

## Production of Crystallized Glucose from Poor Glucose by the Double Salt Method

Hideaki HOSAKA

*Department of Food Chemistry and Technology, Faculty of Fisheries  
and Animal Husbandry, Hiroshima University, Fukuyama*

(Tables 1-8, Figs. 1-6)

In 1927 Mr. S. MATSUURA<sup>1)</sup> determined the mutual solubility of glucose and sodium chloride in ternary system, that is water-glucose-sodium chloride at 24°C. Later N. V. LEBEDEV and B. O. LJUBIN<sup>2)3)</sup> greatly extended the temperature of MATSUURA'S experiment and proved a relation of solid-liquid equilibrium in ternary system at temperatures ranging 0 to 90°C. Furthermore they and A. A. BANNIKOVA<sup>4)</sup> carried out a valuable work on the formation of crystallized glucose by decomposition of double salt.

But it has been found that the glucose crystal formed in the conditions described in the reports is small range from several microns to several ten microns and its centrifugation is not good too. Either the most important point, however, is that a large amount of sodium chloride is left in the crystallized glucose and makes it unsuitable for use.

In the present paper, we shall try crystallization of the double salt by a pan-boiling of test plant similar to the crystallization of sucrose, we shall try also to increase the yield of glucose in the decomposition of crystallized double salt and to decrease the residue of sodium chloride on the washing of glucose.

### 1. The production of double salt by panboiling

In 1964 K. TANEDA and T. ITO<sup>5)</sup> undertook to clarify those points. They represented the yield of glucose in the double salt from the syrup by the following experimental expression.

$$S = \frac{AB - (A - W) D}{AB (1 - 1.21 D)} / 100\%$$

S = expected yield of glucose in the double salt (%)

A = weight of syrup fed into boiling (g)

B = concentration of the syrup (g/100)

W = weight of evaporated water during boiling (g)

D = concentration of the molasses (%)

The experimental equipment was a Calandria type evaporater operated under on reduced pressure. The volume and thermal transmission area were  $0.012 M^3$  and  $0.18 M^2$  respectively. The massecuite was cooled slowly in the evaporater until room temperature and left for 3 hrs. The filter of the massecuite was the centrifugal type.

The glucose solution was prepared according to the following method. The lignocellulose prepared by steamcooking for woodchip was main-hydrolysed with conc. sulfuric acid in the flash mixer. After the lignin was separated, the solution was deacidified by an ion-exchanged membrane and neutralized with calcium hydroxide and sodium carbonate. This neutralized solution was filtered, and purified with ion-exchanged resin and active carbon. This glucose solution was concentrated till 45%.

#### Experiment

Sodium chloride of 16.22% per glucose was added to the concentrated liquid, and then dissolved. The required amount of liquid was weighed put into the panboiler, heated by steam, and concentrated at a temperature of  $60^\circ C$  in vacuum. After the supersaturation of 1.01—1.05, the seed of 60—100 mesh was added, and the pouring of additional syrup into the panboiler began at a constant rate and the boiling was continued. The boiling took 4—5 hrs. for the first salt crystallization, 10—20 hrs. for the second one, and 1—1.5 hrs. for recrystallization.

#### Results:

Several experiments were performed. An example is shown in Table 1. The recrystallized double salt was prepared from the solution that dissolved the first and the second crystallized double salt, and the second crystallized double salt was prepared from the molasses of the first crystallized double salt.

Our experimental results are approximately in accordance with the calculated results of TANEDA's equation. From this experiment we also conclude that the woodhydrolysis sugar solution of more than 90% D.E. (glucose/dissolved material 100) is able to yield more than 60% of glucose as double salt by panboiling, but from a comparison of the panboiling with the double salt, the persaturation of liquid is 1.02—1.20 on the sucrose and 1.02—1.10 on the double salt, it may

