the optimum conditions, the starch aggregates obtained were not completely dry. After inlet air temperature was increased to 135 °C, the aggregates became dry satisfactorily. Accordingly,this temperature was used throughout the rest of the studies.

Native rice flour gave starch aggregates with mean diameter of 105 um. After treatment by crosslinking reaction for 2, 6, 10 hrs., the mean sizes were 135, 100, 120 µm respectively (Table 15 and Fig. 31-32, see size distribution data in table 26,29-31). Moisture contents of 2, 6, 10 hr.-crosslinked rice flours were 9.7, 12.0, and 11.8 % respectively which were higher than that of native starch. No differences in densities, both bulk and tapped, were observed before and after the modification by crosslinking reaction at various time intervals. Percent compressibilities were 15.46, 21.55, 18.52 in comparison with 22.69 of the native, while angles of repose were 30.07, 29.20, and 28.11 when compared to 32.85 of native flour. Flow rates were 13.43, 13.73, and 13.38 g/sec for 2, 6, 10 hr.-crosslinked and 16.94 g/sec for native rice flour, respectively. This showed that crosslinking reaction likely played no effect on the physical properties of starch aggregates.

At 1,000 lb. compressional pressure, friability values of starch aggregates prepared from native and crosslinked rice flour at 2, 6, 10 hrs. were 1.29, 1.04 ,0.55 and 0.01 % respectively (Table 16 and Fig. 33-34). Disintegration time of native and 2, 6 hr.-cross linked rice flour were not different except that of

Table 15 **Effects of Crosslinking on Physical Properties of Starch Aggregates.**

Cl.TIME [hr]	M.Wt.Dia. [µm]	% M.C.	B.D. [g/ml]	T.D. [g/ml]	% Com.	A.O.R. [°]	Fl.R. [g/sec]
0	110	8.93	0.45[0.002]	0.56[0.003]	18.18[1.95]	30.37[0.28]	14.26[1.93]
2	118	9.30	0.44[0.003]	0.53[0.004]	17.50[1.82]	31.18[1.42]	11.82[1.76]
6	114	9.52	0.47[0.002]	0.57[0.005]	18.42[1.67]	29.41[1.57]	13.46[0.82]
10	98	14.48	0.43[0.004]	0.57[0.003]	24.17[1.89]	30.38[1.59]	14.77[0.96]

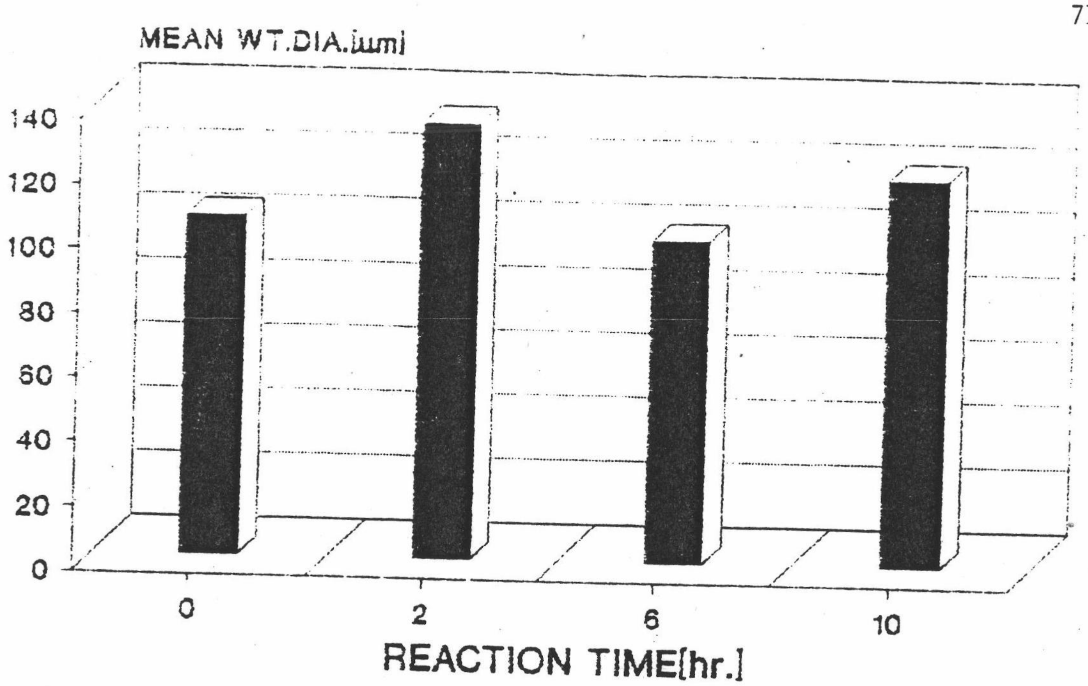


Figure 31 Effects of Crosslinking Time on Mean Wt. Diameters of Starch Aggregates..............

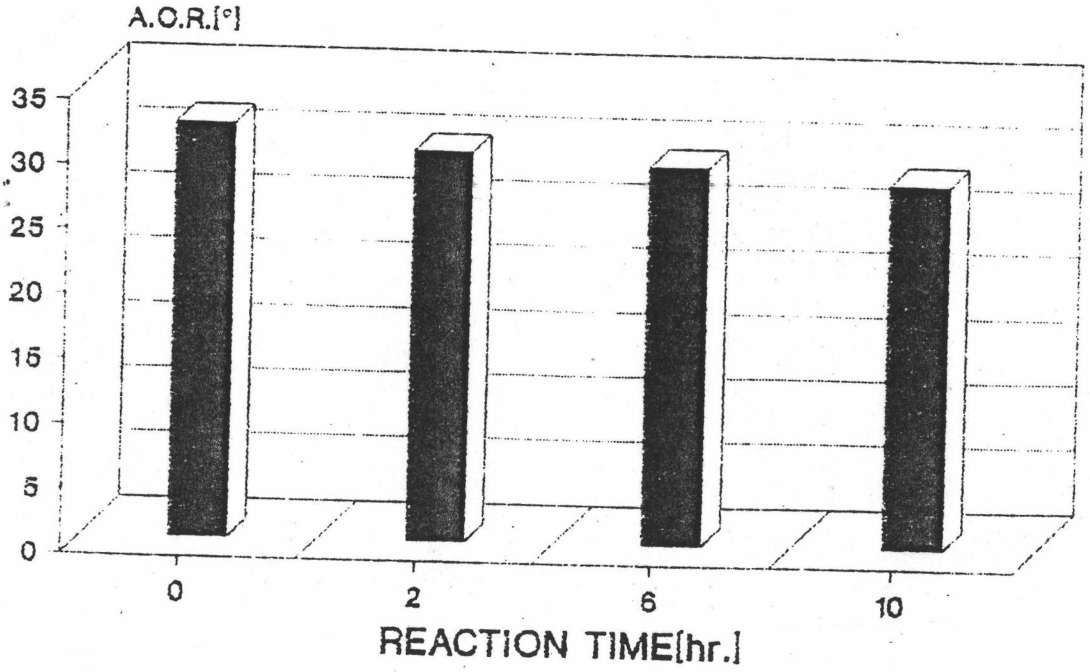


Figure 32 Effects of Crosslinking Time on Angles of Repose of Starch Aggregates.................

Table 16 **Effects of Crosslinking on Tabletting Properties of Starch Aggregates.**

Cl.TIME [hr]	Com.F. [lb]	Av.Wt. [mg]	THICKNESS [mm]	FRIA. [%]	D.T. [min]	HARDNESS [kp]
0	1000	309.9[1.59]	4.30[0.02]	1.29	1.58[0.31]	3.0[0.53]
0	1500	308.9[1.43]	4.06[0.02]	0.97	2.00[0.28]	3.7[1.16]
0	2000	306.6[1.38]	4.04[0.03]	0.58	2.42[0.35]	3.1[0.30]
2	1000	305.9[1.41]	4.31[0.03]	1.04	1.00[0.21]	4.2[0.71]
2	1500	304.9[1.39]	4.01[0.02]	1.12	1.50[0.32]	8.0[0.50]
2	2000	305.5[1.28]	3.81[0.04]	0.55	1.50[0.25]	6.5[0.50]
6	1000	306.1[1.51]	4.34[0.02]	0.59	1.25[0.31]	4.7[0.41]
6	1500	305.9[1.43]	4.14[0.03]	0.61	1.67[0.38]	6.1[0.56]
6	2000	304.7[1.63]	4.04[0.02]	0.58	1.87[0.29]	7.0[0.40]
10	1000	293.2[1.31]	4.10[0.02]	0.01	3.50[0.45]	5.8[0.68]
10	1500	294.9[1.27]	3.88[0.03]	0.02	5.08[0.52]	6.9[0.60]
10	2000	295.9[1.40]	3.77[0.02]	1.21	5.58[0.61]	12.0[1.43]

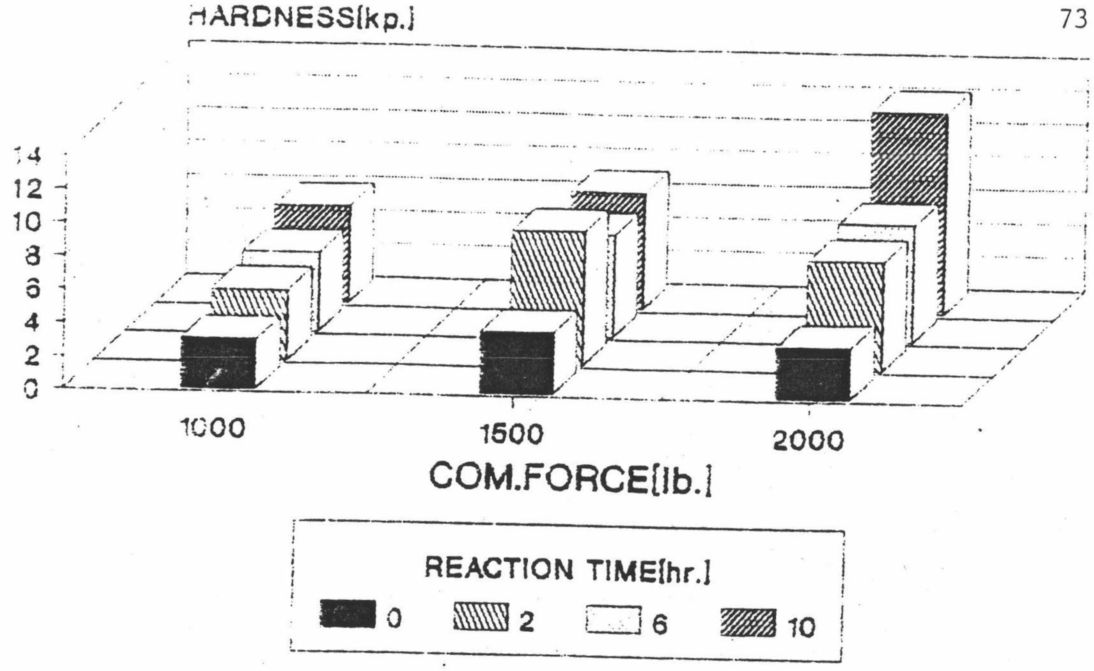


Figure 33 Effects of Crosslinking Time on Hardness of Tablets compressed at 1,000, 1,500 and 2,000 lbs..

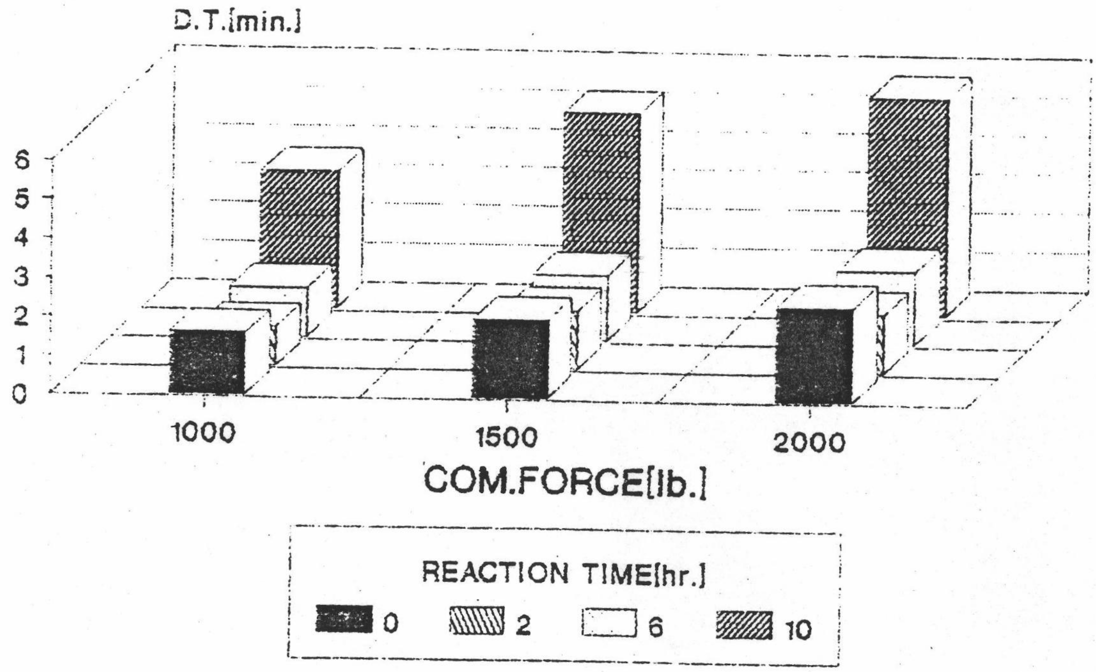


Figure 34 Effects of Crosslinking Time on Disintegration Time of Tablets compressed at 1,000, 1,5000, and 2,000 lbs.

10 hr.-crosslinked which was longer, while hardness were 3.0, 4.2, 4.7, and 5.8 kp for native and crosslinked flour at 2, 6, 10 hrs. respectively. When pressure was increased to 1,500 lb., friability data were 0.97, 1.12, 0.61, and 0.02 % respectively. Disintegration time were 2:00, 1:30, 1:40 and 5:05 min., while hardness were 3.7, 8.0, 6.1 and 6.9 kp. respectively. At the maximum pressure (2,000 lb.), friability values were all lower except for that crosslinked 10 hrs, which was out of limit at 1.21 % Disintegration time were longer, reaching the maximum at 5:35 min. for that crosslinked 10 hrs. Hardness were also higher, reaching the maximum at 12.0 kp. for that crosslinked 10 hrs.

4. <u>Effects of Deproteinization and Crosslinking on Physical and Tabletting Properties of Spray-dried Starch aggregates</u>

Mean weight diameters of deproteinized rice flour with and without crosslinking treatment for 2, 6, and 10 hrs. were close to one another ranging from 110, 118, 114, and 98 µm respectively (Table 17 and Fig. 35-36). Moisture contents were in the range of 8.93-9.52 % except for that crosslinked for 10 hrs. which

Table 17 Effects of Crosslinking on Physical Properties of Starch Aggregates (Deproteinized).

CL.TIME [hr]	M.WT.DIA. [µm]	% M.C.	B.D. [g/ml]	T.D. [g/ml]	% COM.	A.O.R. [o]	FL.R. [g/sec]
0	110	8.93	0.45[0.002]	0.56[0.003]	18.18[1.95]	30.37[0.28]	14.26[1.93]
2	118	9.30	0.44[0.003]	0.53[0.004]	17.50[1.82]	31.18[1.42]	11.82[1.76]
6	114	9.52	0.47[0.002]	0.57[0.005]	18.42[1.67]	29.41[1.57]	13.46[0.82]
10	98	14.48	0.43[0.004]	0.57[0.003]	24.17[1.89]	30.38[1.59]	14.77[0.96]

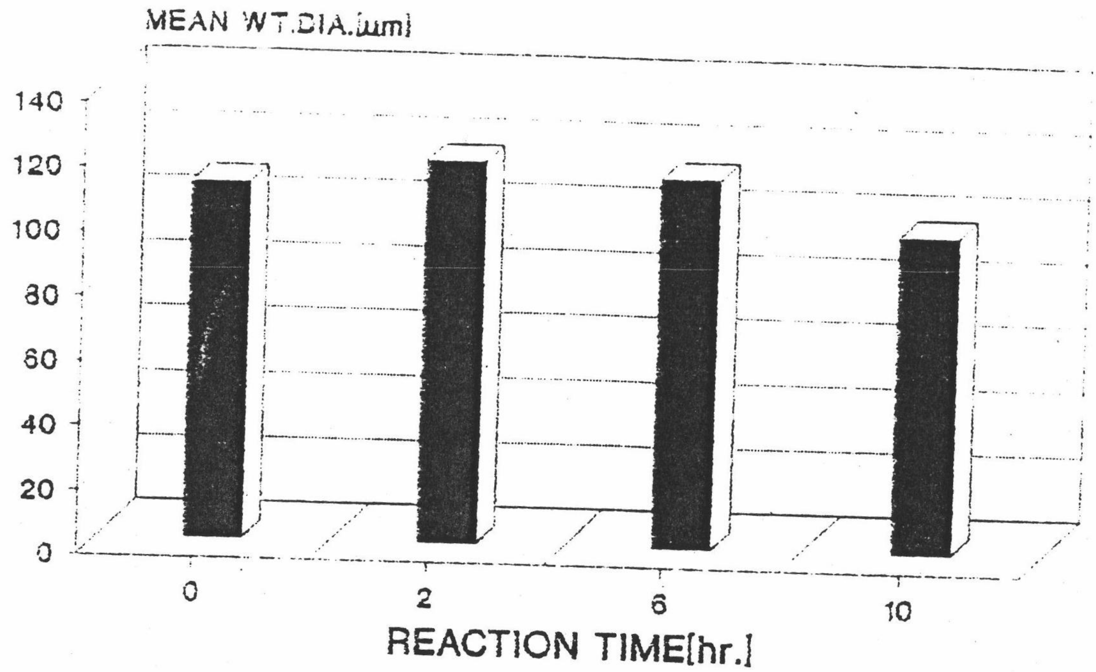


Figure 35 Effects of Deproteinization and Crosslinking on Mean Wt. Diameters of Starch Aggregates...

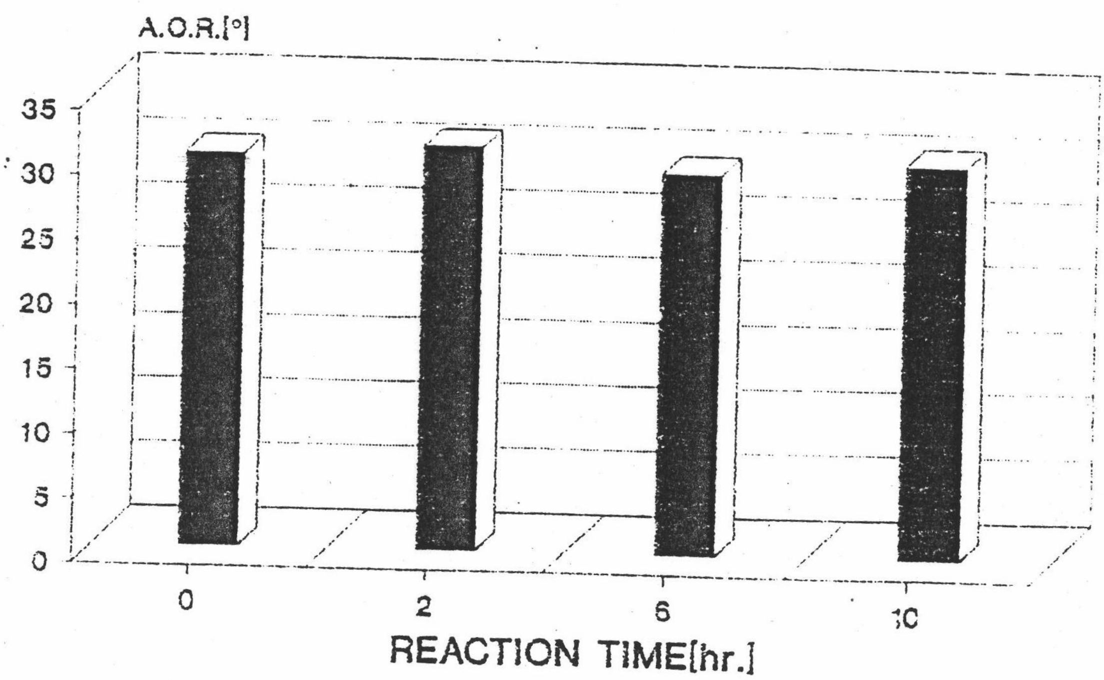


Figure 36 Effects of Deproteinization and Crosslinking on Angles of Repose of Starch Aggregates....

was higher at 14.48 % Bulk density values were nearly equal, ranging from 0.43-0.47, while tapped density were not different , ranging from 0.53-0.57. Compressibility values ranged from 17.50-18.42 % , with the maximum at 24.17 % for that crosslinked for 10 hrs. Angles of repose were in the range between 29.41 and 31.18 , good flow rates were attained, ranging from 11.82 to 14.77 g./sec.

For tablets prepared from deproteinized rice flour at 1,000, 1,500, and 2,000 lb., hardness were higher, from 8.1, 12.3, and more than 20 kp., and friability values were low, ranging from 0.56, 0.30, and 0.64 % respectively (Table 18 and Fig. 37-38). Disintegration time of tablets were also shorter, ranging from 2:35, 3:20, and 4:40 min. Starch crosslinked for 2 hrs. exhibited higher hardness value with lower friability but longer disintegration time when compared with native starch at all compressional forces. When crosslinking time was increased to 6 hrs., more friable tablets were obtained, and disintegration time were shorter, while exhibited highest hardness values, from 18.8 and more than 20 kp.. When crosslinked for 10 hrs., the contrary results were observed. Friability values were out of limit,

Table 18 Effects of Crosslinking on Tabletting Properties of Starch Aggregates (Deproteinized).

CL.TIME [hr]	COM.F. [lb]	AV.WT. [mg]	THICKNESS [mm]	FRIA. [%]	D.T. [min]	HARDNESS [kp]
0	1000	305.6[1.69]	4.37[0.03]	0.56	2.58[0.28]	8.1[0.73]
0	1500	303.8[1.75]	4.08[0.02]	0.30	3.33[0.35]	12.3[0.69]
0	2000	309.7[1.82]	3.95[0.04]	0.64	4.67[0.43]	>20.0[0.15]
2	1000	307.4[1.72]	4.21[0.05]	0.21	4.67[0.37]	15.6[1.78]
2	1500	307.7[1.62]	4.01[0.04]	0.14	5.00[0.48]	18.0[2.43]
2	2000	308.5[1.76]	3.91[0.03]	0.09	5.75[0.42]	>20.0[0.47]
6	1000	314.5[1.91]	4.19[0.02]	0.54	3.00[0.47]	18.8[1.32]
6	1500	311.7[1.83]	4.02[0.03]	0.52	4.00[0.52]	>20.0[0.14]
6	2000	308.8[1.71]	3.91[0.04]	0.50	4.25[0.59]	>20.0[1.63]
10	1000	305.5[1.62]	4.33[0.04]	1.88	4.33[0.72]	7.8[0.66]
10	1500	305.0[1.69]	4.08[0.02]	1.90	5.25[0.81]	10.9[1.25]
10	2000	303.8[1.54]	3.92[0.03]	0.82	6.00[0.93]	17.7[1.15]

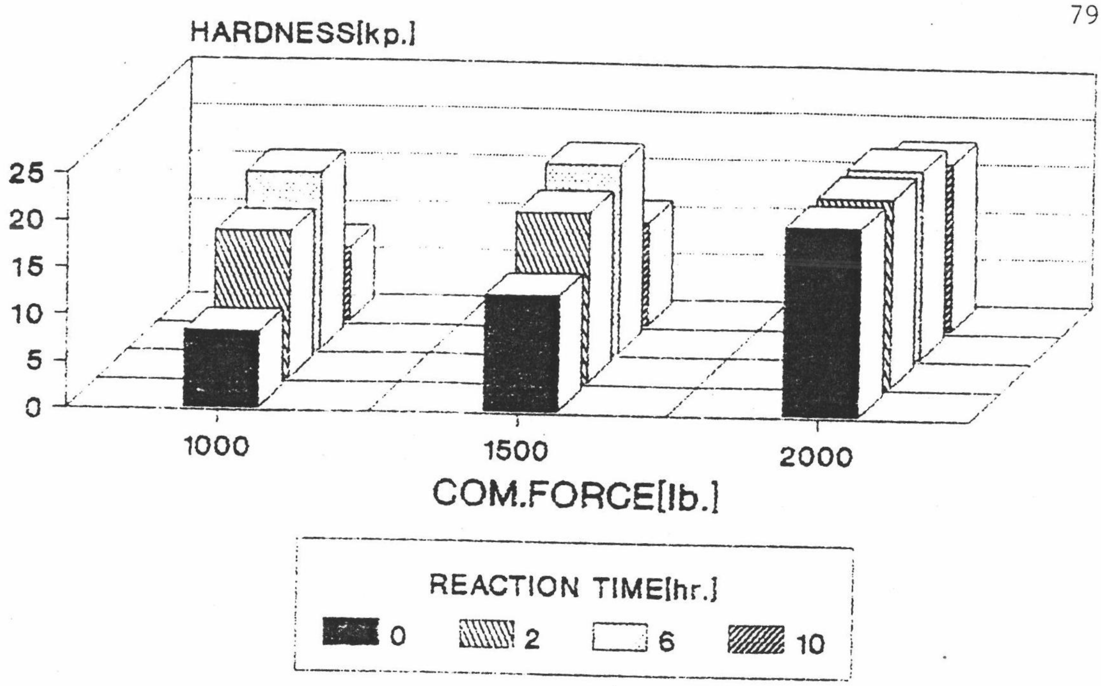


Figure 37 Effects of Deproteinization and Crosslinking on Hardness of Starch Aggregates Tablets compressed at 1,000, 1,500, and 2,000 lbs.

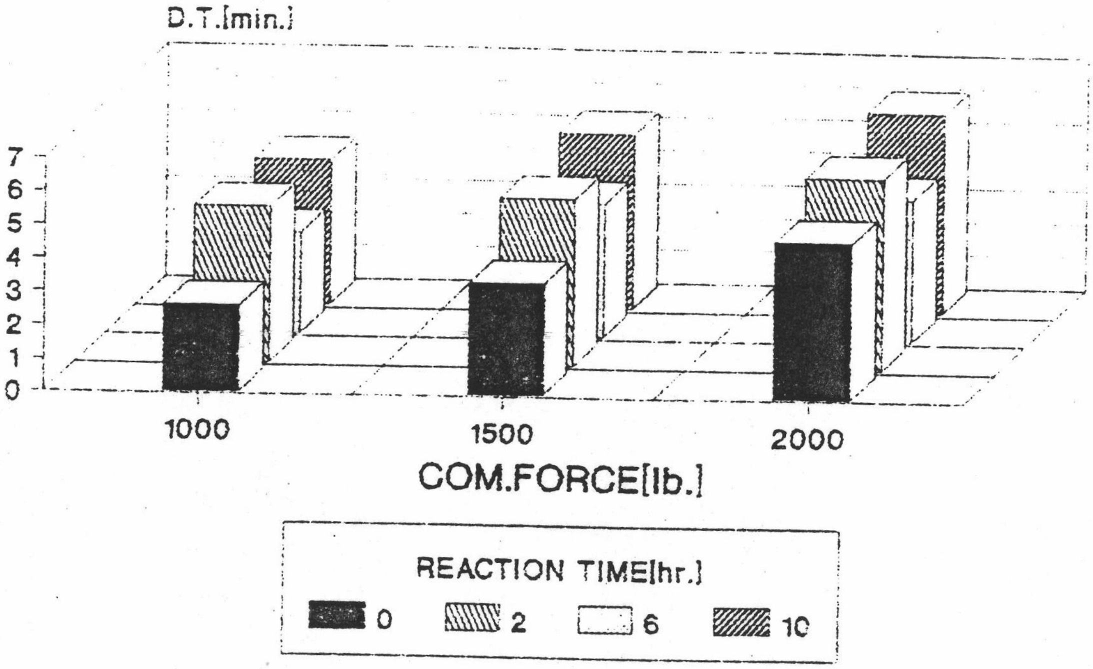


Figure 38 Effects of Deproteinization and Crosslinking on Disintegration Time of Starch Aggregates Tablets compressed at 1,000, 1,500, and 2,000 lbs.

disintegration time were also longer, and lower degree of compressibility was observed, ranging from 7.8, 10.9 and 17.7 kp. respectively. These results showed that starch aggregates crosslinked for 10 hrs.exhibited lower hardness than those crosslinked for 6 or 2 hrs.

5. <u>Physical and Tabletting Properties of Comparative Starch Products</u>

Table 19 showed the physical properties of Starch 1500^R and Eratab^R employed as comparative materials in evaluation of tabletting properties of modified rice starch products. The mean weight diameter of starch 1500^R was 80 µm. Moisture content was 11.50 % with bulk and tapped densities of 0.56 and 0.79 g/ml respectively. Percent compressibility was high, reaching 29.11 % but angle of repose was low, only 29.88 with good flow rate at 15.32 g/sec. Eratab^R had the mean weight dia meter of 88 µm. Moisture content was a little higher at 13.54 % with bulk and tapped densities at 0.50 and 0.63 g/ml respectively. Percent compressibility was low, 21.13 %, while angle of repose was high, but acceptable at 34.67 with good flow rate of 15.94 g/sec.

Friability of Starch 1500^R, when compressed at 1,000; 1,500; and 2,000 lb., were high, but within 1 %

Table 19 Physical Properties of Comparative Starch Products

NAME	M.Wt.Dia. [μm]	% M.C.	B.D. [g/ml]	T.D. [g/ml]	% Com.	A.O.R. [°]	Fl.R. [g/sec]
STARCH 1500	80	11.50	0.56[0.003]	0.79[0.005]	29.11[1.97]	29.88[2.17]	15.32[1.65]
ERATAB	88	13.54	0.50[0.004]	0.63[0.004]	21.13[1.81]	34.67[3.72]	15.94[1.10]

limit(Table 20). However,it exhibited long disintegra tion time, more than 30 min. at all three pressures. Hardness values were fairly good, between 7.4 and 12.3 kp. Friability of Eratab[R] tablets compressed at the same pressures were lower, 0.45-0.47 % and exhibit ed fastest disintegration. Hardness at various com pressional forces were also good at 12.7, 16.5 and 17.4 kp.

6. Viscosity characteristics of Various Modified Starches

6.1 Viscosities of Crosslinked Rice Flours

At room temperature(25 °C), the viscosity of native rice flour was about 22 B.U.(Fig.39) It did not change when the temperature was increased to 95 °C at the rate of 3 °C/min. When the temperature reached 95 °C, the viscosity began to rise gradually to 80 B.U. after 9 min. had passed. It then increased instantly to its peak at 700 B.U. at 26 min. of holding time. The viscosity then decreased gradually to 570 B.U. about 18 min. after the end of holding time. However, it rose slightly to 600 B.U. at 40 °C.

When rice flour was crosslinked for 2 hrs., the viscosity curve differed greatly from the uncrosslinked

Table 20 Tabletting Properties of Comparative Starch Products

NAME	Com.F. [lb]	Av.Wt. [mg]	THICKNESS [mm]	FRIA. [%]	D.T. [min]	HARDNESS [kp]
STARCH 1500	1000	299.8[1.32]	4.08[0.02]	0.93	>30[0.00]	7.7[0.52]
	1500	300.7[1.45]	3.94[0.03]	0.85	>30[0.00]	10.8[0.58]
	2000	300.6[1.35]	3.88[0.02]	0.71	>30[0.00]	12.3[0.98]
ERATAB	1000	298.3[1.47]	4.09[0.03]	0.45	1.75[0.62]	12.7[1.04]
	1500	298.3[1.47]	3.88[0.02]	0.37	3.42[0.75]	16.5[2.23]
	2000	297.8[1.38]	3.83[0.03]	0.47	3.42[0.69]	17.4[1.81]

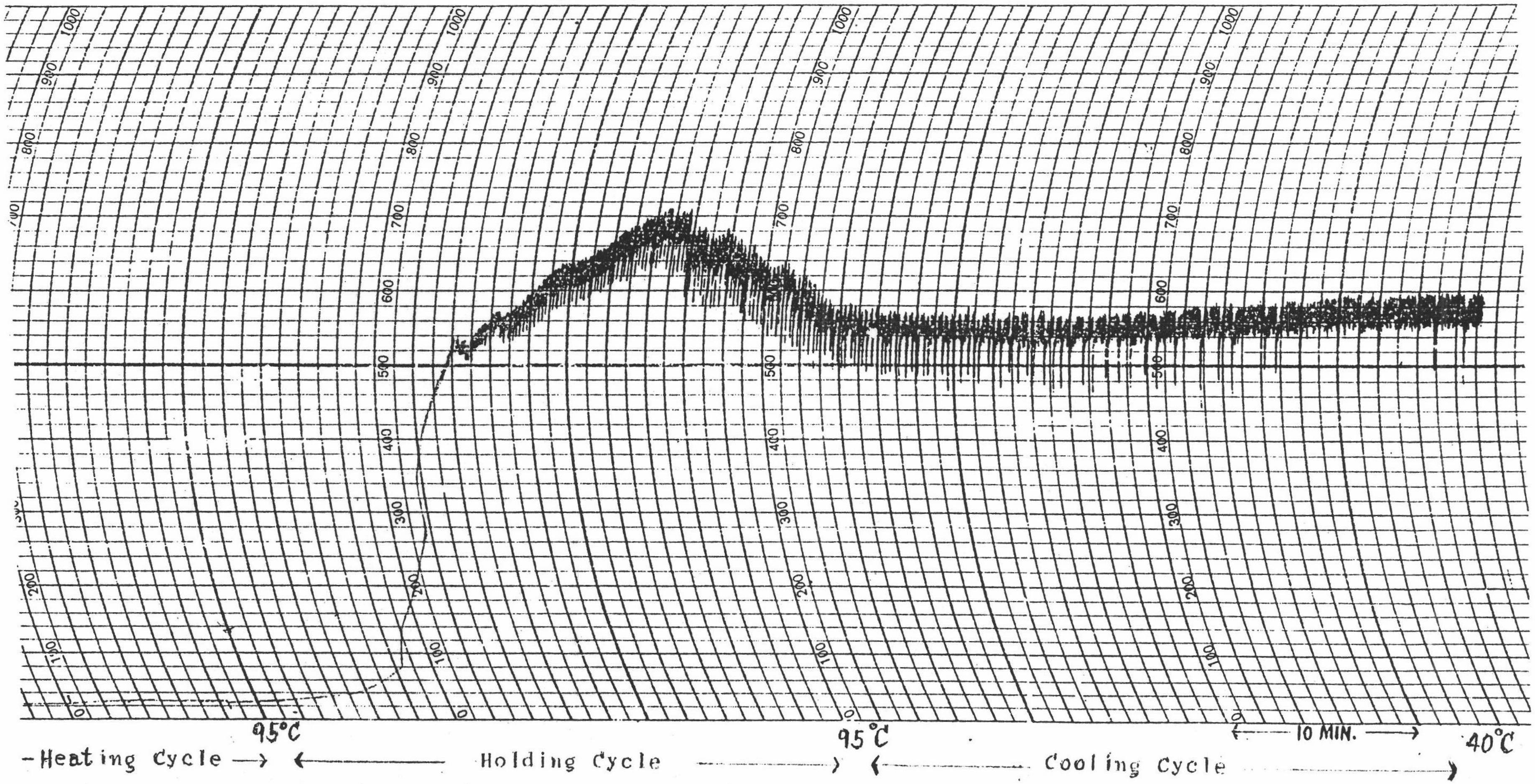


Figure 39 Brabender Viscosity Curve of Rice Flour (native).

starch (Fig. 40). At first, the viscosity remained unchanging at 22 B.U. when the starch dispersion was heated from 25 °C to 95 °C. It began to rise gradually after 8 min. of holding time had passed, and still rose continuously without its peak even after holding cycle had completed. At the end of holding time, the viscosity was 180 B.U. During cooling cycle, at 40 °C,it was about 270 B.U. after 30 min. had passed.

The 6 hr.-crosslinked rice flour showed a different picture from those previously mentioned (Fig. 41). The viscosity remained to unchange at 24 B.U. after heating, holding, and cooling cycles. When crosslinked for 10 hrs. (Fig. 42), the viscosity curve was similar to that crosslinked for 6 hrs. It was constant at 22 B.U. for the whole course of measurement, very slightly lower than the 6 hr.-crosslinked.

6.2 <u>Viscosities of Deproteinized and Crosslinked Rice Flours</u>

Deproteinized rice flour gave the pattern of viscosity curve that was similar to that of the native one(Fig.43). The viscosity remained to unchange at 20 B.U. from room temperature to 95 °C, then it increased instantly to its peak at 720 B.U. after

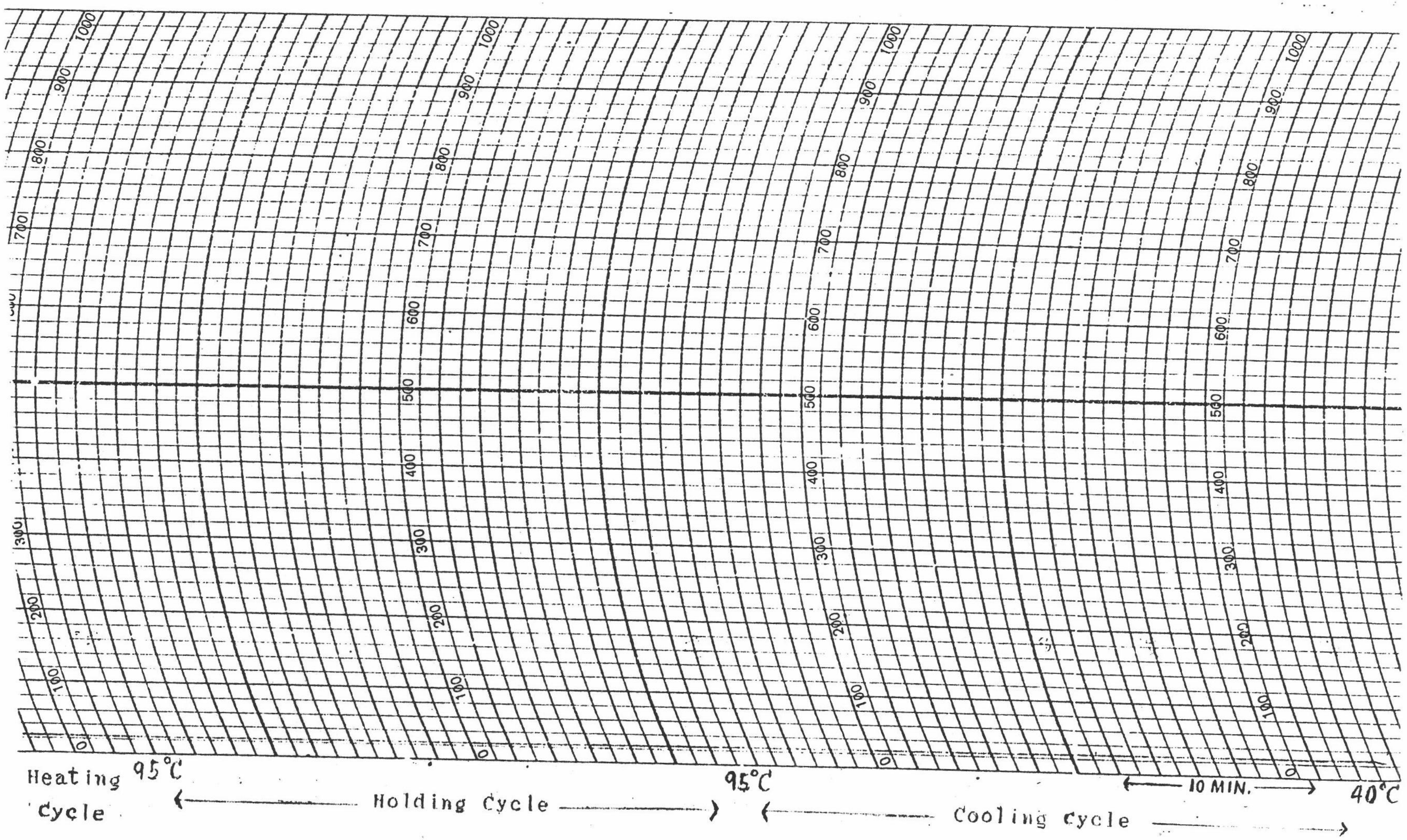


Figure 40 Brabender Viscosity Curve of Rice Flour, Crosslinked 2 hrs.

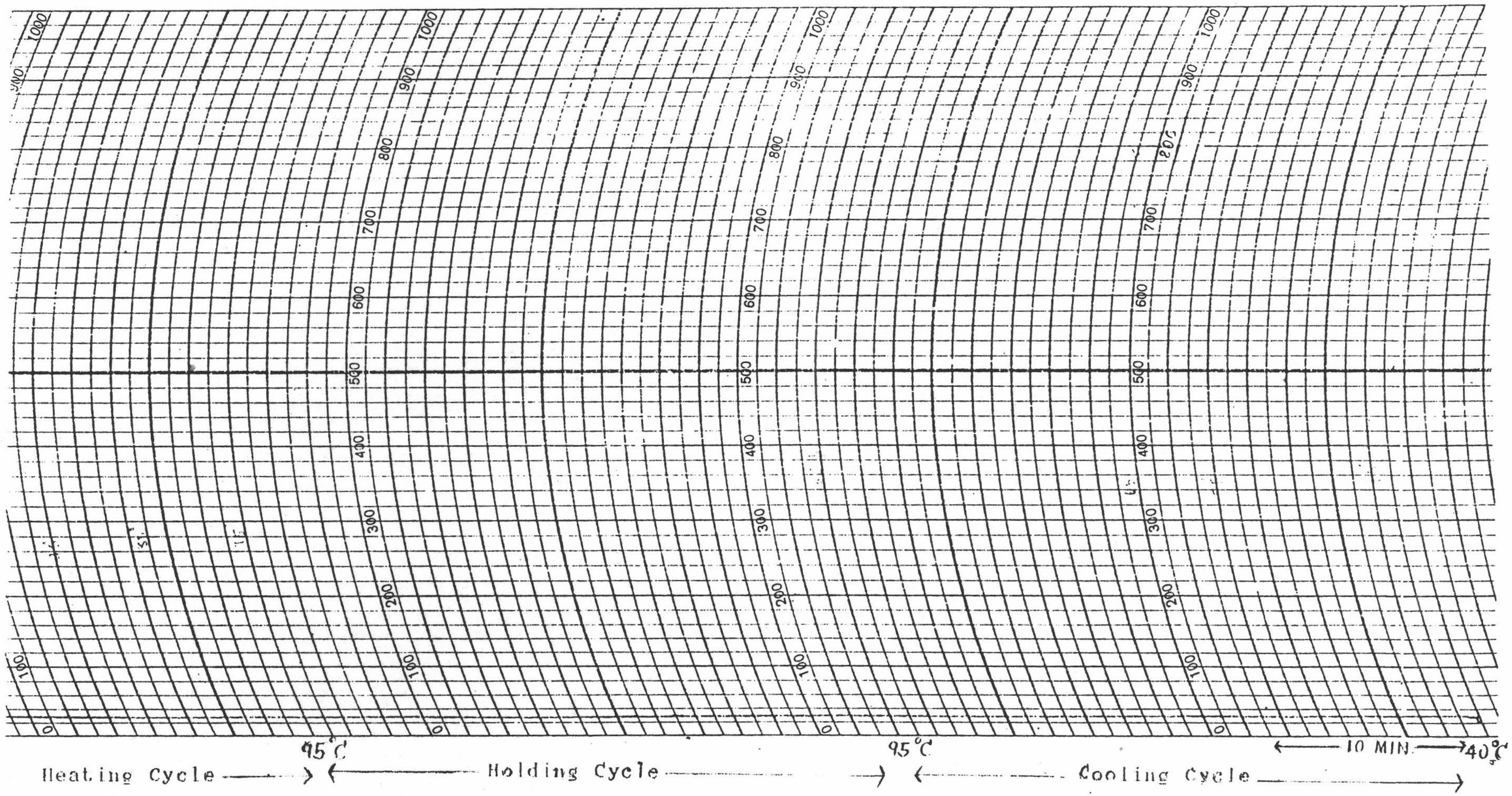


Figure 41 Brabender Viscosity Curve of Rice Flour, Crosslinked 6 hrs.