Table 1. Crystallization of double salt from poor glucose syrup by vacuum panboiling

		first crystallization	recrystallization	second crystallization
D. E.		94.6	99.6	87.2
composition of starting sugar solution	reducing sugar (%)	43.8	48.9	36.7
	NaCl (%)	7.2	7.8	6.1
starting sugar solution (g)		710	6000	1200
additional sugar solution (g)		2130	1990	2540
massecuite (g)		1695	5290	2420
composition of double salt	glucose (%)	80.0	83.1	78.6
	NaCl (%)	14.1	13.7	13.8
composition of molasses	reducing sugar (%)	61.8	61.1	42.7
	NaCl (%)	9.6	9.9	4.6
glucose yield (%)		63.3	66.2	49.7
calculated glucose yield* (%)		60.9	65.9	50.2

remarks 1) \* from TANEDA's equation

2) evaporated water (W) of TANEDA's equation is water in starting sugar solution, additional sugar solution and massecuit

concluded that the double salt panboiling yields more than sucrose panboiling.

It is difficult to obtain the high yield of the first crystallization in the case of a low D. E., because if the yield of first crystallization is high, the second crystallization will be low and the more difficult. According to our experiments it is more usual that the yield of the crystallization is 60% in case the of 90% D. E. at the first crystallization.

In the case of no-seeding the cake is separable from the massecuit by centrifugal effect at about 1000 g in 15—30 minutes. But in case of seeding the diameter of the crystal is 400—800 $\mu$ , theremore the cake is separable by the centrifugal effect at about 500 g in a few minutes.

With the results described as well as with TANEDA's report, made up a commercial plant. The flow sheet of the commercial plant is shown in Fig. 6. The crystallizer is a Calandria type; heat transfer area 58 M<sup>2</sup>. The settling tank is a cooling type tube; volume 11 M<sup>3</sup>, cooling area 17 M<sup>2</sup>. The glucose solution of purified wood hydrolysis is concentrated by a double effect evaporator at 80°C, and ca 1% of seed and sodium chloride are added. After panboiling the massecuite is transfered to the settling tank and cooled off slowly untill 35°C, while

stirred. The cooling requires 9 hrs. at the first massecuit, and 18 hrs. for second.

The result of the operation is shown in Fig. 1. The operation of this apparatus began Aug. 1963. At first the yield of double salt was low, because we were not well acquainted with the apparatus and the hydrolyzed solution was too poor. But in 1964 the actual yield was higher than we had beforehand. It seems quite all right to keep a long settling time.

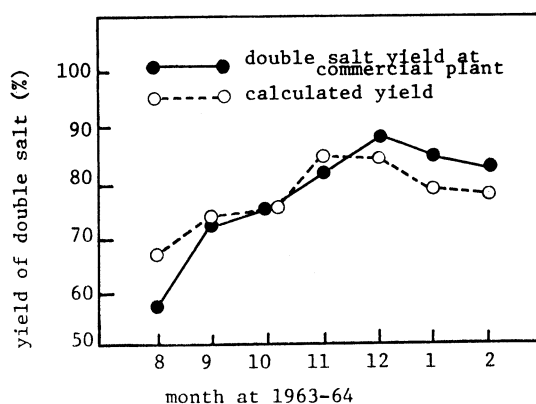


Fig. 1. The yield of double salt at commercial plant

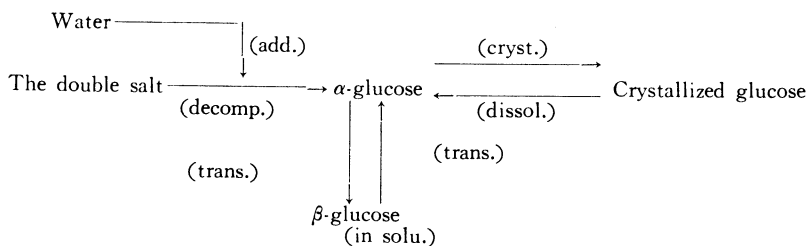
## 2. The decomposition of double salt

N. V. LEBEDEV found out that if when the formed crystallized glucose had separated itself much before the liquid-solid equilibrium phase, the deal of crystallized glucose produced was higher than the quantity calculated beforehand by the triangular diagram. That means that in the case of the decomposition carried out at a temperature of 20°C, the maximum yield calculated by the diagram is 21.6%, yet the yield of crystallized glucose reaches in fact 67.8% at 30 minutes after the beginning of the decomposition.