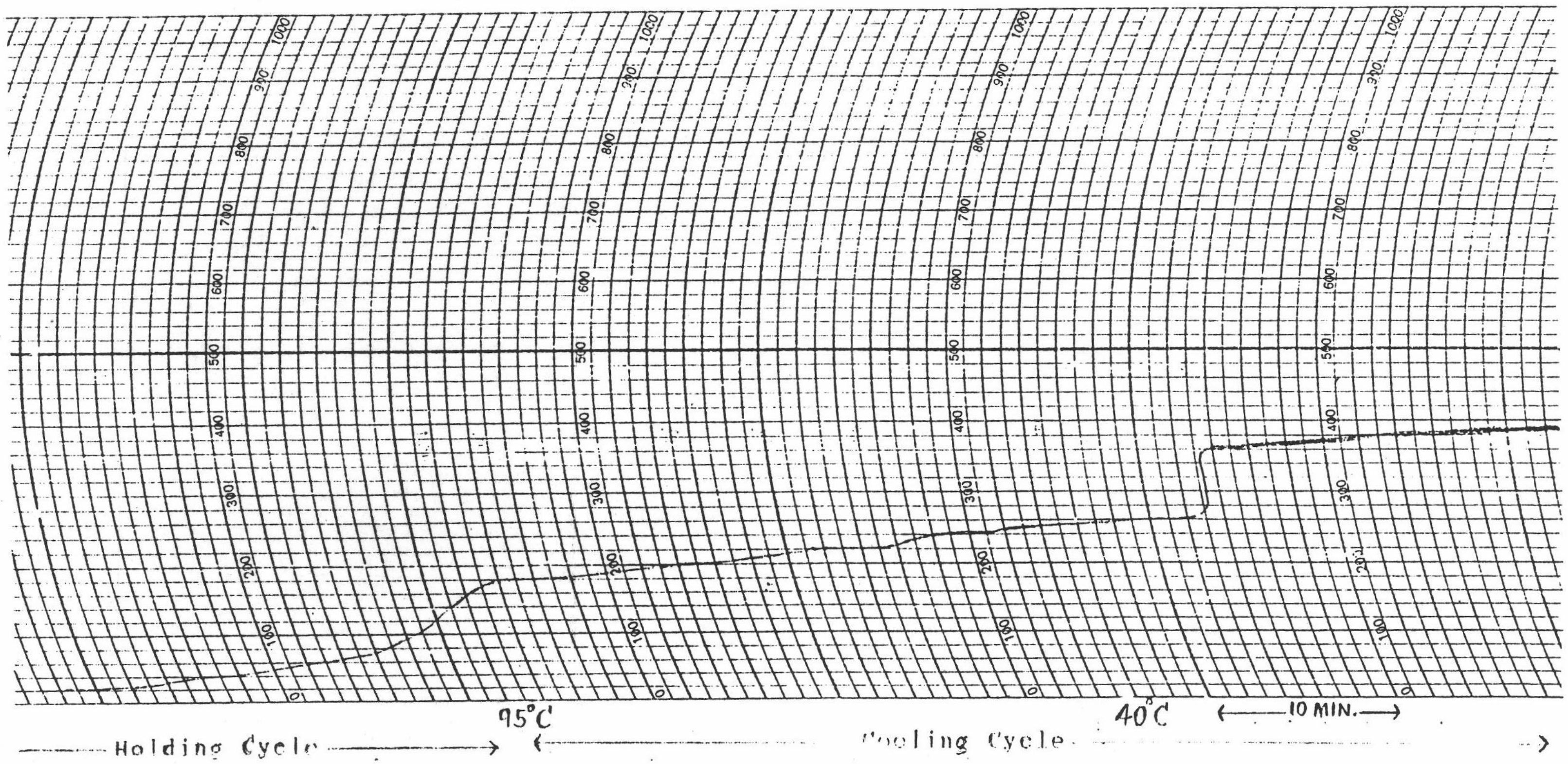


Figure 42 Brabender Viscosity Curve of Rice Flour, Crosslinked 10 hrs.

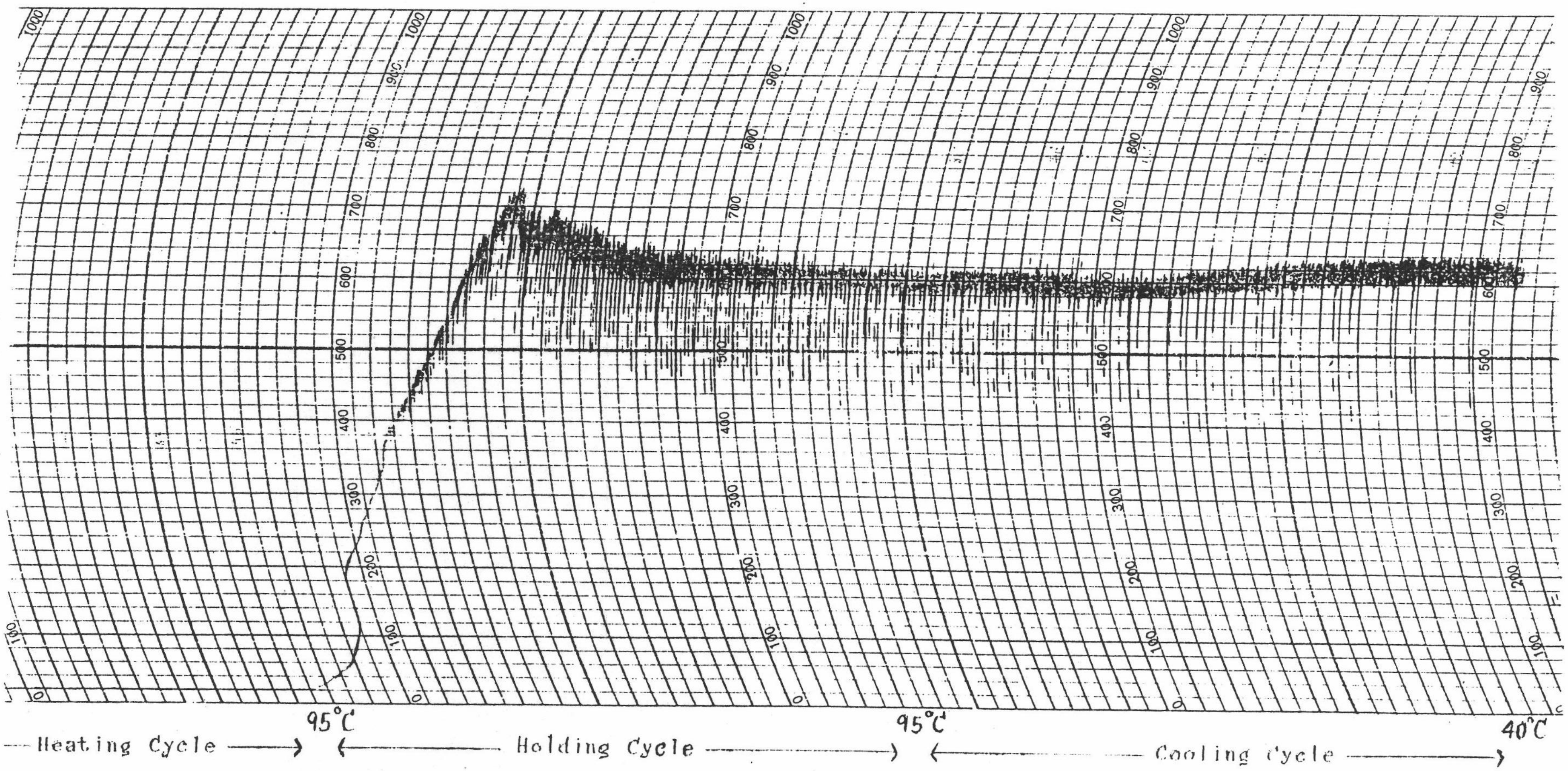


Figure 43 Brabender Viscosity Curve of Deproteinized Rice Flour...................................

14 min. of holding cycle. It then decreased gradually to 600 B.U. at 60 °C during cooling cycle and rose slightly to 640 B.U. at 40 °C.

Deproteinized and 2 hr.-crosslinked rice flour showed the different pattern (Fig. 44). After remaining at 10 B.U. during the heating cycle, it increased appreciably during the holding cycle and reached 350 B.U. at the end of the cycle. It then increased gradually during the cooling cycle. reaching 450 B.U. at 40 °C.

Viscosity curves of those deproteinized and crosslinked for 6 & 10 hrs. were very similar (Fig. 45-46). They remained to unchange throughout the three cycles at 16 and 12 B.U. respectively.

In conclusion, it was seen that the viscosity of native rice flour was reduced from 600 B.U. to 26, 30,and 250 B.U. after crosslinked for 2, 6, and 10 hrs. respectively (Table 21 and Fig. 47). As well as, the viscosity of deproteinized rice flour decresased after it was crosslinked at the same intervals (Table 22 and Fig. 47).

7. <u>Swelling Power of Various Modified Rice Flours</u>

Swelling Power of native rice flour was 696.3 %,

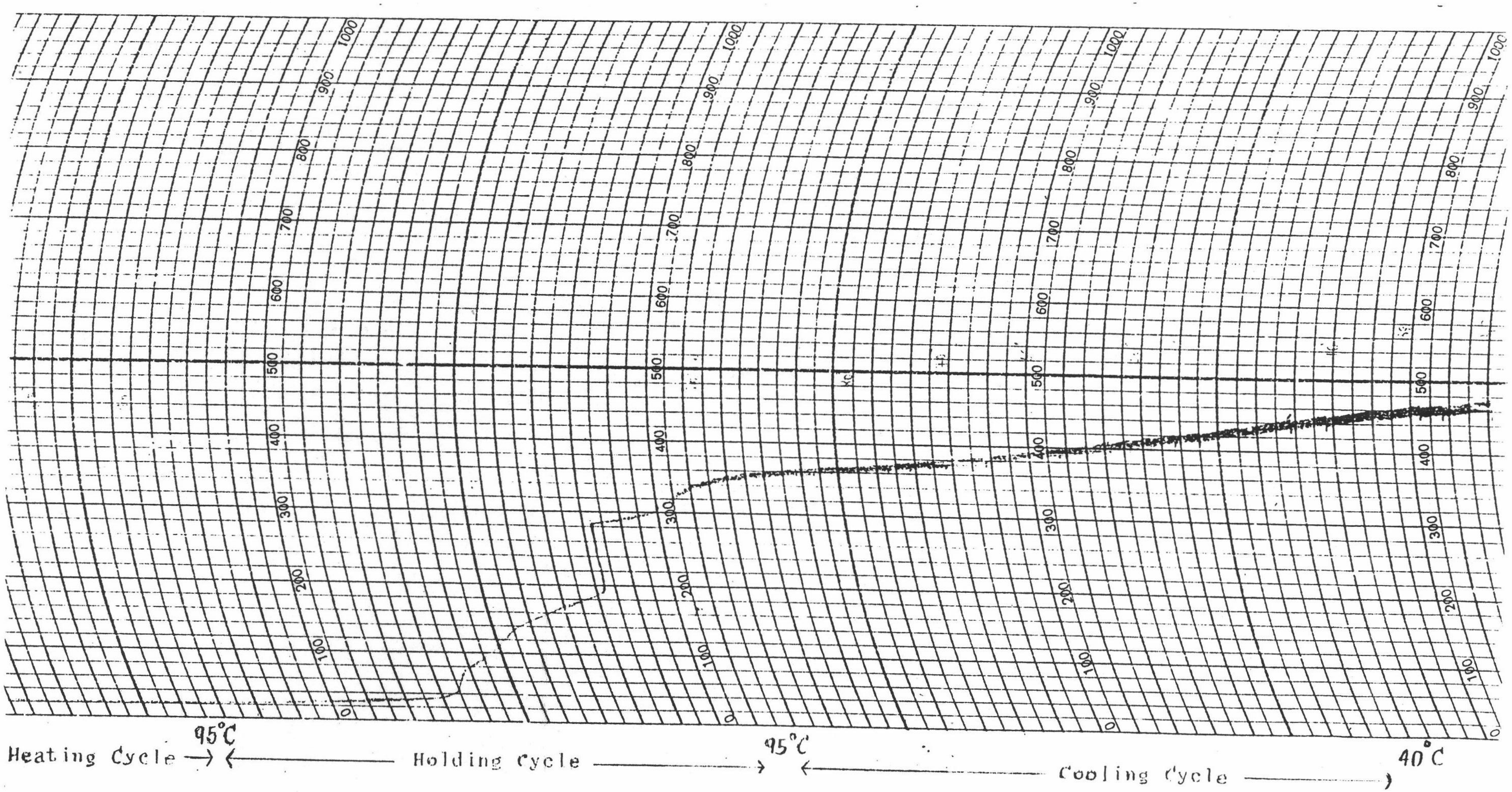


Figure 44. Brabender Viscosity Curve of Deproteinized Rice Flour, crosslinked 2 hrs.

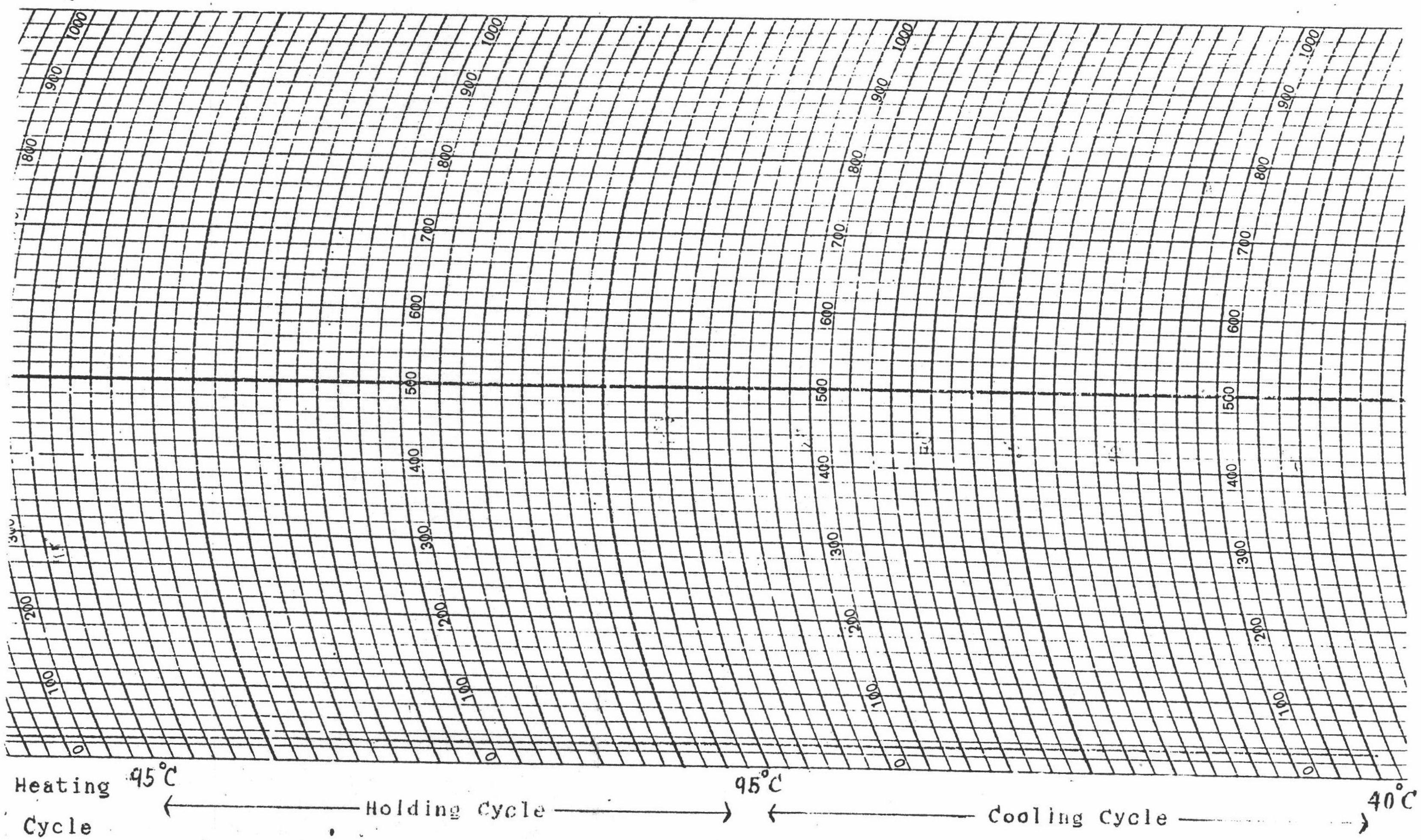


Figure 45 Brabender Viscosity Curve of Deproteinized Rice Flour, crosslinked 6 hrs.

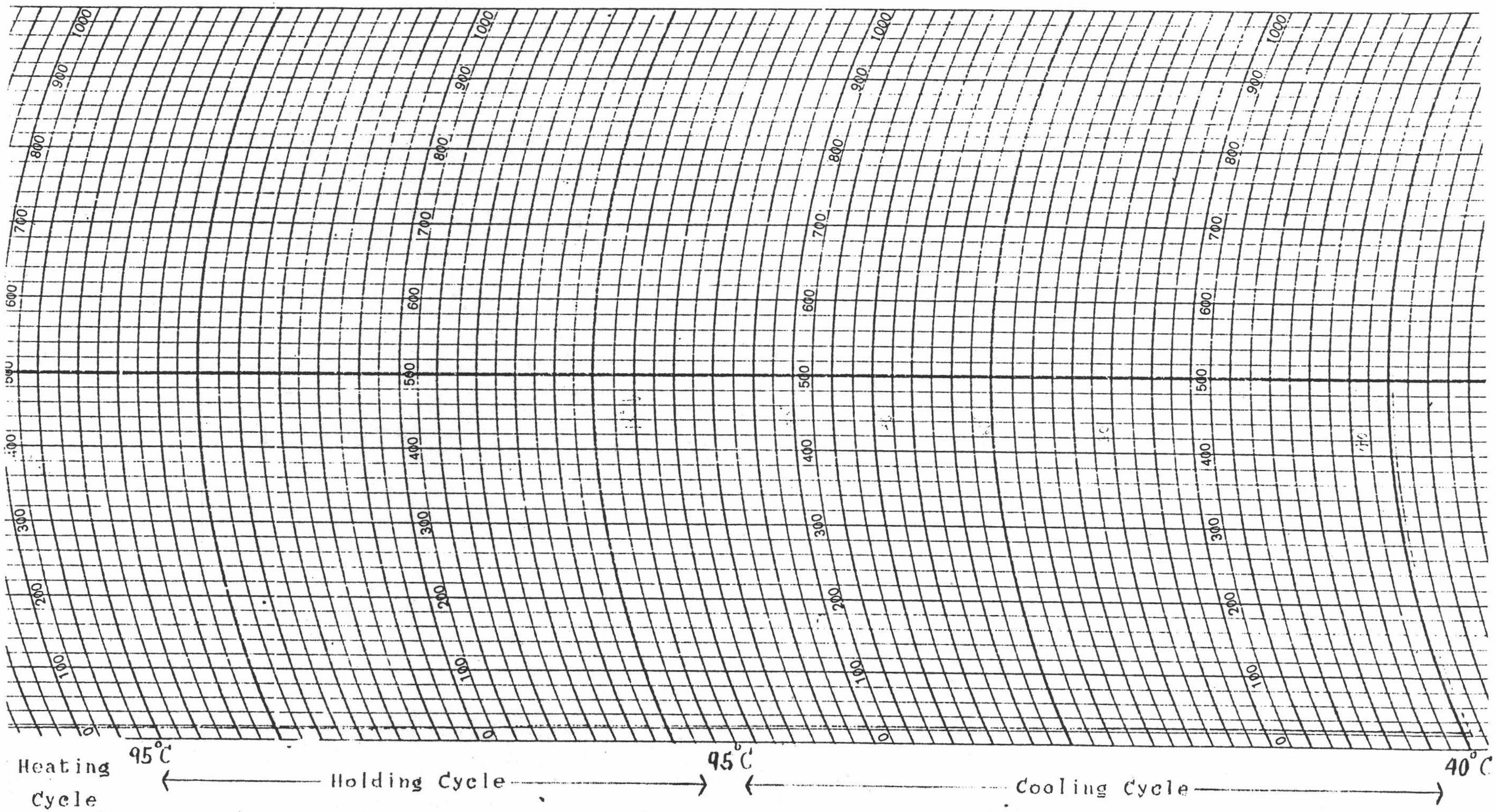


Figure 46 Brabender Viscosity Curve of Deproteinized Rice Flour, crosslinked 10 hrs.

Table 21 Viscosities of Crosslinked Rice Flours.

CL. TIME [HRS.]	VISCOSITY [B.U.]
0	600
2	26
6	30
10	250

Table 22 Viscosities of Crosslinked Rice Flours (Deproteinized).

CL. TIME [HRS.]	VISCOSITY [B.U.]
0	640
2	450
6	34
10	25

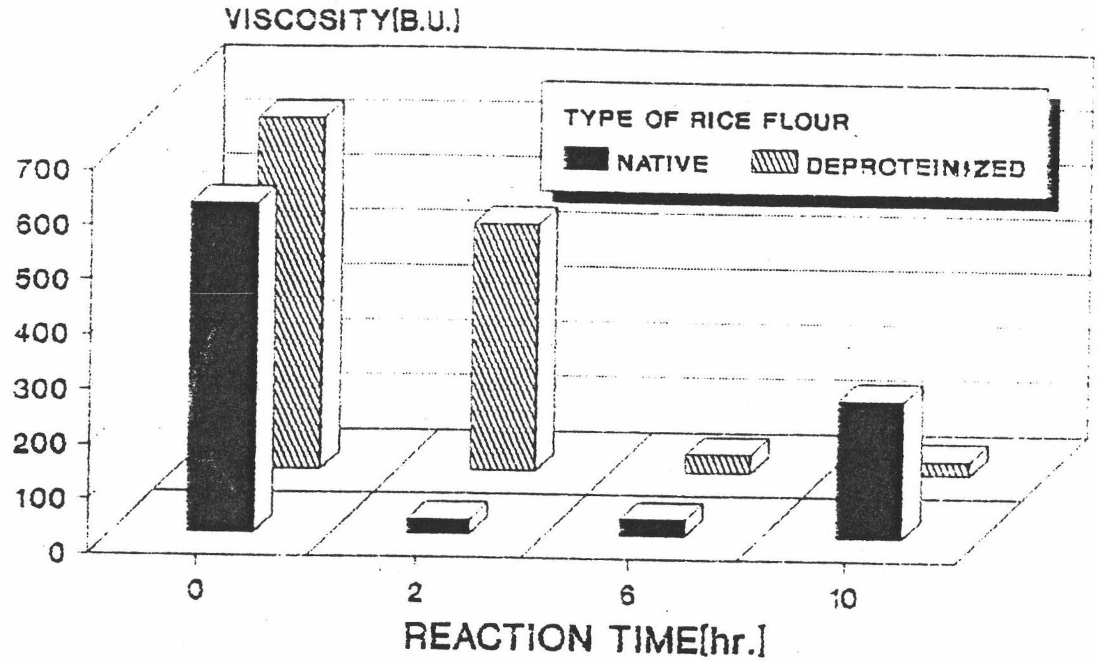


Figure 47 Viscosities of Rice Flour at 40 °c (Native & Deproteinized) at various crosslinking times.