K. TANEDA compared both crystallizations of glucose, namely the direct method which required many hours and the double salt method and estimated that in the direct method,  $\beta$ -glucose that may be considered rather to hinder transport of  $\alpha$ -glucose in case of crystallization is abundant in the solution, while in the double salt method, the obstacles rather scarce in the solution. Therefore it may be assumed that diffusion in both methods differ enormously from each other.

The course of the transformation of glucose at the double salt decomposition

is represented as follows:



K. TANEDA suggested the following new method of decomposition that was based on his dynamic experiment. Namely: relatively warm water was used to drop the degree of supersaturation flase grain, thereafter the masseccuite was gradually cooled with comparing to dropping velocity of  $\alpha$ -glucose concentration by its crystallization and the trans-formation to the  $\beta$ -form for increasing of crystallized glucose. A summary of his results is as follow: temperature of decomposition 9—14°C, time 60—100 minutes, yield of glucose 60—65%, and remaining salt in glucose 0.6—0.8%.

The remaining salt in glucose that has his report is relatively large compared to the crystallised glucose on the maket which contains 0.03% ash. This large amount of remaining salt is a hindrance for industrialization.

We studied a methode for producing in a simple way and a good yield of glucose with as less as possible remaining sodium chloride. Our experimental decomposition is as follow;

- 1) diameter of the seed
- 2) combination of decomposing water and washing water
- 3) additive method of double salt

We think that the diameter naturally affects the yielding of glucose. The sodium chloride in glucose is due to the presence of molasses adhering to the cake of crystallized glucose or to the double salt that remained slightly in the cake. If much water used in the washing, much crystallized glucose will dissolve in to water, therefore it is important to remove effectivly the remained sodium chloride with less water. The effects of the diameter of the seed, the volume of decomposing water and the volume of washing water were studied by means of analysis of the variance.

#### Experiment

The water for decomposition on a constant temperature was put in a beaker

of 2 L, double salt of 1000 g and seed were added gradually with under continuous stirring. After the massecuite had cooled off, the crystallized glucose was separated from the molasses by a small centrifugal machine in a short time. The separated cake was sprayed with cooled off water, and separated again by centrifugal force.

The data of this experiment are:

temperature of the decomposition water	20°C
times for decomposition	10 min.
cooling temperature of massecuite	8°C
cooling time of massecuite	25 min.
weight of seed per glucose	10%
temperature of the washing water	2°C
effect of centrifugal	950 g
time of centrifugal	3 min.
weight of double salt in the washing at a time	500 g
diameter of seed	under 200 mesh, 100—500 mesh, 35—65 mesh
percentage of decomposing water per glucose	80, 85, 90, 95, 100%
percentage of washing water	20, 15, 10, 5%

Table 2. results of salt decomposition and washing

mesh of seed	double salt decomposition				washing				total yield (%)	rate of total desalting (%)	salt in crystal glucose (%)	diameter of crystal ( $\mu$ )
	decomposition water %/sugar	yield (%)	salt in cake (%)	rate of desalting (%)	washing water %/sugar	yield (%)	salt in cake (%)	rate of desalting (%)				
200	80	72.20	2.84	79.93	20	87.90	1.15	65.18	63.43	92.19	1.17	185
	85	67.81	2.17	84.67	15	92.74	0.69	69.37	62.88	95.30	0.71	185
	90	68.20	1.83	87.20	10	91.58	0.25	86.75	62.45	98.30	0.26	195
	95	67.99	1.32	90.93	5	90.71	0.42	69.17	61.67	97.20	0.43	140
	100	63.94	0.98	93.14	—	—	—	—	63.94	93.14	1.02	165
100—150	80	75.81	3.11	68.22	20	89.92	1.01	71.82	69.09	94.51	1.03	270
	85	67.41	1.80	87.43	15	91.10	0.49	73.57	62.90	96.68	0.51	275
	90	65.88	1.20	91.91	10	92.75	0.22	76.96	61.96	98.94	0.23	225
	95	63.32	0.52	96.52	5	96.22	0.12	77.97	60.92	99.23	0.12	250
	100	67.31	0.93	92.98	—	—	—	—	67.31	92.98	0.96	255
35—65	80	69.96	3.01	79.61	20	85.34	0.92	69.69	63.02	93.68	0.95	295
	85	68.57	1.33	91.03	15	89.84	0.23	84.89	62.79	98.64	0.23	310
	90	62.25	0.66	95.60	10	93.35	0.03	99.60	61.94	99.97	0.03	315
	95	63.40	0.51	96.16	5	93.59	0.14	75.39	62.38	99.06	0.14	265
	100	70.67	0.51	97.64	—	—	—	—	70.67	97.64	0.51	315