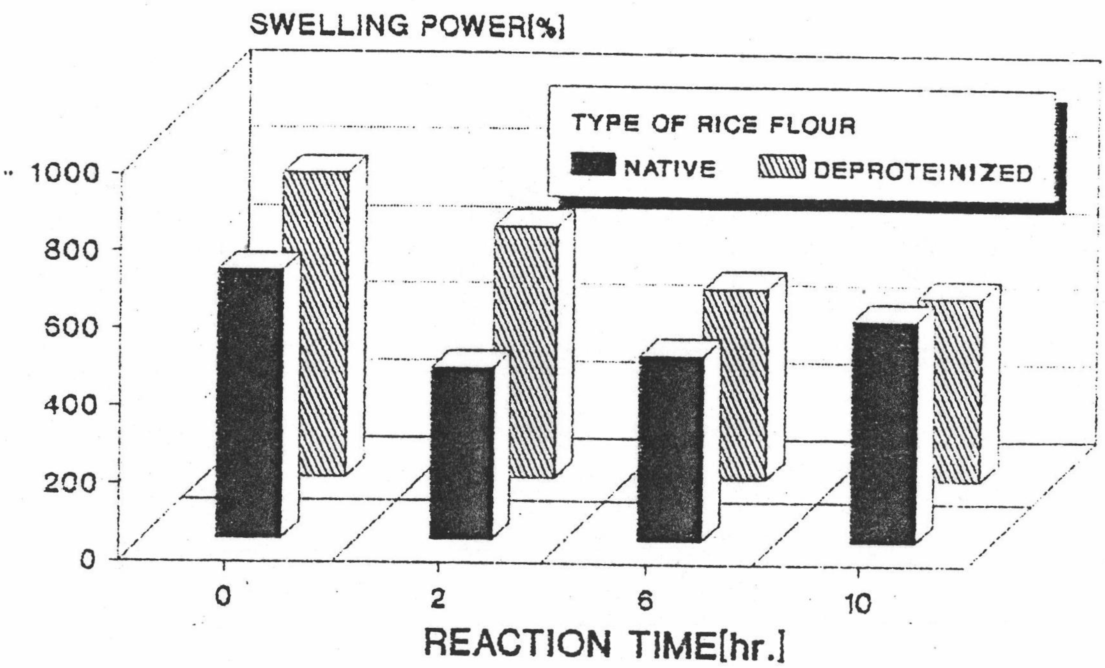


Figure 48 Swelling Powers of Rice Flour (Native & Deproteinized) at various crosslinking times.

but it decreased to 444.8 % for the 2 hr.-crosslinked flour (Table 23 and Fig. 48). It then increased to 479.8 and 574.3 % when crosslinked for 6 and 10 hrs.

Swelling Power of deproteinized rice flour was higher than the native, reaching 787.3 % . The values decreased to 650.4, 493.7, and 473.5 % for those crosslinked for 2,6 and 10 hrs. respectively (Table 24 and Fig. 48).

8. <u>Differential Thermal Analysis of Starches</u>

All samples of starches were tested with thermal analyser apparatus (Shimadzu, Japan). The concentrations used were 1:1 W/V starch-water ratio. Reference cell was alumina.

The enthalpy change (endothermic) for native rice flour began at 70 °C and ended at 100 °C (Fig. 49). The AUC (area under the curve) was small. The enthalpy change of deproteinized rice flour also took place and ended at 70 and 100 °C respectively, but AUC was larger. The results of starch aggregates prepared from native rice flour spray dried at 130 and 135 °C were similar to the deproteinized. The shapes, the beginning and ending points and AUC'S were not different.

The different patterns of DTA were detected for

Table 23 Swelling Powers of Crosslinked Rice Flours

CL. TIME [HRS.]	SW.POWER [%]
0	696.3
2	444.8
6	479.8
10	574.3

Table 24 Swelling Powers of Deproteinized and Crosslinked Rice Flours

CL. TIME [HRS.]	SW. POWER [%]
0	787.8
2	650.4
6	493.7
10	473.5

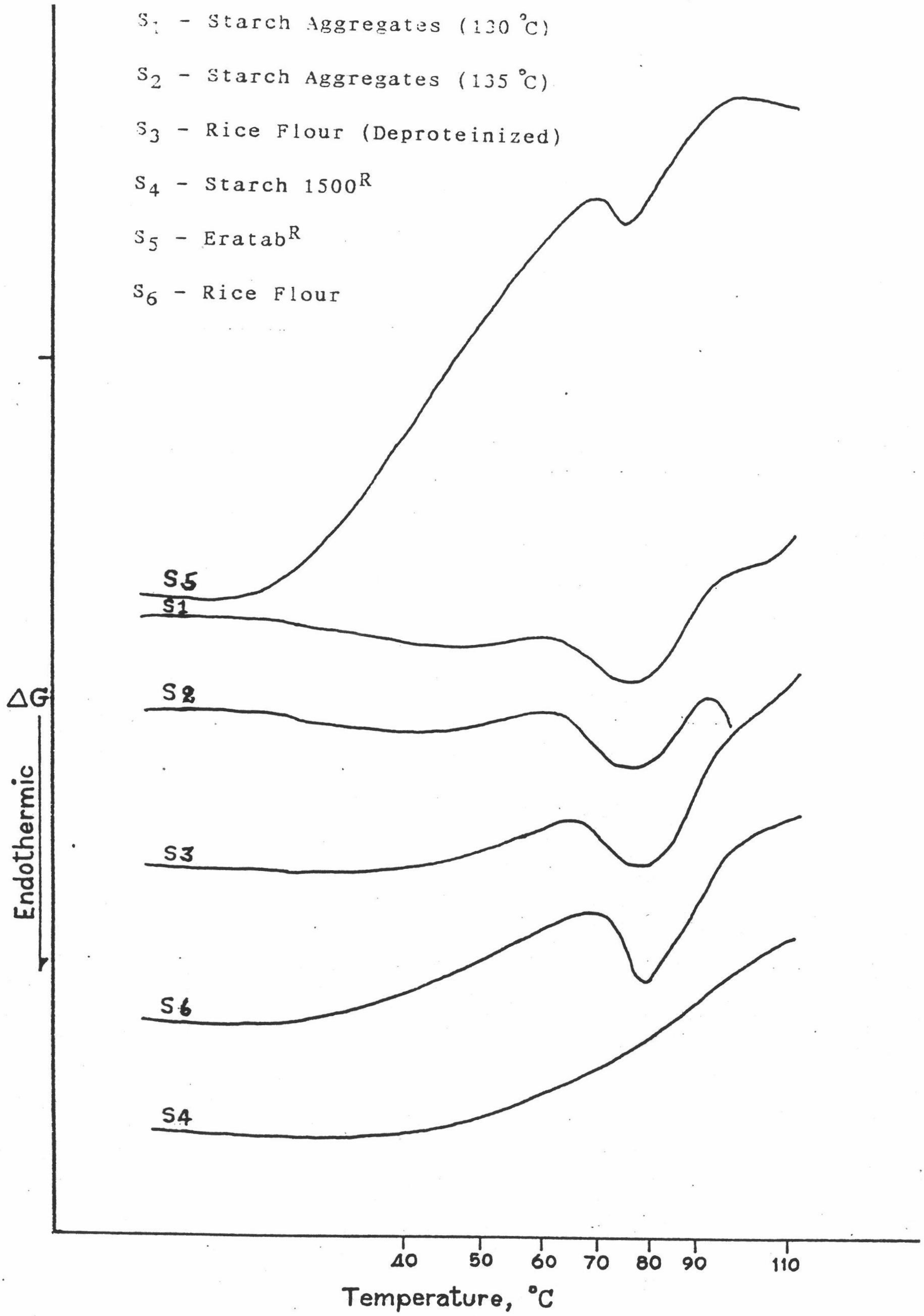


Figure 49 Differential Thermal Analysis of Various Starches.

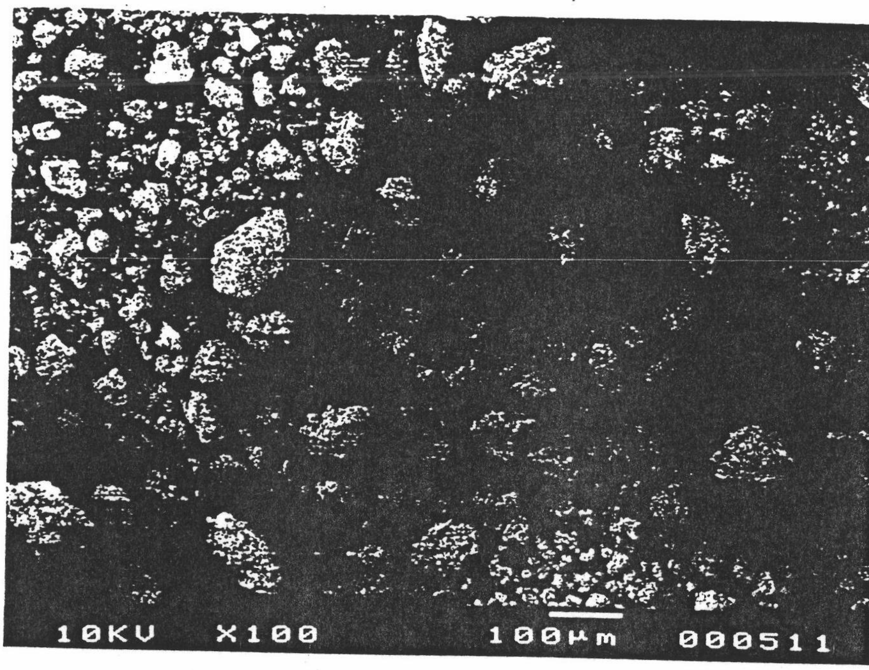
commmercial starch products. Starch 1500^{R} showed no peak up to 110 °C, while Eratab^{R} demonstrated a small peak beginning and ending at 70 and 100 °C respectively. However, the AUC was the smallest of all due to very short peak.

10. Physical Properties of Spray-dried Rice Starch Aggregates

10.1 Size and Shape

Under scanning electron microscope, native rice flour (Fig. 50) was seen as irregular shape particles with varying sizes at low magnification (x 100). Higher magnification (x 500) revealed that they were the aggregates of rice starch granules ranging from a few granules to many thousands. When rice flour dispersion was spray-dried at 30 % concentration, the shapes of the particles changed from the non-uniform irregular to much more uniform, nearly spherical ones and many became spherical (x 150) (Fig. 51). High magnification (x 1000) clearly showed that the spheri cal particles were made up of a large number of rice starch granules attached together. At 40 % concentration (Fig. 52), the picture resembled that of 30 %. The difference was that 40 % concentration pro

A



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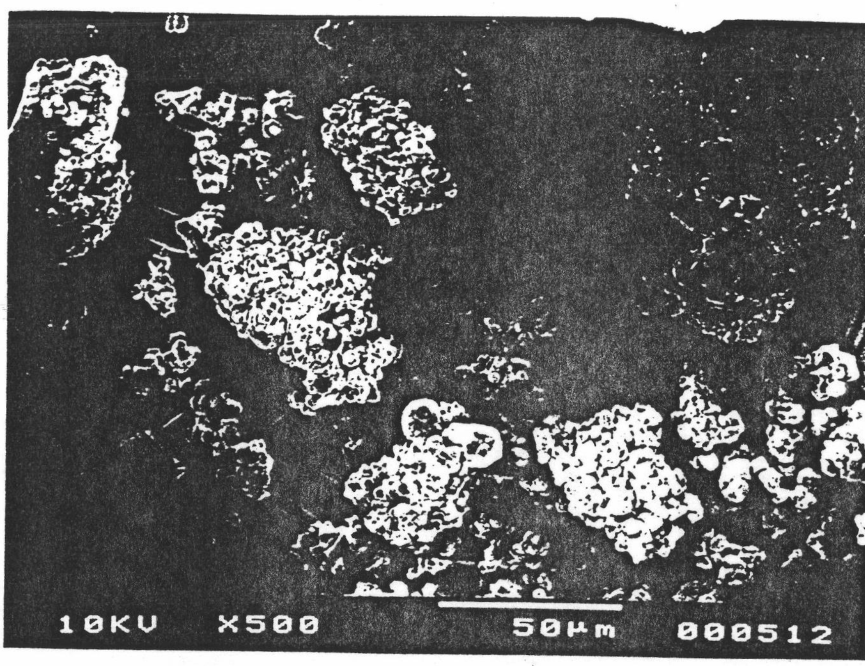
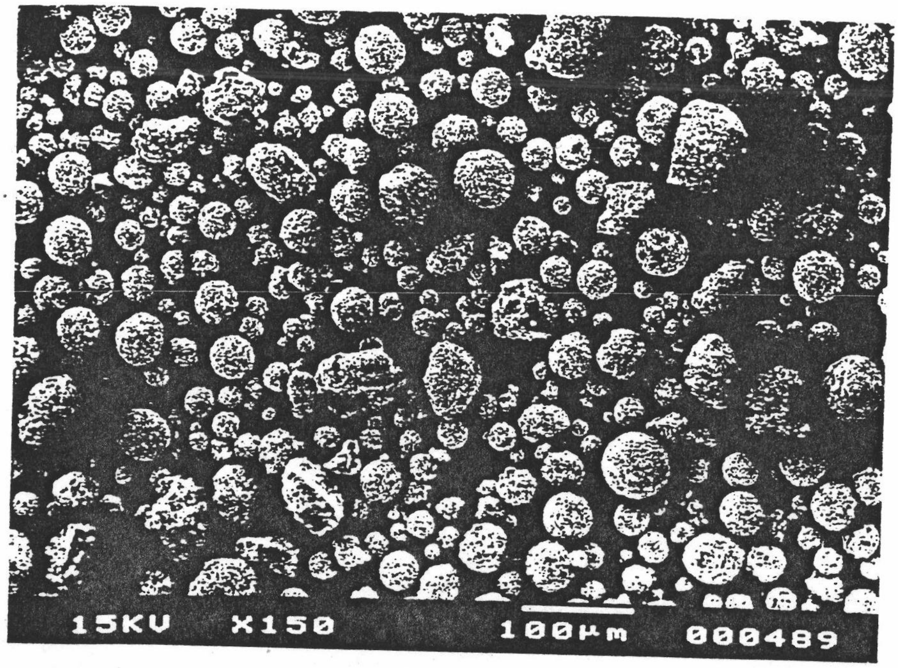


Figure 50 Photomicrograph of Rice Flour (Native)
A x 100 B x 500.

A



B

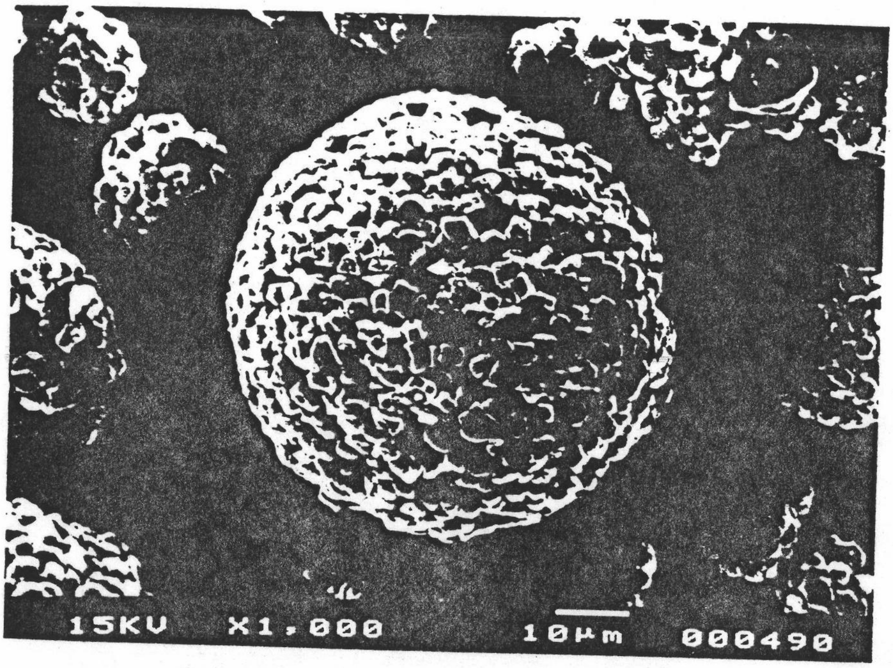


Figure 51 Photomicrograph of Starch Aggregates (30 % Conc., FR.12.96 g/min, Temp.130 °C, P.1.5 bar) A x 150 B x 1000..........................

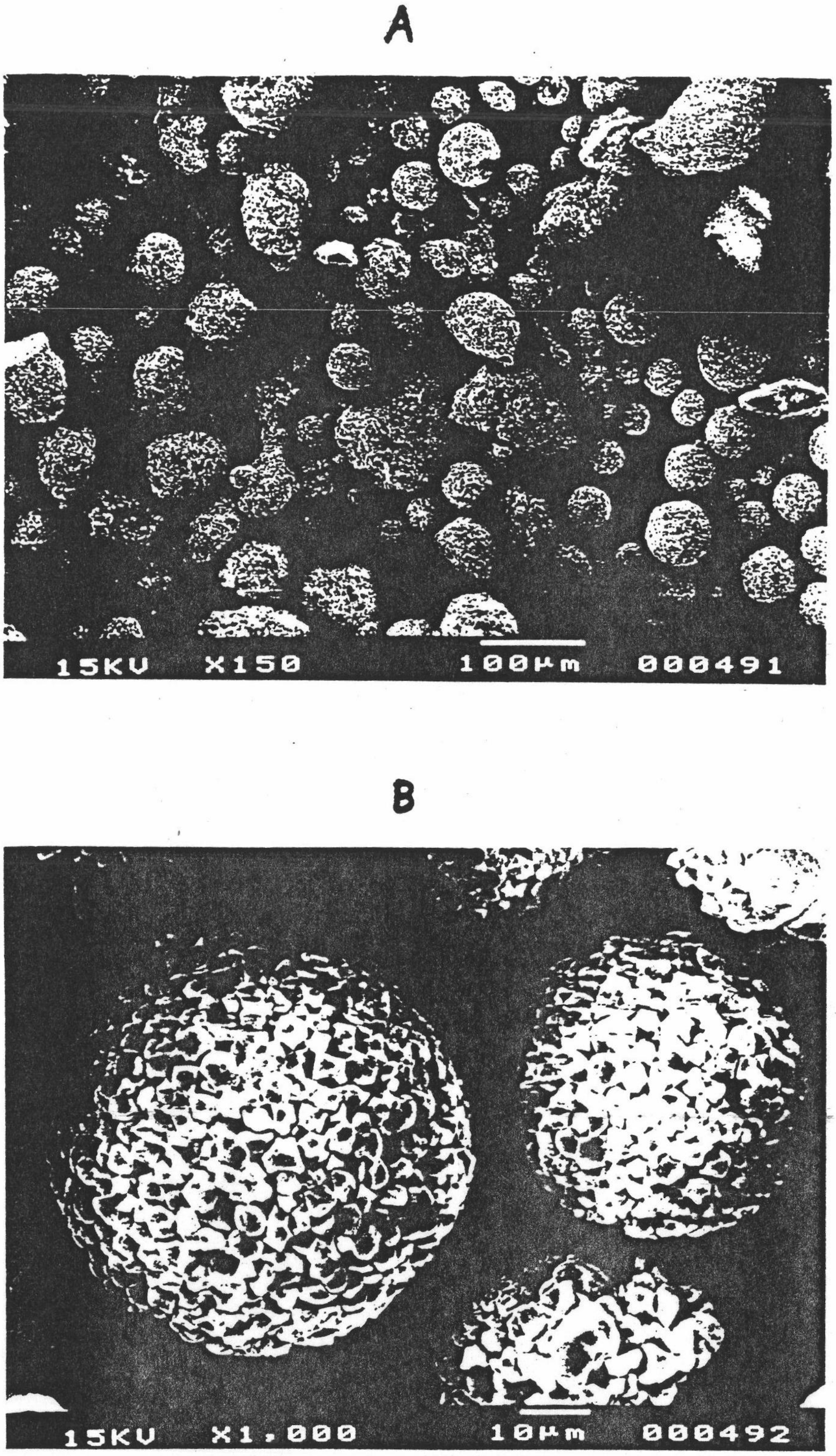
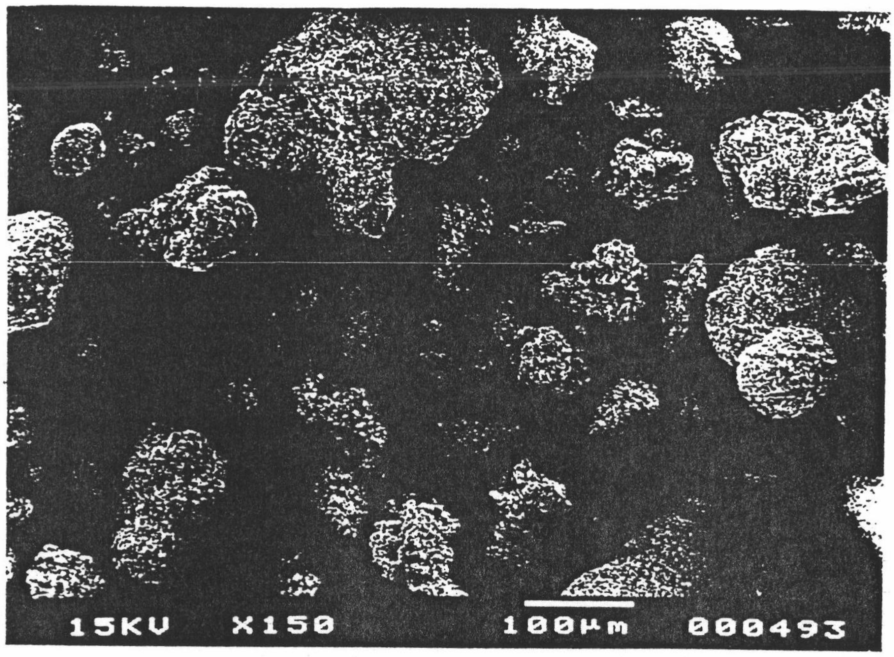


Figure 52 Photomicrograph of Starch Aggregates (40 % Conc., FR.12.96 g/min, Temp.130 °C, P.1.5 bar) A x 150 B x 1000.........................

duced the particles which were larger than 30 %. The particles at 50 % concentration (Fig. 53) were similar to that of 40 %, but with larger sizes and more irregular shapes. The particles at 50 % concentration, spray-dried at 130 °C showed similar results, while those spray-dried at 135 °C exhibited slightly larger sizes (Fig. 54). When rice flour was crosslinked for 2, 6, and 10 hrs. and spray-dried (at 50 % concentration, the results and starch aggregates obtained were so similar to those produced from native flour (Fig. 55 -57).