Table 3. Analysis of variance table (No. 1)

	factorial effect	sum of squar	degree of freedom	mean square	F-test on the obser- vation
yield on the decomposition	seed	3.5	2	1.8	0.21
	vol. of decomp.	112.9	4	28.2	0.33
	water error	67.9	8	8.5	
	total	184.3	14		
percentage of desalting on the composition	seed	74.3	2	37.2	2.9
	vol. of decomp.	723.4	4	180.9	14.0**
	water error	103.4	8	12.9	
	total	901.1	14		
yield on the dewatering	seed	9.4	2	4.8	1.2
	vol. of decomp.	57.9	3	19.3	4.8*
	water error	23.8	6	4.0	
	total	91.1	11		
percentage of desalting on the washing	seed	237.6	2	118.8	2.7
	vol. of decomp.	629.8	3	209.9	4.6
	water error	271.3	6	45.2	
	total	1138.7	11		
total yield	seed	6.0	2	3.0	0.52
	vol. of decomp.	65.5	4	16.4	2.82
	water error	46.5	8	5.8	
	total	118.0	14		
percentage of total desalting	seed	16.6	2	8.3	8.9
	vol. of decomp.	73.3	4	18.3	19.7**
	water error	7.3	8	0.93	
	total	97.3	14		
	seed	0.30	2	0.15	12.0**
	vol. of decomp.	1.74	4	0.44	38.8**
	water error	0.10	8	0.13	
	total	2.12	14		

These conditions were projected for the analysis of variance by two way square.

#### Results:

The results of the experiment shown in table 2. A summary of the results on the analysis of variance of two way square is given in a table 3. When the diameter of seed is large, both total desalting and the diameter of the crystal will be large, and the amount of remaining salt will be little. The main effect of the