Starch 1500^R showed different morphology. At low magnification(x 100),the shapes of the particles were irregular and the sizes varied widely (Fig. 58). High magnification (x 500) clearly demonstrated that actually corn starch granules melted to form the particles of starch 1500^R and if carefully scrutinized, it would be seen that a number of corn starch granules remained intact. Eratab^R (Fig. 59), on the other hand, yielded results that resembled those of 50 % concentration (whether crosslinked or not). However, the pictures showed very clearly that its particles were more uniform and spherical. When rice starch (flour) was deproteinized before crosslinked and spray

A



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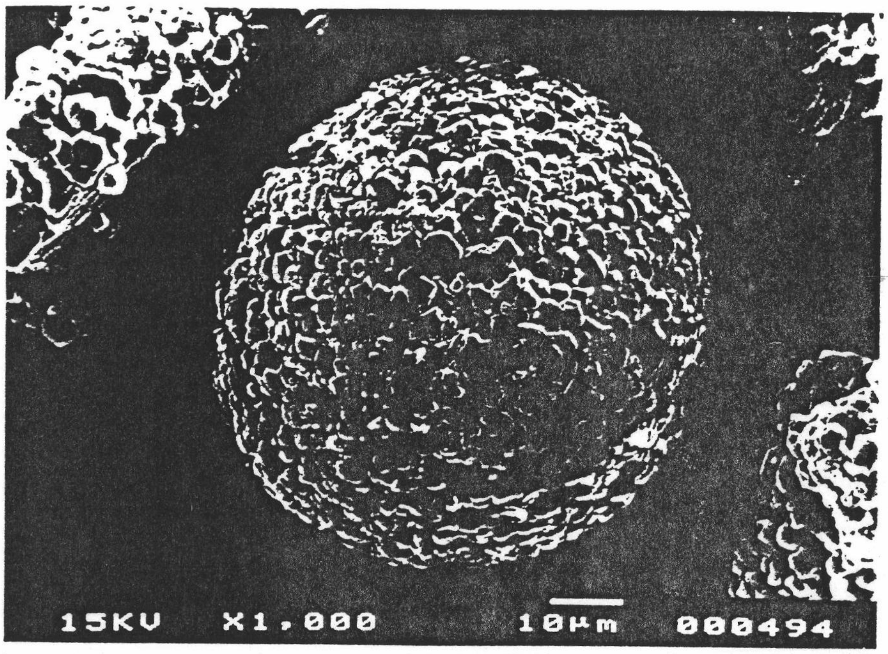
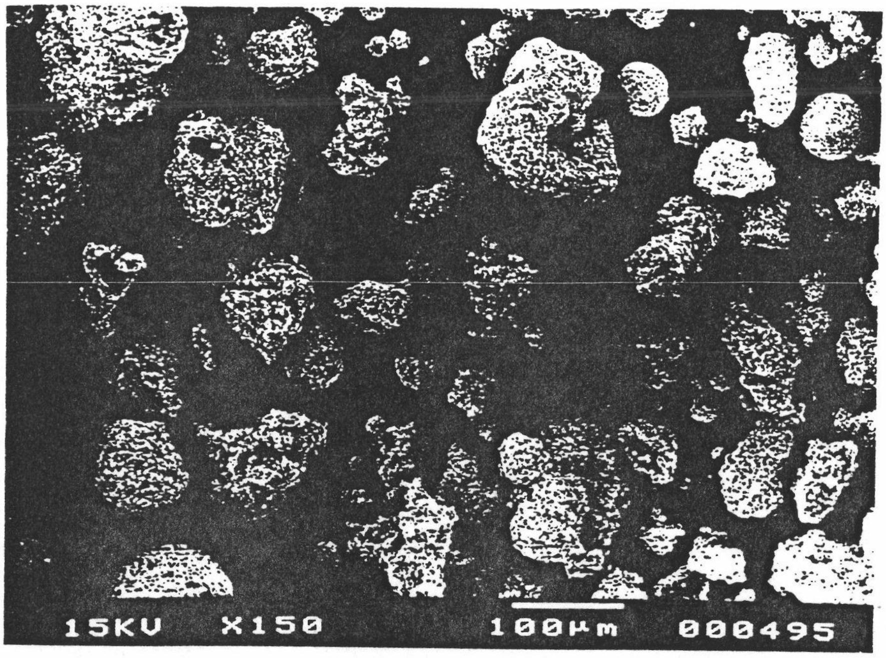


Figure 53 Photomicrograph of Starch Aggregates (50 % Conc., FR.12.96 g/min, Temp.130 °C, P.1.5 bar) A x 150 B x 1000............................

A



B

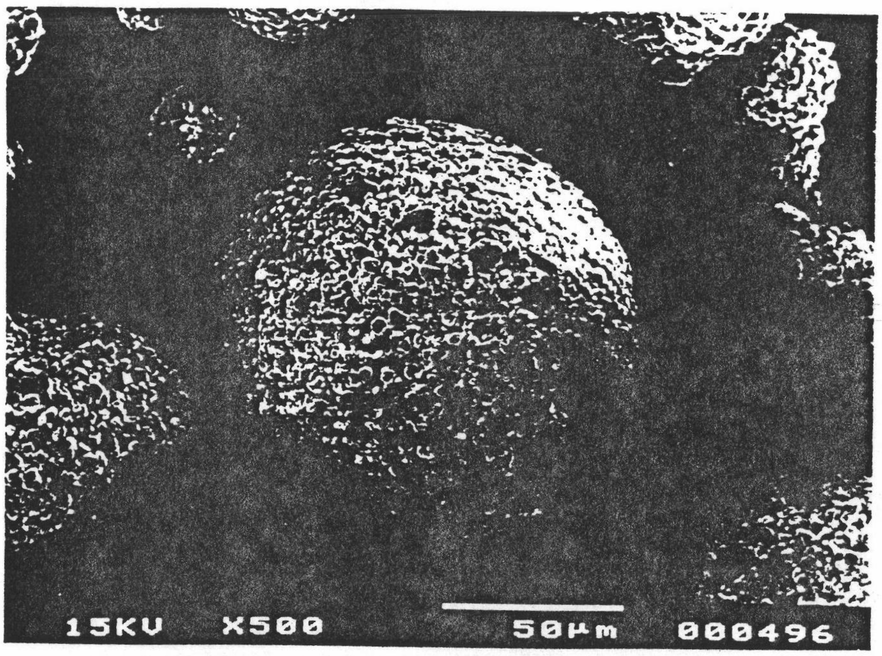
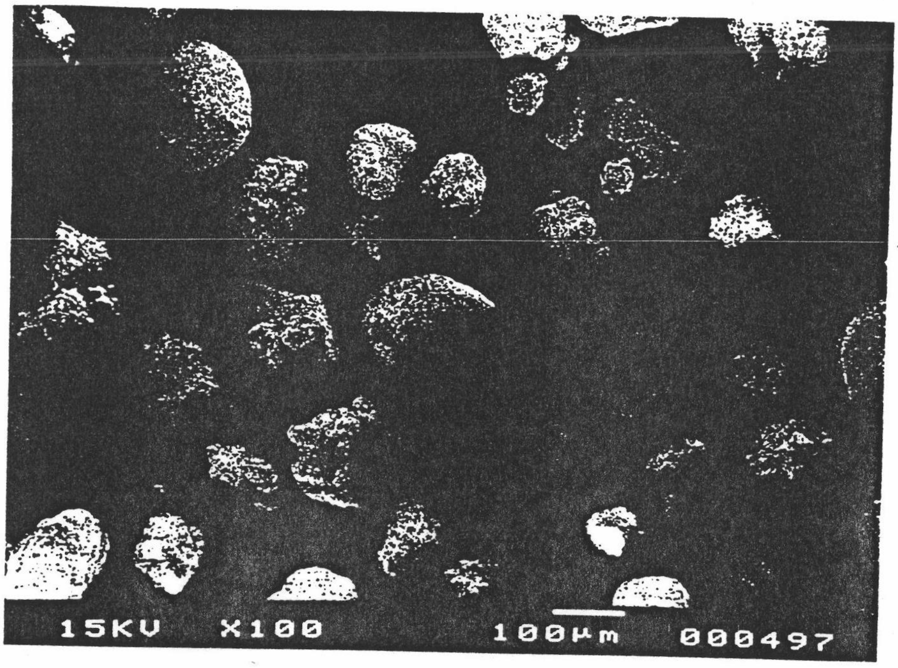


Figure 54 Photomicrograph of Starch Aggregates (50 % Conc., FR.12.96 g/min, Temp.135 °C, P.1.5 bar) A x 150 B x 1000...........................

A



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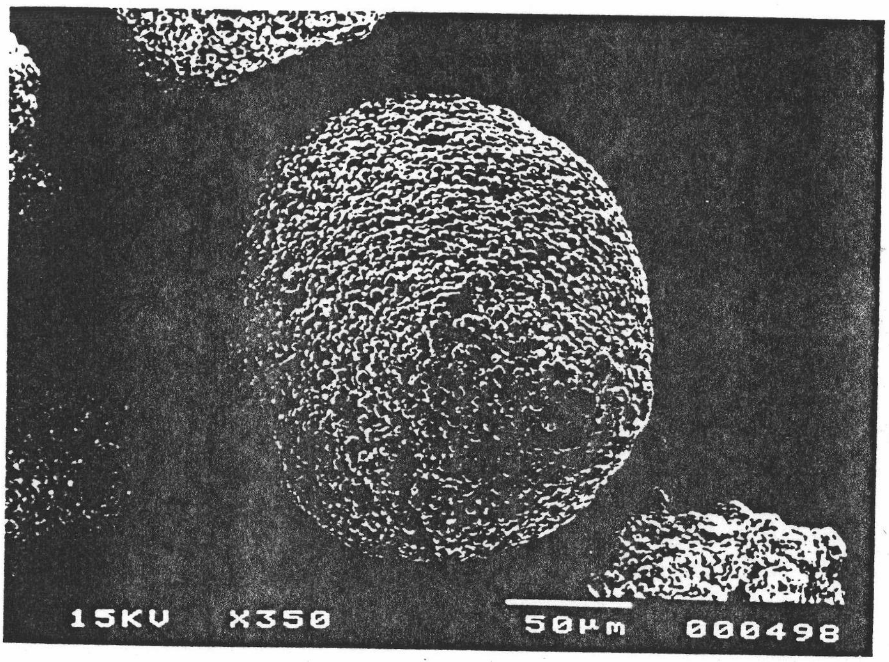
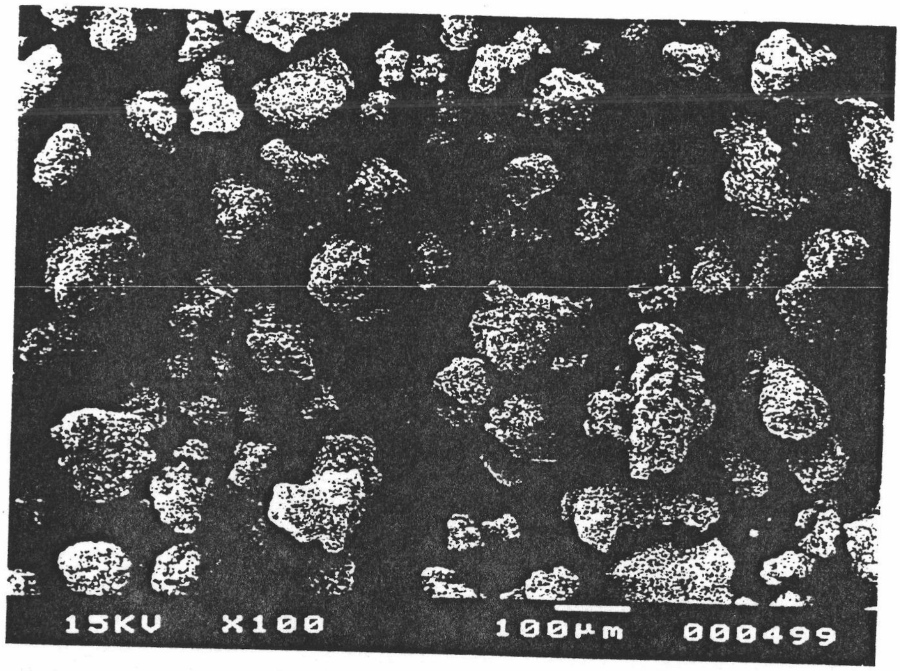


Figure 55 Photomicrograph of Starch Aggregates, crosslinked 2 hrs. (the same conditions as Fig.54) A x 100 B x 350..................

A



B

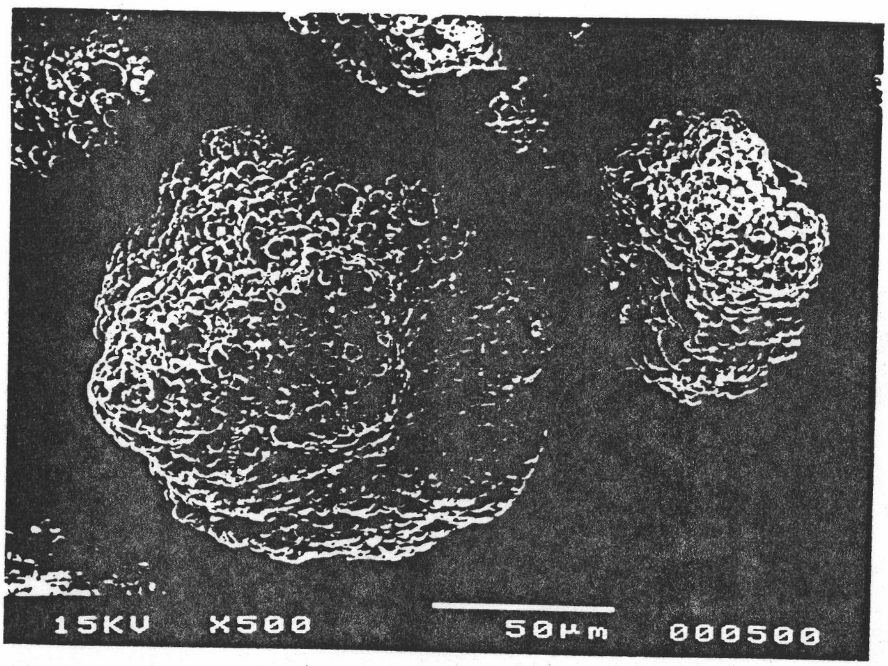
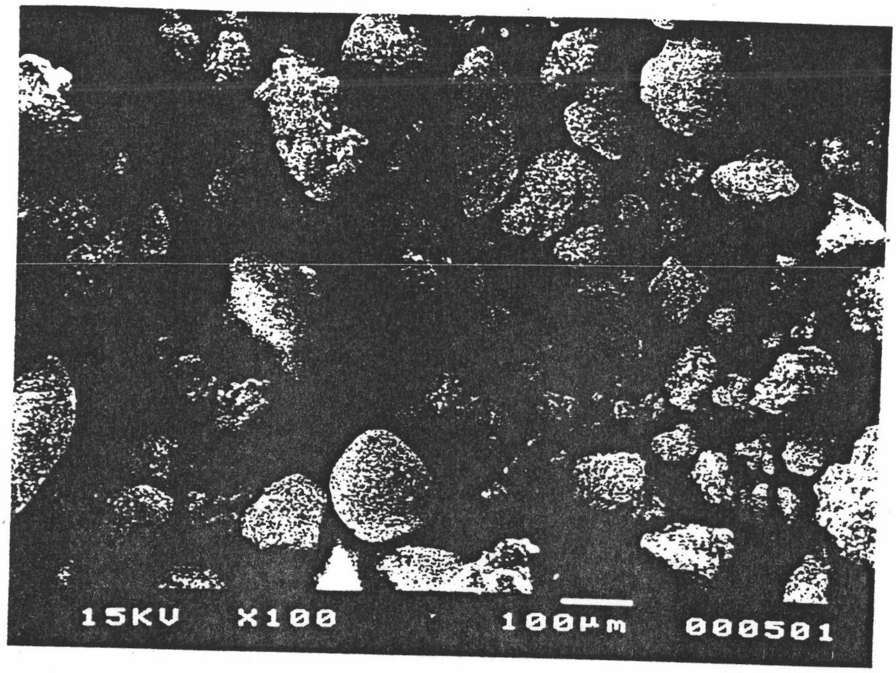


Figure 56 Photomicrograph of Starch Aggregates, crosslinked 6 hrs. (the same conditions as Fig.54) A x 100 B x 500..................

A



B

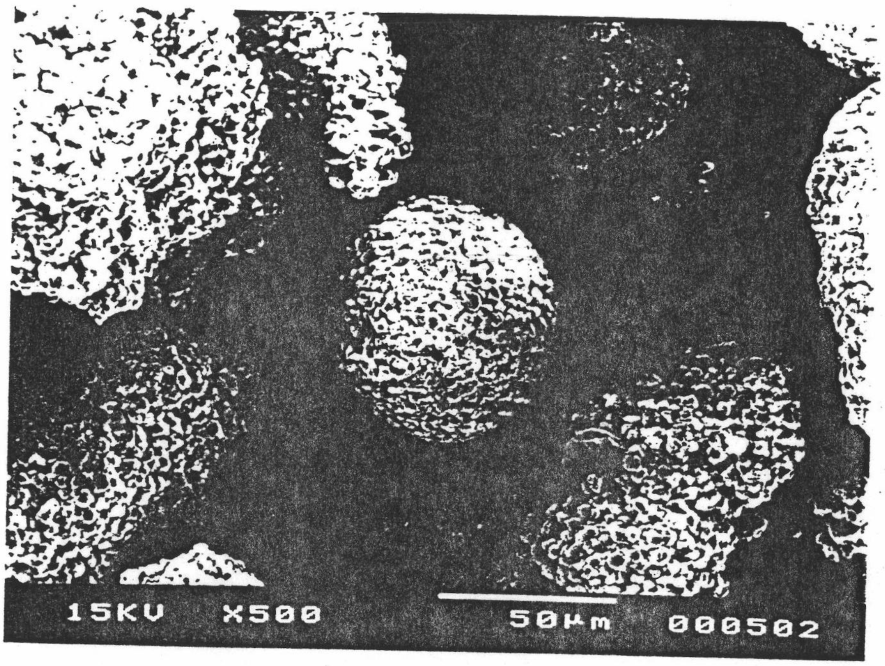


Figure 57 Photomicrograph of Starch Aggregates, crosslinked 10 hrs. (the same conditions as Fig.54) A x 100 B x 500 C x 3500.......

C

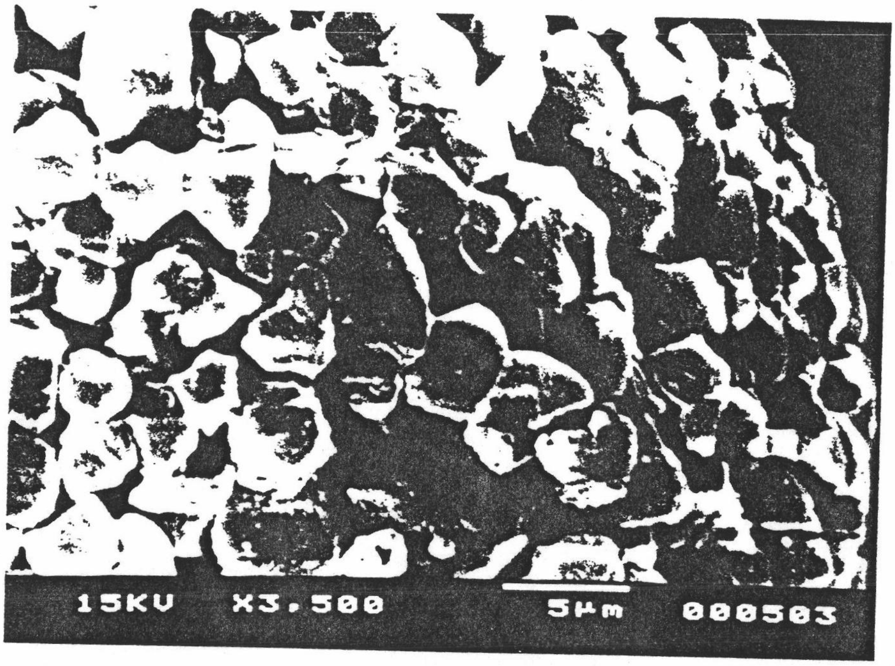


Figure 57 Cont.

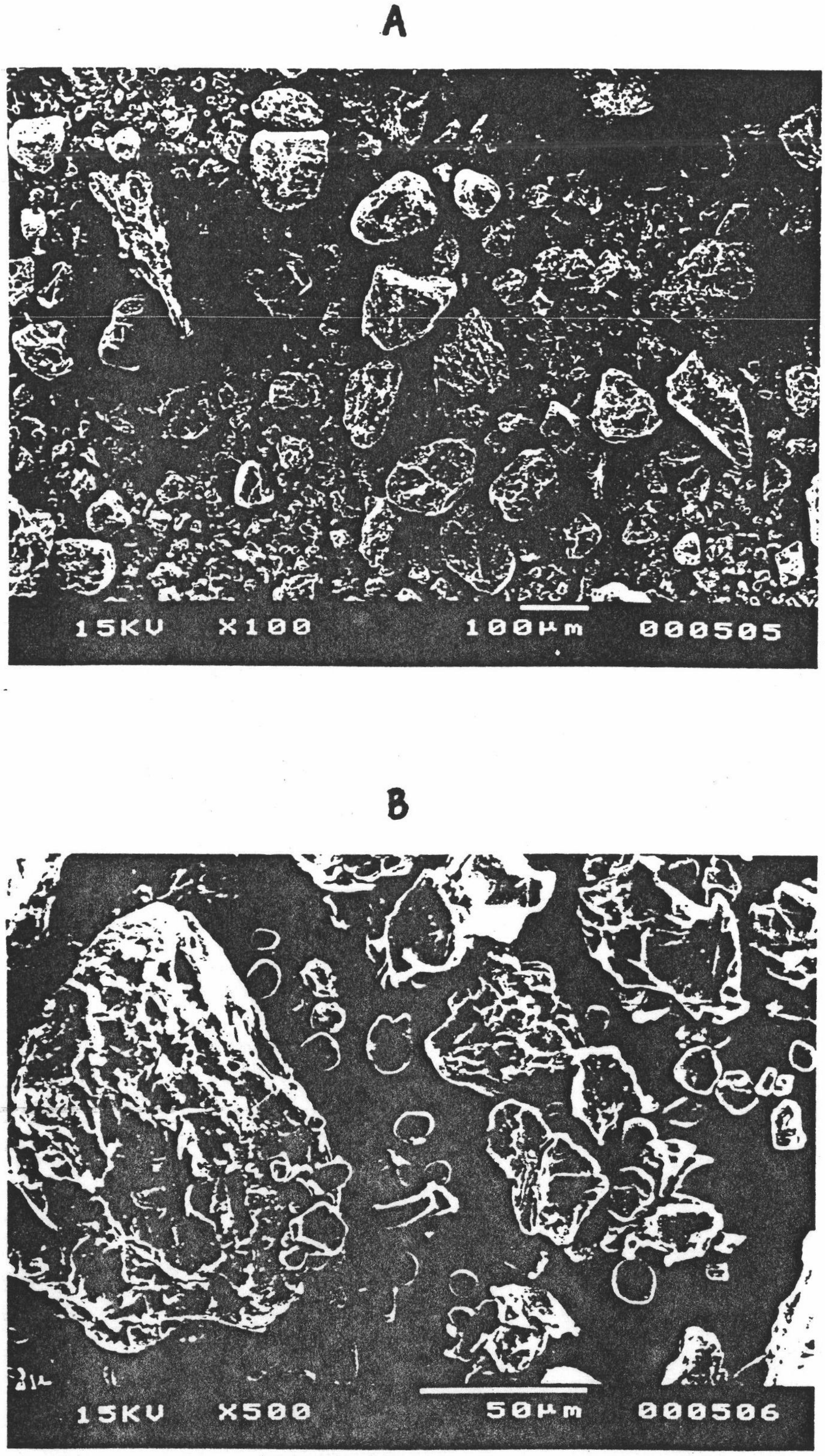
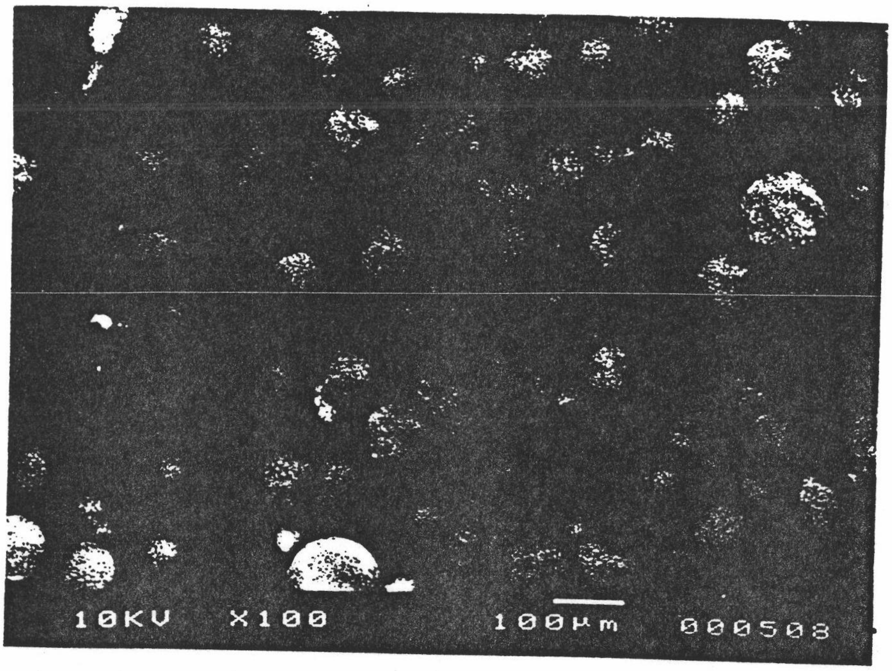


Figure 58 Photomicrograph of Starch® 1500
A x 100 B x 500

A



B

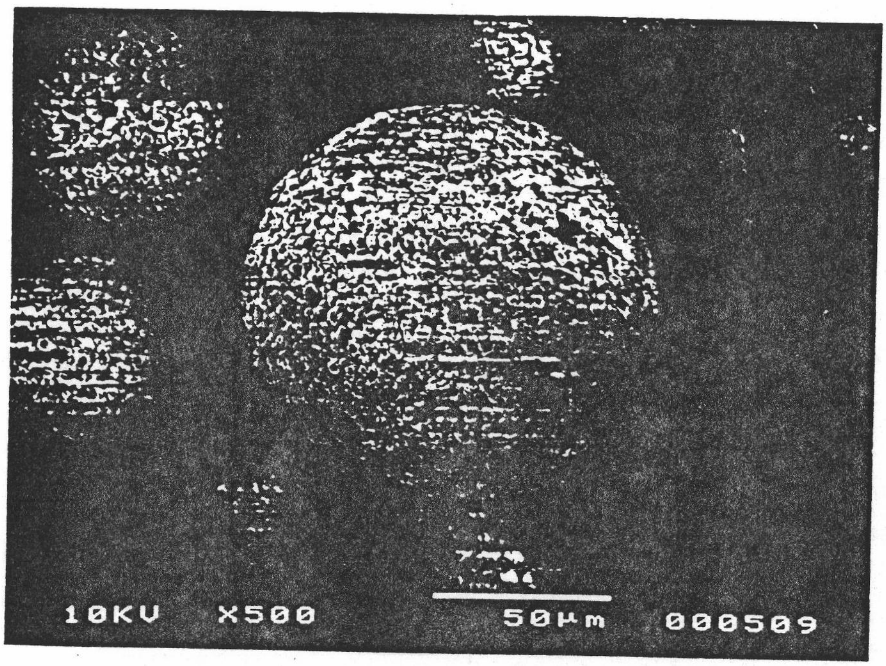


Figure 59 Photomicrograph of Eratab^{R}
A x 100 B x 500 C x 3500

C

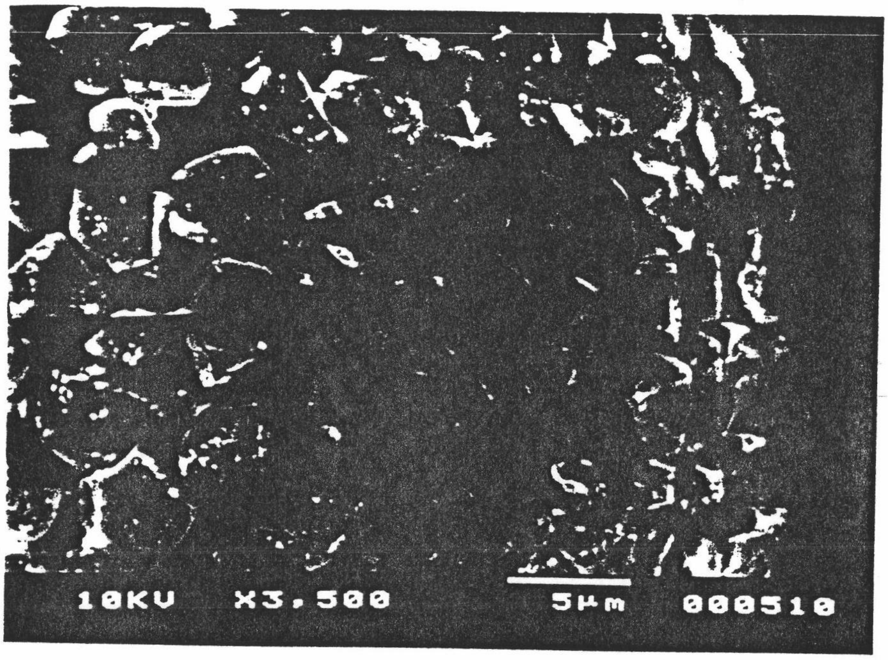


Figure 59 Cont.

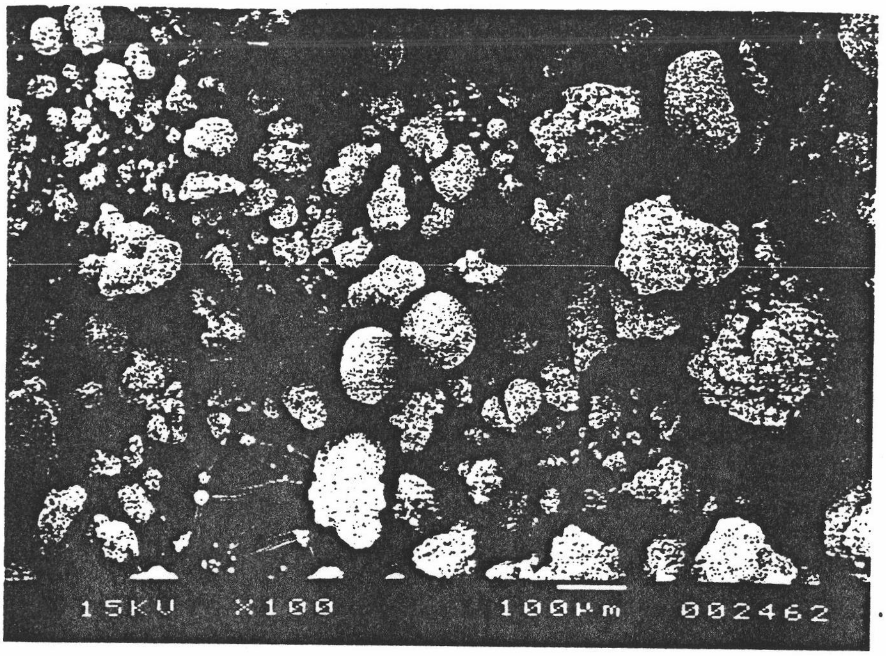
-dried, the final products looked similar to those mentioned earlier. Fig. 60 was obtained from deproteinized rice flour. The shapes of the particles were irregular with a small number of spherical starch aggregates. Deproteinized rice flour crosslinked for 2 hrs. showed similar results but somewhat larger sizes (Fig. 61). Deproteinized rice flour crosslinked for 6 and 10 hrs. were similar to that crosslinked 2 hrs. (Fig. 62-63). The electron photomicrograph with highest magnification (x 7500) showed clearly that rice starch granules melted and linked to one another at their contacting parts (Fig. 63 D).

10.2 <u>Particle Size Distribution by Sieve Analysis</u>

Fig. 64 and data in Table 25 in Appendix presented particle size distribution of starch aggregates prepared from rice flour at 50 % W/W concentration, temperature 130 °C, feed rate 12.96 g/min, atomizing pressure 1.5 bar. The percent weight retained of the smallest partiles(under 45 µm sive size)was 5.9, then increased to the highest percentage of 20.4 % at 45 µm sieve size, and decreased gradually to 2.7 % at 425 µm sieve size.

The mean weight diameter obtained by

A



B

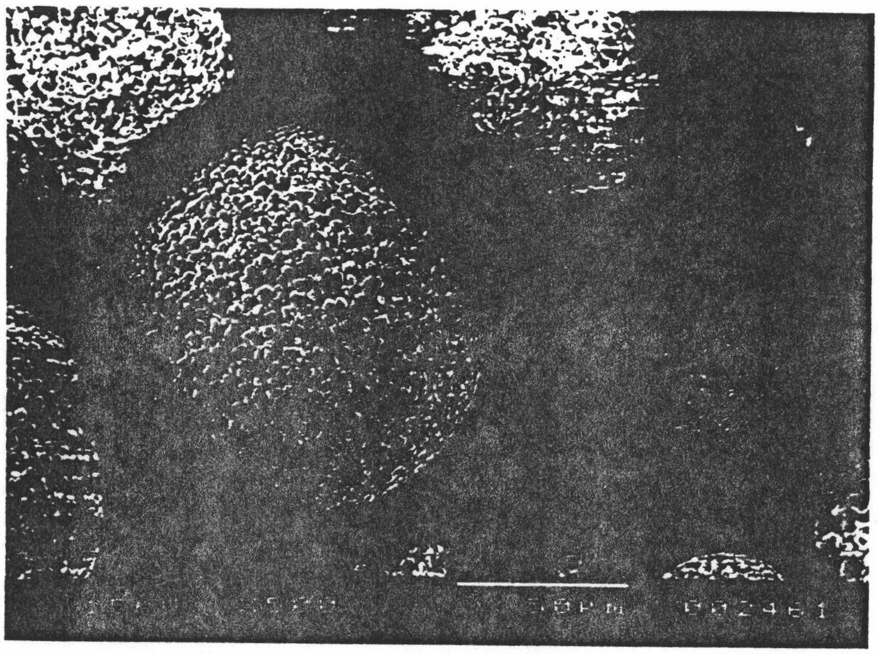
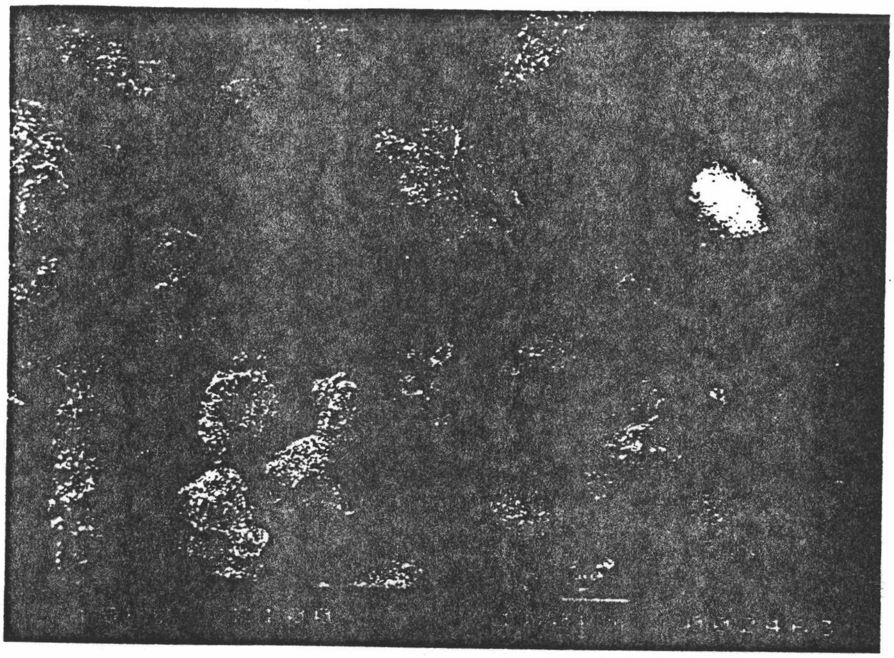


Figure 60 Photomicrograph of Deproteinized Starch Aggregates A x 100 B x 500...............

A



B

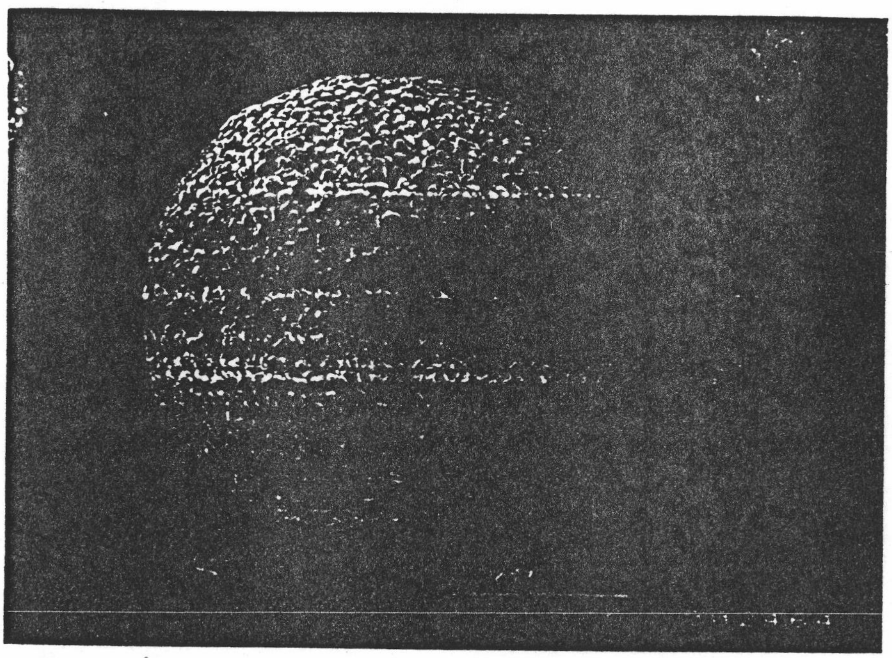
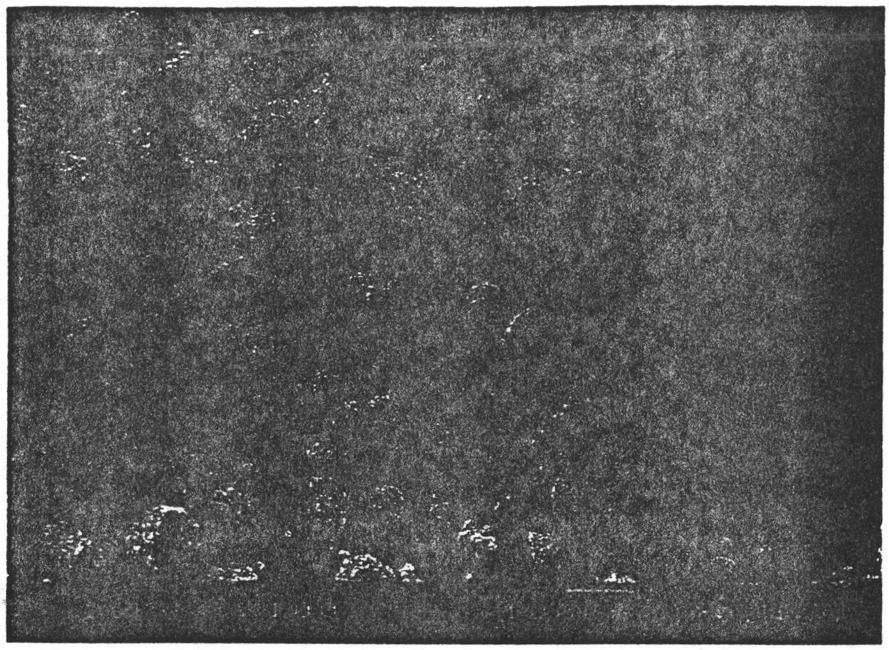


Figure 61 Photomicrograph of Starch Aggregates (Deproteinized & crosslinked 2 hrs.) A x 100 B x 500.

A



B

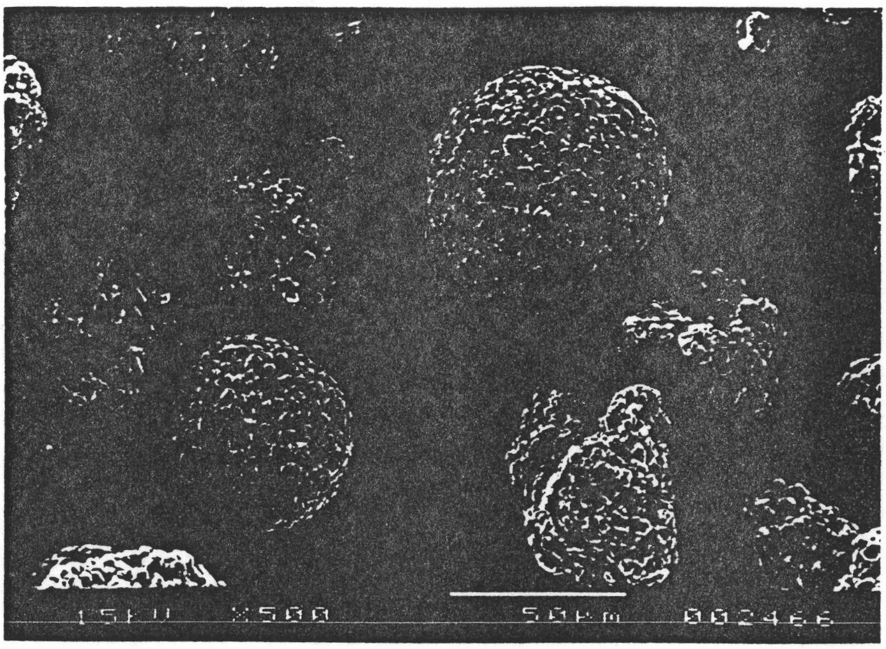
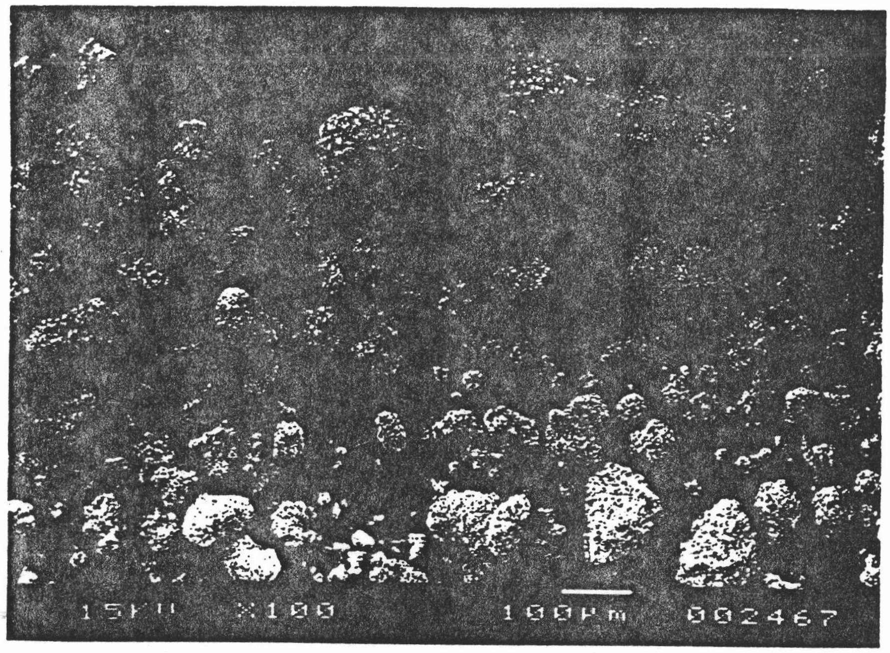


Figure 62 Photomicrograph of Starch Aggregates (Deproteinized & crosslinked 6 hrs.) A x 100 B x 500.