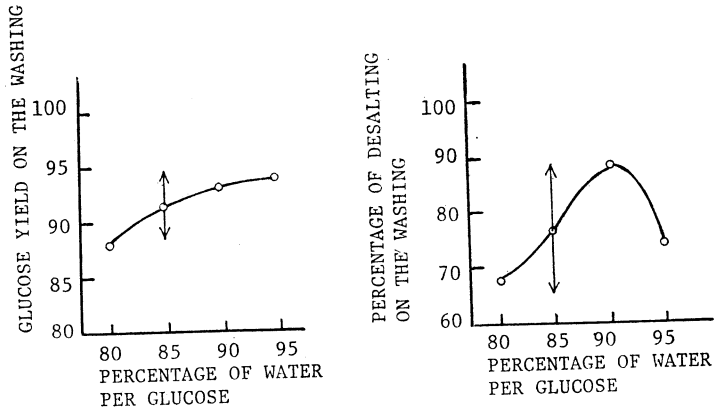


Fig. 2. Average estimation on washing

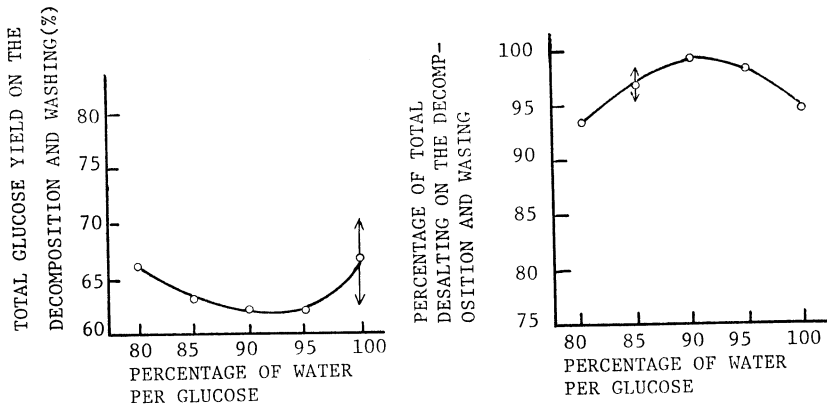


Fig. 3. Total average estimation on the decomposition and washing

seed's diameter may have a significance of 1% on the desalting, none on the yields. therefore a large diameter of seed has a good desalting effect (Fig. 2, 3, 4).

The condition of water used does not affect the glucose yielding in the decomposition, but has a significance of 1% on the glucose yield of the washing and desalting. The most desirable condition of water used is 90% per glucose on the decomposition, and 10% per glucose on the washing to get rid of the desalting effect on the decomposition. The presumed average total yield and the presumed average sodium chloride contained in crystallized glucose produced under these conditions are as follows:



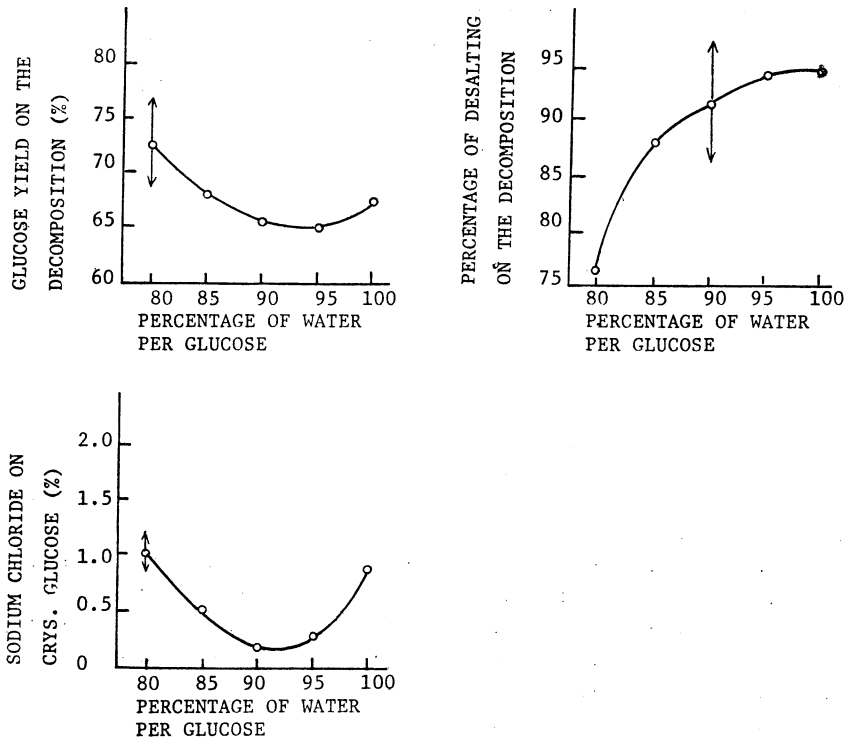


Fig. 4. Average estimation on the decomposition

diameter of seed	presumed average total yielding	presumed average sodium chloride contained in the glucose
200 mesh under	$60.90 \pm 7.17$	$0.34 \pm 0.24$
100—150 mesh	$62.30 \pm 7.17$	$0.19 \pm 0.24$
35—65 mesh	$62.20 \pm 7.17$	$0.00 \pm 0.24$

Decrease of the decomposing water seems to have a tendency to increasing the desalting, for instance if the decomposing water decreases to 80% from 90%, the desalting will increase 15.5%. When rearranging the results, in case of 3% upper limited control on the contained sodium chloride in the crystallized glucose, the conditions of operation are seed of 35—65 mesh, decomposing water of 90—95% per glucose and washing water of 5—10%.

But it is not practical to use seed of 35—65 mesh on a commercial base,

generally the particle collected in the cyclone on the drying are used for seeding, so that their diameter is 200 mesh under. therefore the following experiments were made for the case of 3% upper limited control on the contained sodium chloride in the glucose. The conditions of the experiment were the same as the last time. The calculated results which were obtained in the way described above are shown Table 4. A summary of the results on the analysis variance of two way square is shown in Table 5.

Table 4. Results of double salt decomposition and washing by the seed of 200 mesh under

double salt decomposition				washing			rate of desalting (%)	total yield (%)	rate of total desalting (%)	salt in dry crylized glucose (%)
decomposing water %/sugar	yield (%)	salt in cake (%)	rate of desalting (%)	washing water (%)	yield (%)	salt in cake (%)				
90	63.9	1.17	89.4	10	89.5	0.33	78.9	57.2	97.8	0.33
90	63.5	0.94	93.7	10	94.5	0.16	74.5	53.9	98.4	0.17
90	64.7	1.14	92.2	30	79.2	0.04	96.2	51.2	99.7	0.04
90	66.7	11.6	92.1	30	79.9	0.07	94.0	53.3	99.5	0.07
90	63.4	1.08	92.8	50	76.7	0.04	96.4	48.6	99.7	0.04
90	62.3	1.09	91.9	50	70.5	0.04	96.7	43.9	99.8	0.04
100	63.4	0.98	93.4	—	—	—	—	63.4	93.4	1.00
100	63.7	0.93	93.7	—	—	—	—	63.7	93.7	0.93
100	63.2	0.98	93.1	20	81.2	0.04	95.9	51.3	99.7	0.05
100	61.4	0.77	94.8	20	82.9	0.05	93.3	50.9	99.7	0.05
100	61.7	0.77	94.7	40	71.2	0.04	95.2	43.9	99.8	0.04
100	59.2	0.83	94.3	40	70.0	0.03	96.4	41.4	99.8	0.03

The increase of water used decreases the yield of glucose, namely in case of 140% per glucose it is 50% under. The decrease of contained sodium chloride increases water used, but the approximate constant quantity in case of more than 120% per glucose is a residue of sodium chlorid of  $0.06 \pm 0.13$  or  $0.05 \pm 0.13\%$ .

The 99% confidence interval that is estimated from the error variance in this experiment is  $\pm 0.13\%$ . This value is very high, therefore this value can be made smaller on an industrilized scale. If the upper control line is 0.3%, the water used will be 100% per glucose, in case of 0.1%, water used will be 120%.

The relation of the decomposing water for washing has little consequence on the yield of crystal and the percent of desalting between 90%+30% and 100%  $\pm 20\%$  of water used in the case of 120% water used per glucose.

The above experiment adopted the decomposing method that adds the double

Table 5. Analysis of variance table (No. 2)

	factorial effect	sum of squar	degree of freedom	mean square	F-test on the observation
yield on the decomposition	A	11.8	1	11.8	4.53
	B	25.7	10	2.6	
	total variation	37.5	11		
percentage of desalting on the decomposition	A	11.8	1	11.8	9.20*
	B	12.8	10	1.3	
	total variation	24.6	11		
yield on the washing	A	345.2	4	87.0	12.70**
	B	34.1	5	6.8	
	total variation	379.3	9		
percentage of desalting on the washing	A	570.6	4	142.6	44.02**
	B	16.2	5	3.24	
	total variation	586.8	9		
total yield	A	534.6	5	106.9	29.21**
	B	21.9	6	36.6	
	total variation	556.5	11		
percentage of total desalting	A	61.1	5	12.2	305.30**
	B	0.3	6	0.4	
	total variation	61.4	11		
	A	135.6	5	27.1	104.30**
	B	1.6	6	0.3	
	total variation	137.2	11		

remarks 1) A ; volume of decomposing water

2) B ; analytical data at each water

salt to continue saturation of  $\alpha$ -glucose gradually. But it is possible to add it all at one time too. This way the control of the operation is easier and enables the simplifying of an apparatus on the industrializing base. Both method were analysed according to the Graeco-latin square ( $2^3$  type) for the yield and the percentage of desalting. The result which were obtained by these methods are shown in Table 6, 7. Their significant difference did not appear from this result. Therefore it is clear that do not matter to add the decomposing salt all in one time.