A



B

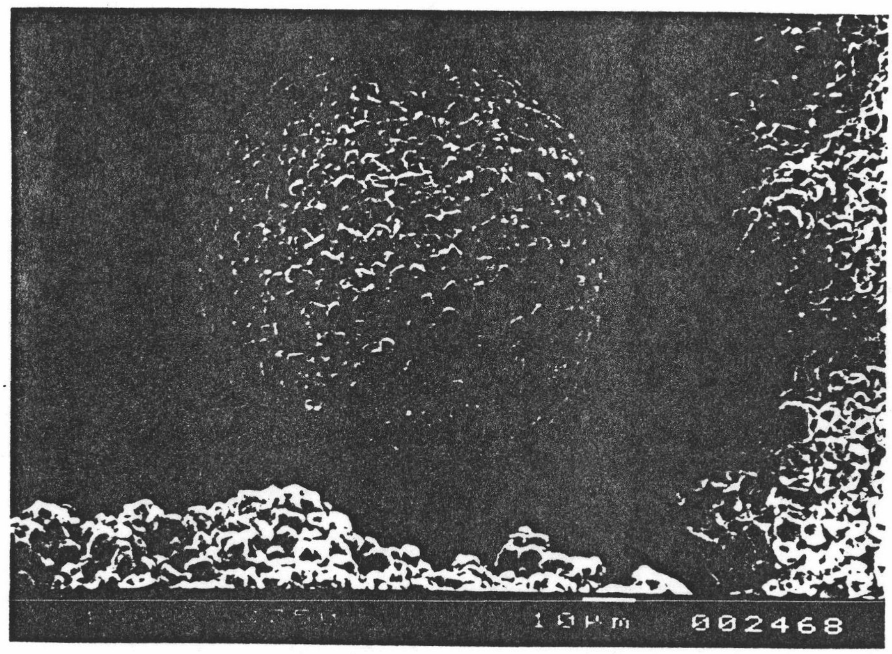
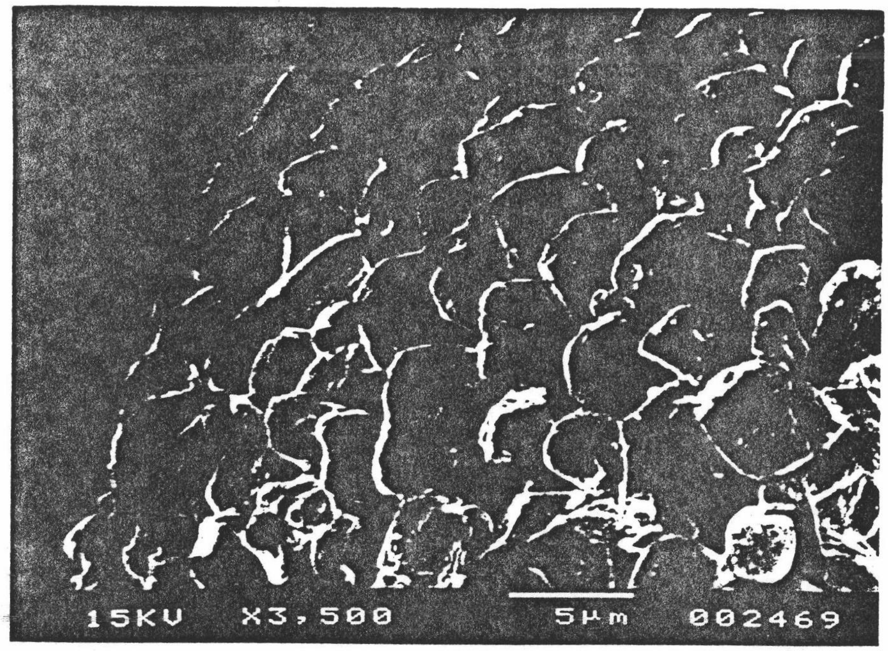


Figure 63 Photomicrograph of Starch Aggregates (Deproteinized & Crosslinked 10 hrs.)
A x 100 B x 500 C x 3500 D x 7500

C



D

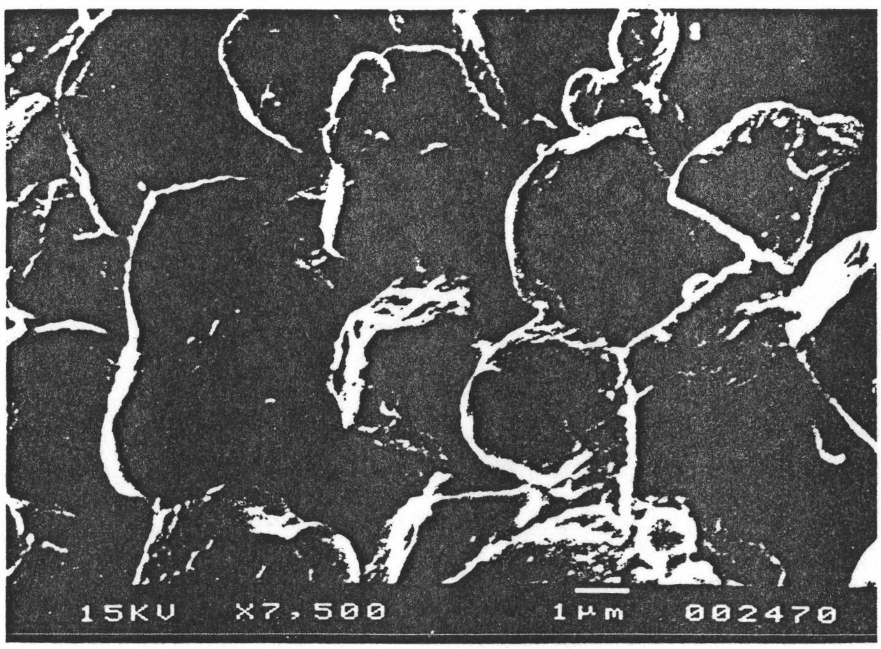


Figure 63 Cont.

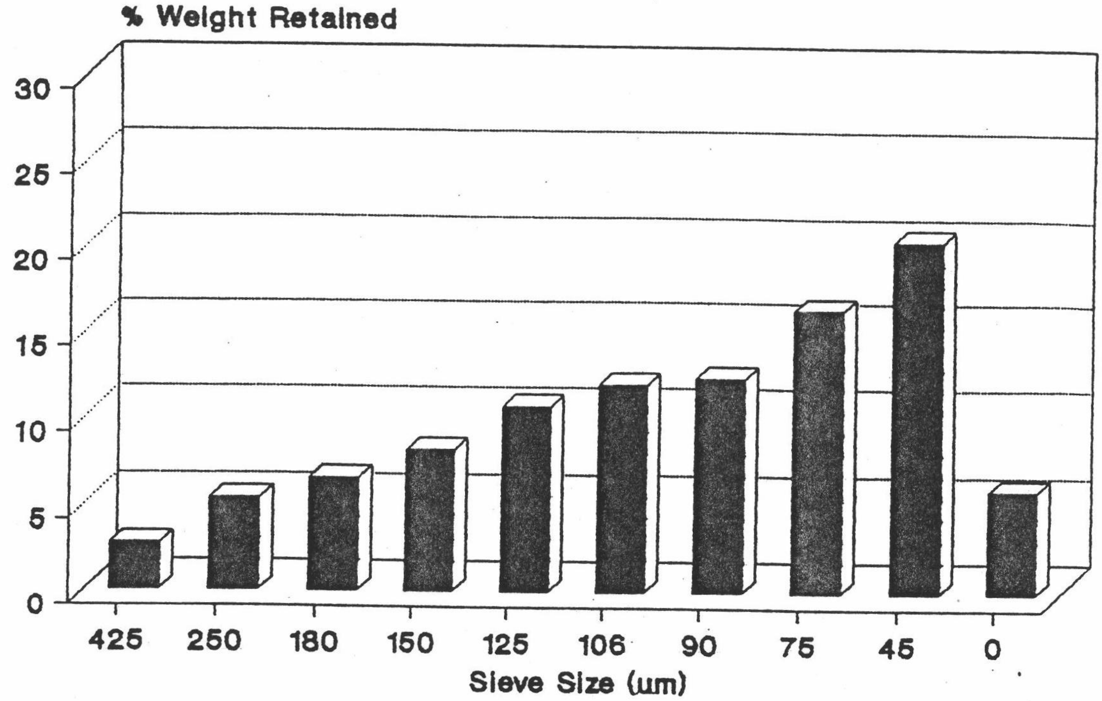


Figure 64 Particle Size Distribution of Starch Aggregates prepared by spraying at inlet air temperature 130 °C (Conc. 50 %, F.R. 12.96 g./min., P. 1.5 bar)........................

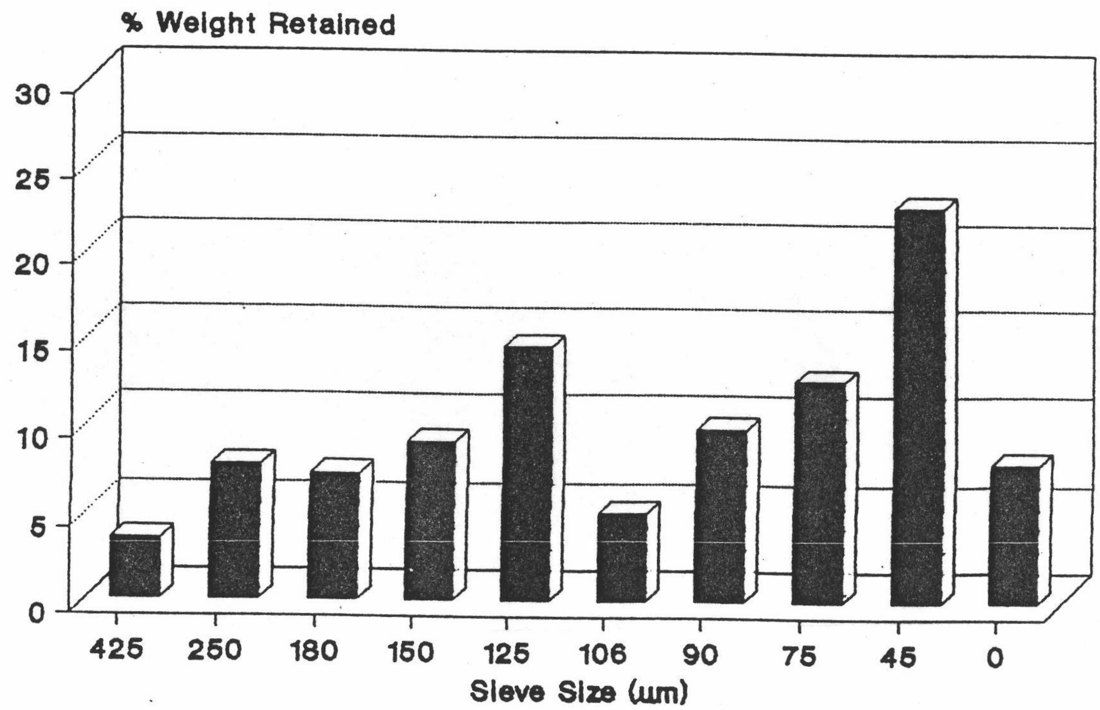


Figure 65 Particle Size Distribution of Starch Aggregates prepared by spraying at inlet air temperature 135 °C (Conc. 50 %, F.R. 12.96 g./min., P. 1.5 bar)........................

plotting cumulative percent oversize for each sieve size on log-probability scale was 102 µm(Appendix 1).

Size distribution of starch aggregates prepared under the same conditions except the temperature was changed to 135 °C was shown in Fig. 65 and data in Table 26 in Appendix. It was similar to that prepared at 130 °C. The mean weight diameter was 105 µm(Appendix 2).

Fig. 66-67 and data in Table 27-28 in Appendix showed the particle size distributions of starch aggregates produced at different feed rates. The mean weight diameters were determined to be 108 and 106 µm for feed rates at 4.32 and 21.6 g/ml (Appendix 3 and 4). It was apparent that feed rate did not affect the mean weight diameter of starch aggragates obtained.

Fig. 68 and Table 29 gave particle size distribution of starch aggregates prepared from rice flour crosslinked for 2 hrs. under the same conditions as Fig. 65. Most of starch aggregates produced were re tained on 180 µm sieve(15.6 %), then the percent weight retained decreased gradually to 8.7 % at 90 µm sieve size and rose again to 13.3 % at 45 µm sieve size. The percent of the smallest particle size (under 45 µm) was only 3.2 %. The mean weight diameter was 135 µm (Appen dix 5).

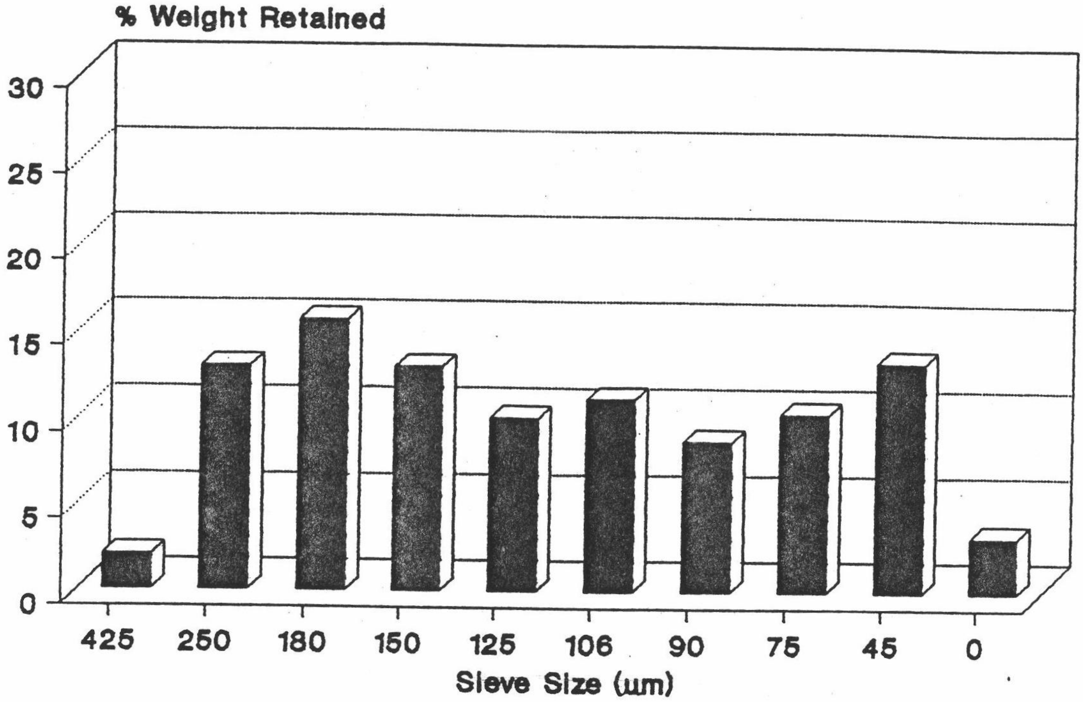


Figure 66 Particle Size Distribution of Starch Aggregates prepared by spraying at feed rate 4.32 g./min. (Conc. 50 %, Temp. 130 °C, P. 1.5 bar)......................................

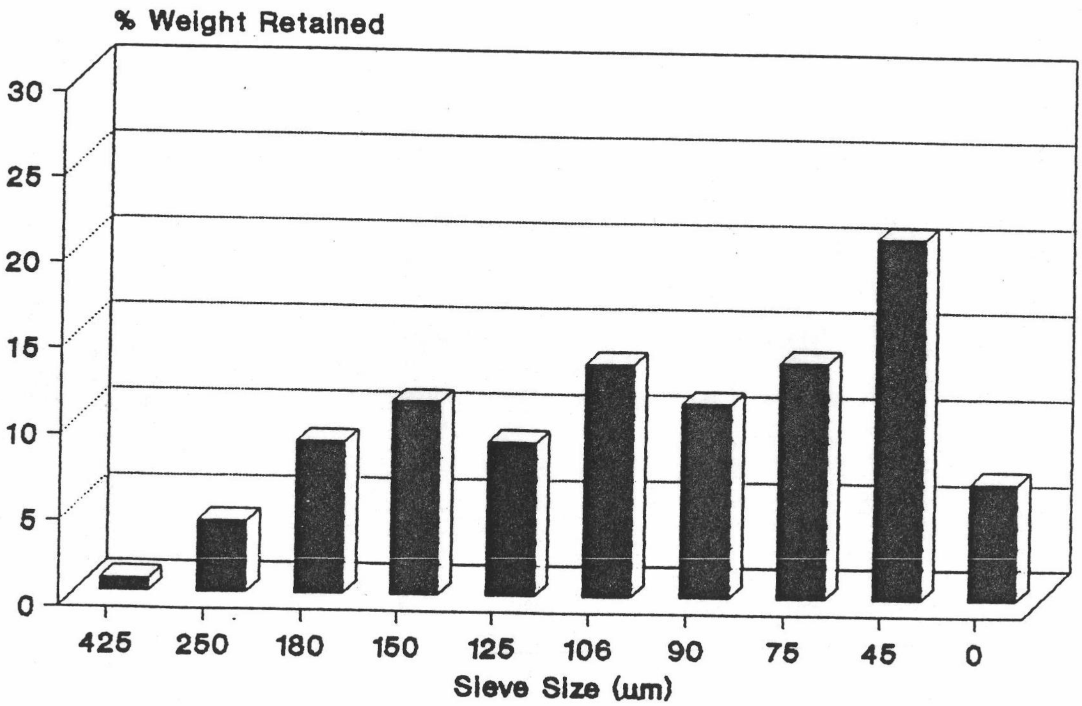


Figure 67 Particle Size Distribution of Starch Aggregates prepared by spraying at feed rate 21.60 g./min. (Conc. 50 %, Temp. 130 °C,P. 1.5 bar)......................................

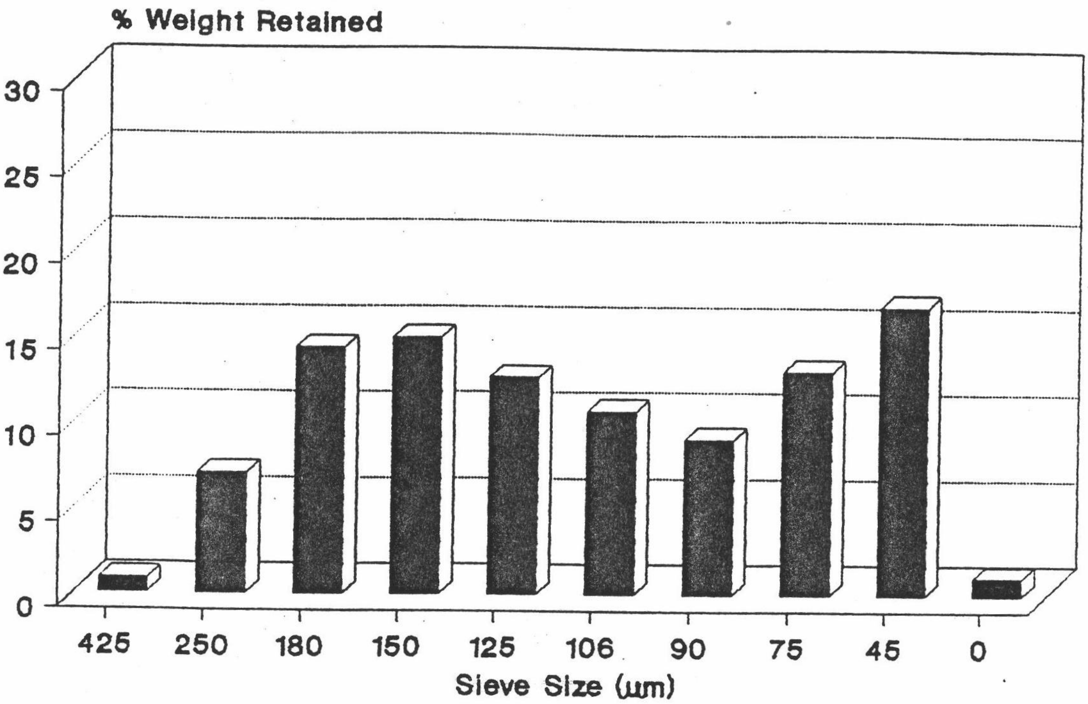


Figure 68 Particle Size Distribution of 2-hr. crosslinked Starch Aggregates (the same conditions as Figure 67)..................