When comparing the D. E. of glucose in the direct crystallization to the double salt method, we conclude that the double salt method is far efficient than the direct crystallization (Fig. 5). This conclusion is based on the calculations of the experimental data above. The analytical results obtained on the comercial plant are shown in Table 8.

Table 6. Results of decomposition by two method

	D <sub>1</sub> group		80% per glucose		100% per glucose		D <sub>2</sub> group		80% per glucose		100% per glucose	
yield	A-method	35-65 mesh	66.7%	200 mesh	65.8%	A-method	200 mesh	62.2%	35-65 mesh	59.0%		
	B-method	200 mesh	62.7%	35-65 mesh	58.9%	B-method	35-65 mesh	63.4%	200 mesh	55.0%		
percentage of desalting	A-method	35-65 mesh	68.2%	200 mesh	98.2%	A-method	200 mesh	69.4%	35-65 mesh	91.3%		
	B-method	200 mesh	68.0%	35-65 mesh	91.0%	B-method	35-65 mesh	61.2%	200 mesh	92.1%		

Table 7. Analysis of variance table (No. 3)

		sum of squar	degree of freedom	mean square	F-test on the obser- vation
yield	volume of decomposing water	33.2	1	33.2	4.46
	decomposing method	23.5	1	23.5	3.15
	diameter of mode	0.6	1	0.6	0.09
	group	26.3	1	26.3	3.52
	error variation	22.4	3	7.5	
	total	106.0	7		
percentage of desalting	volume of decomposing water	1260.0	1	1260.0	272.7**
	decomposing method	11.1	1	11.1	2.4
	diameter of mode	14.1	1	14.1	3.0
	group	4.5	1	4.5	1.0
	error variation	13.9	3	4.6	
	total	1303.6	7		

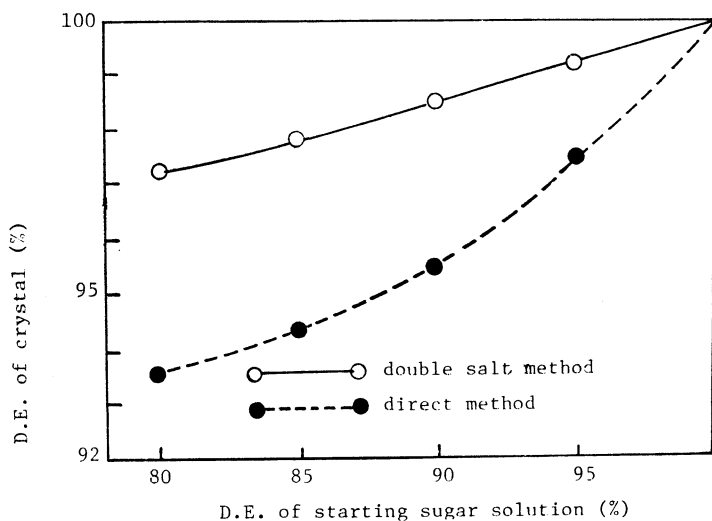


Fig. 5. Comparison of direct method and double salt method

Table 8. The analysis of crystallized glucose at commercial plant

		A	AA
water	%	8.28±0.33 <sup>b</sup>	8.45±0.51
ash	%	0.19±0.05	0.065±0.025
sodium chloride	%	0.17±0.05	0.057±0.022
reducing sugar	%	99.52±0.19	99.61±0.21
purity (as glucose)		99.16±0.31	99.20±0.43
acidity (1/10 HCl ml)		0.66±0.11	0.60±0.31
whiteness	%	96.79±0.30	97.03±1.28
pH		6.29±0.29	6.09±0.25
H. M. F.	ppm	none	none