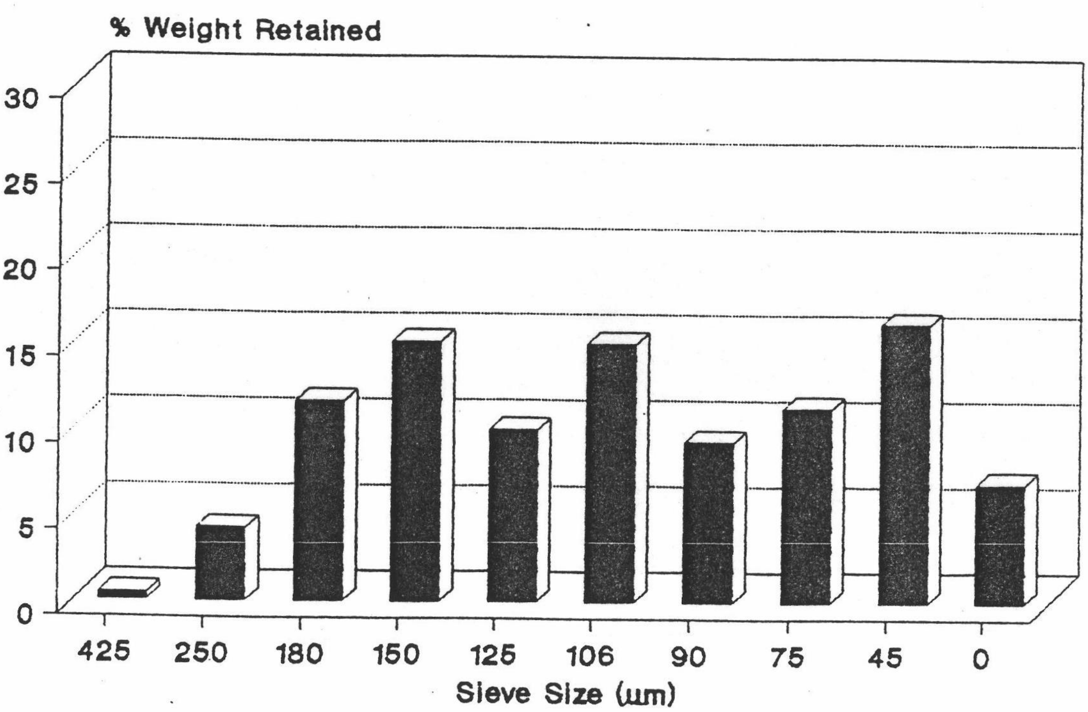


Figure 69 Particle Size Distribution of 6-hr. crosslinked Starch Aggregates (the same conditions as Figure 67)..................

Fig. 69 and Table 30 showed the values of those crosslinked for 6 hrs. under the same conditions as Fig. 68. The picture was opposite to Fig. 68. The high est percentage was 21.0 at 45 µm sieve size and de clined to the lowest, 0.7 at 425 µm sieve size. The mean weight diameter was 100 µm (Appendix 6).

Fig. 70 and Table 31 were obtained from those crosslinked for 10 hrs. (under the same conditions as Fig. 69). The peak was 16.8 % for 45 µm sieve size, and declined to 9.0 % at 90 µm and rose again to 14.9 % at 150 µm and declined again to the lowest, 0.8 % at 425 um sieve size. The mean weight diameter was 120 µm (Ap pendix 7).

When rice flour was deproteinized and then spray dried under the same conditions as Fig. 65, except feed rate was changed to 30.24 g./min. The result was shown in Fig. 71 and Table 32. The percent of the smallest particles (under 45 µm) was 6.9 %, while those on 45 µm sieve size reached the maximum at 16.2 % . The particles on larger sieve size were nearly equal, varying between 9.3 % (90 µm) and 15.1 % (150 µm), while the largest (over 425 µm) was very low, only 0.4 %. The mean weight diameter was 110 µm (Appendix 8).

Fig. 72 and Table 33 showed the result of

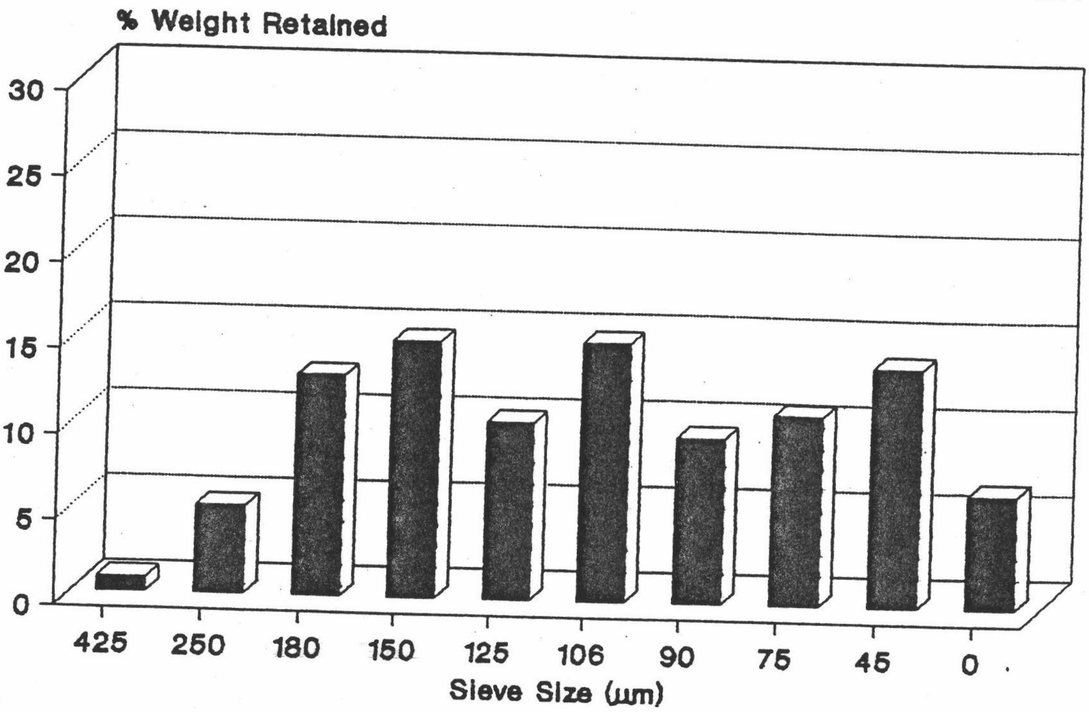


Figure 70 Particle Size Distribution of 10-hr. crosslinked Starch Aggregates (the same conditions as Figure 65)...................

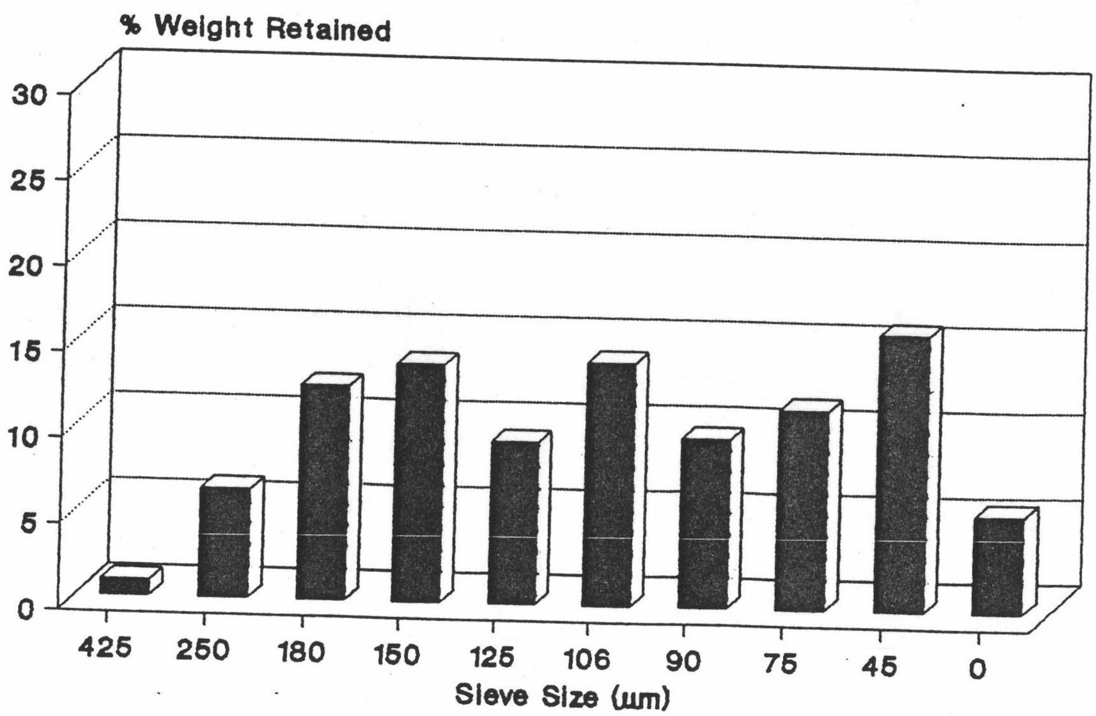


Figure 71 Particle Size Distribution of Deproteinized Starch Aggregates (Conc. 50 %, Temp. 135 °C, F.R. 21.6 g./min., P. 1.5 bar)..............

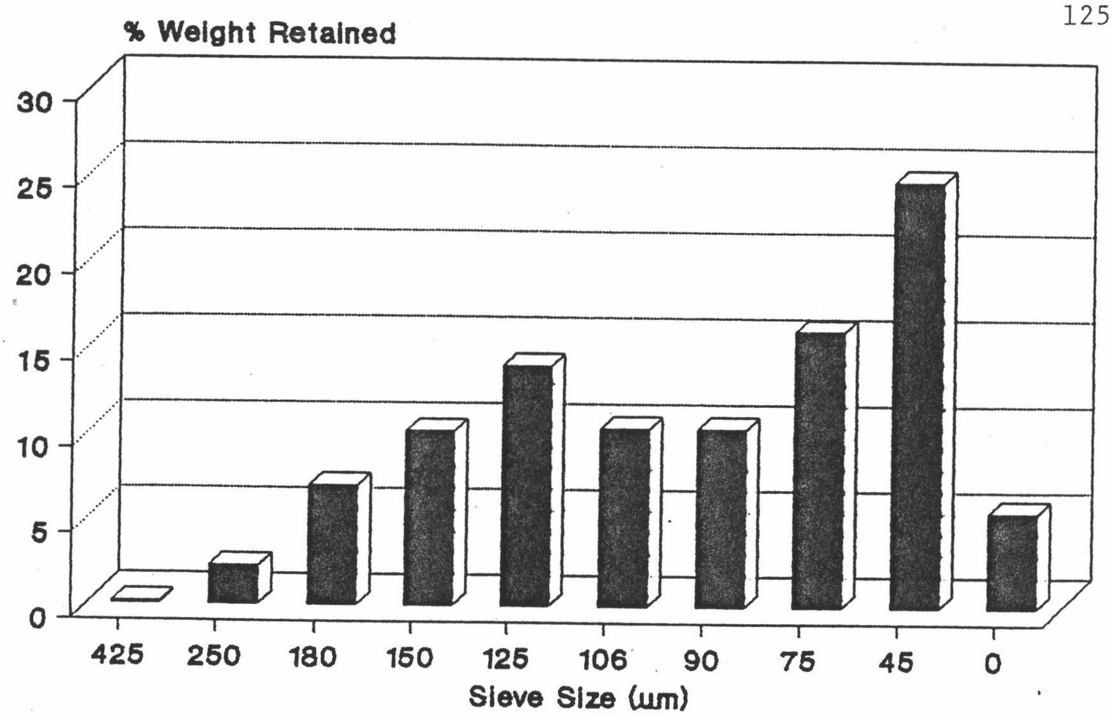


Figure 72 Particle Size Distribution of Deproteinized and 2-hr. Crosslinked Starch Aggregates (the same conditions as Fig.71).............

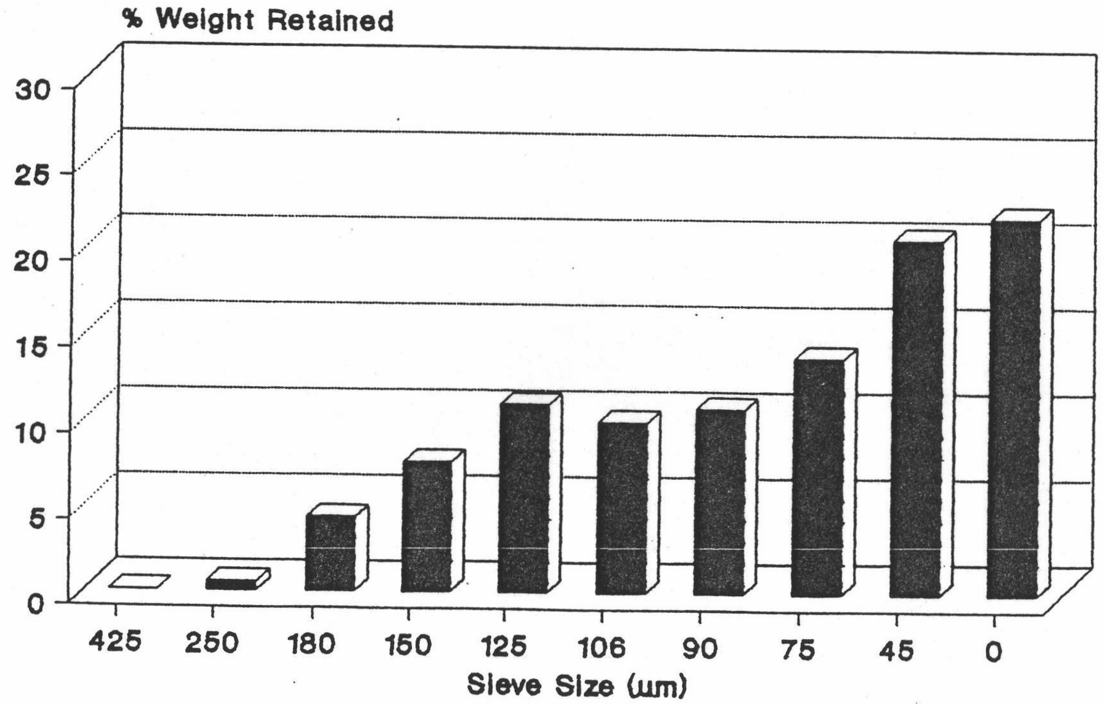


Figure 73 Particle Size Distribution of Deproteinized and 6-hr. Crosslinked Starch Aggregates (the same conditions as Fig.71).............

deproteinized rice flour crosslinked for 2 hrs. before spray-dried. The result was very similar to Fig. 73. The mean weight diameter was 118 µm (Appendix 9).

Fig. 73 and Table 34 was obtained from those starch aggregates, deproteinized and crosslinked for 6 hrs. The result was similar to Fig. 74. The mean weight diameter was 114 µm (Appendix 10).

Fig. 74 and Table 35 stood for those, deproteinized and crosslinked for 10 hrs. The result was also similar to Fig. 75 except the percent weight retained of 45 µm sieve size was higher, reaching 24.7 %. The mean weight diameter was 98 µm (Appendix 11).

Fig. 75 and Table 36 showed particle size distribution of Starch 1500[R]. The percent weight retain ed of the smallest size (under 45 µm) was highest, reaching 21.9, and then declined a little to 20.6 for 45 µm sieve size. It still declined gradually to 5.5 % for 250 µm except the slightly higher value 10.9 % for 125 µm sieve size. The mean weight diameter was 80 µm (Appendix 12).

Fig. 76 and Table 37 showed that of Eratab[R]. The percent retained of the smallest size was low, only 5.8, while that on 45 µm sieve size was highest, reaching 27.2 %. The percent of 75, 90, and 106 µm

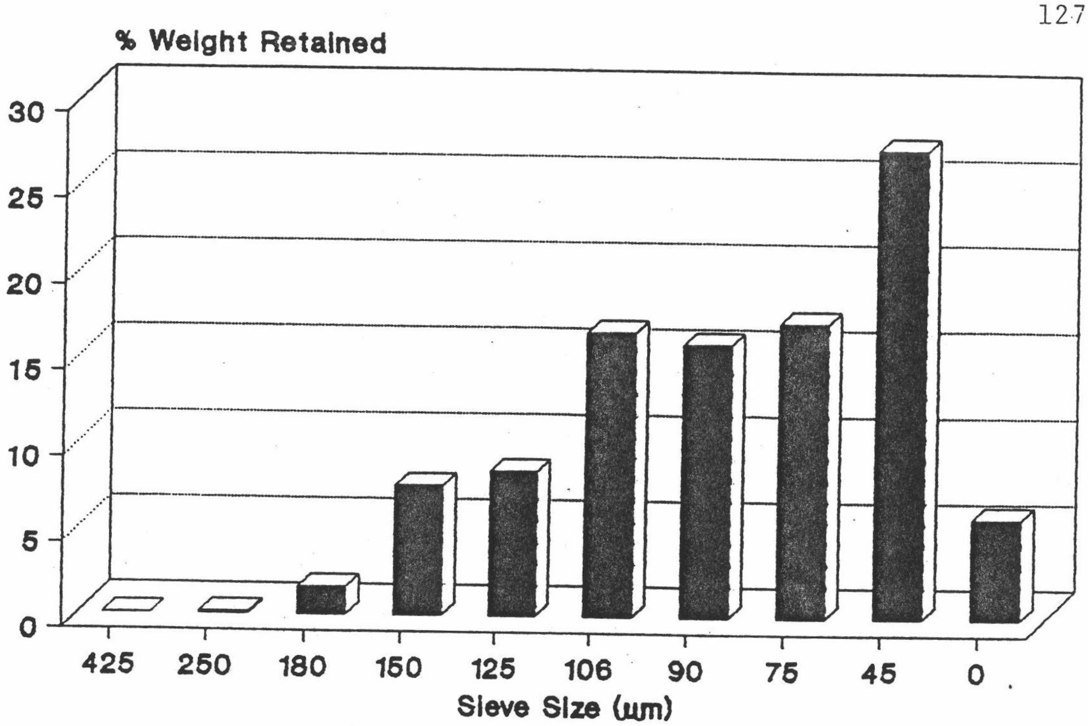


Figure 74 Particle Size Distribution of Deproteinized and 10-hr. Crosslinked Starch Aggregates (the same conditions as Fig.73).............

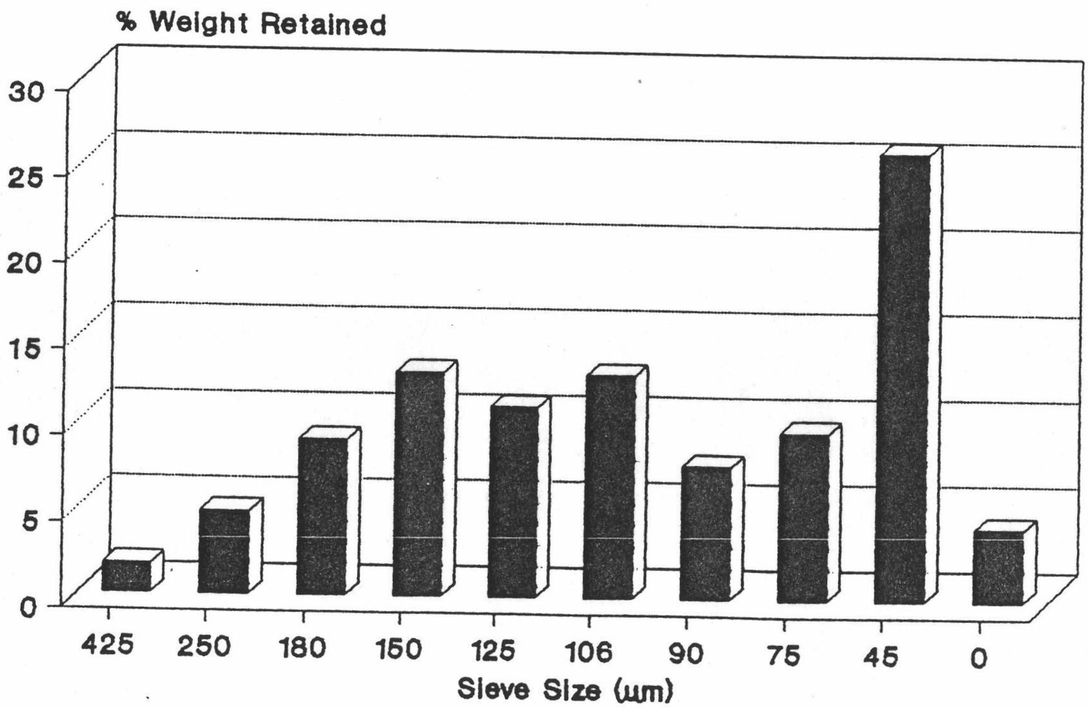


Figure 75 Particle Size Distribution of Starch 1500.

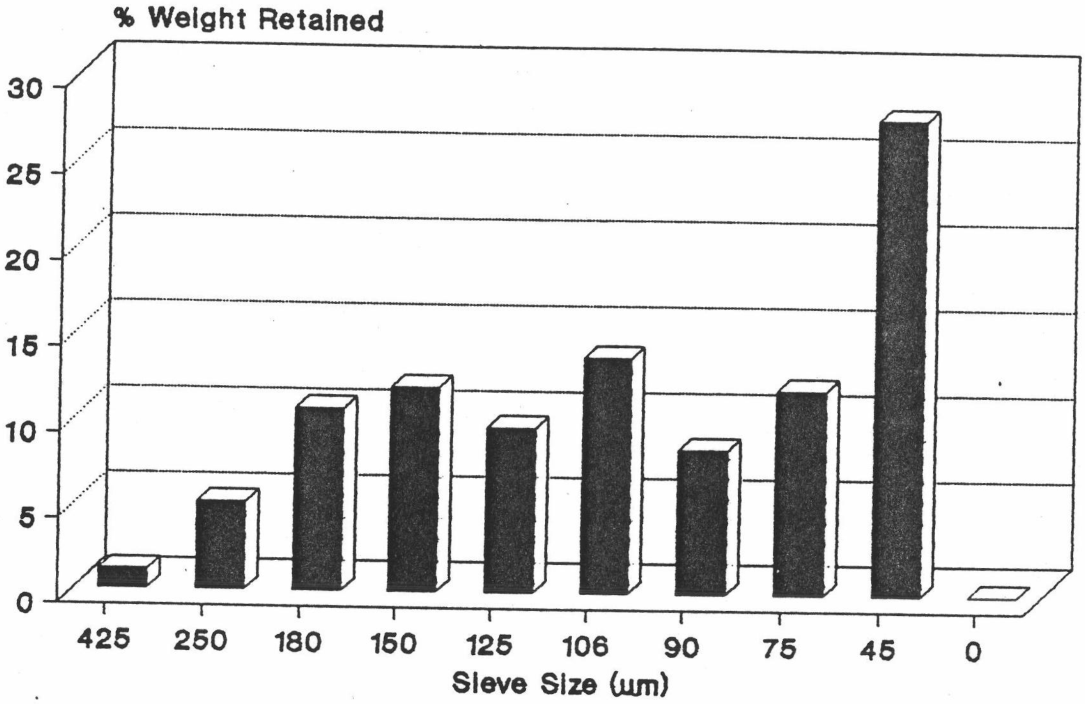


Figure 76 Particle Size Distribution of Eratab.

sieve size were nearly equal, varying between 15.8 and 17.1, while the largest (over 250 µm) was very low, only 0.1 %. The mean weight diameter was 88 µm (Appen dix 13).