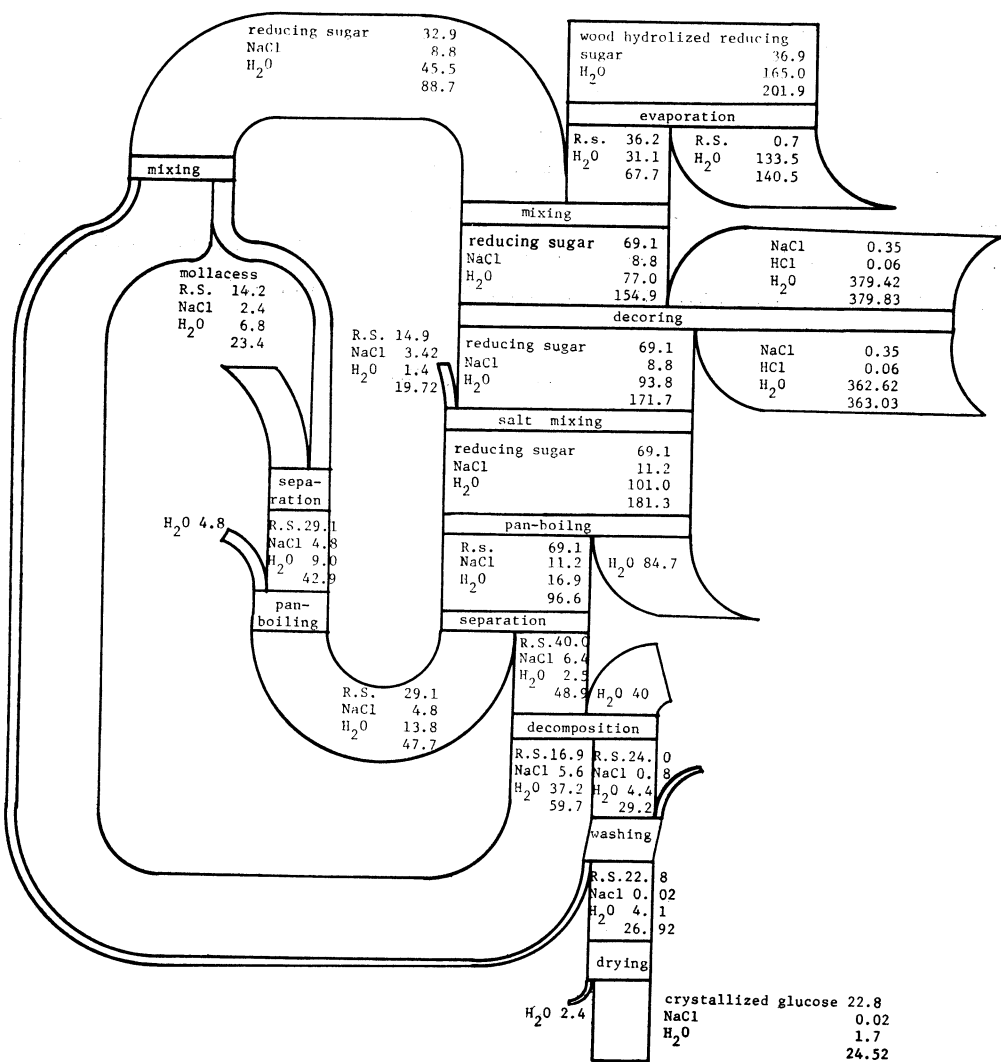


Fig. 6. Material Balance on the Crystallization of Wood hydrolyzed Glucose

These decomposing condition is as follows: The decomposed volume of double salt in the one batch is 600 kg; the temperature of the decomposing water 27—35°C; the decomposing time 10 minutes; the settling temperature under 10°C, 120% decomposing water per double salt for 0.1—0.2% of residual sodium chloride and 140% for under 0.1%.

### 3. Summary

1) About the formation of the double salt: the panboiling method is possible in case of the D.E. is above 90%, the yield is more than 80%. This yield almost coincides with TANEDA'S equation in laboratory. Also the yield increases more than his equation by using longer settling times in a commercial plant.

2) The yield of crystallized glucose on the decomposition changes remarkably by mean of the permissible quantity of sodium chloride that is left in the crystallized glucose. The quantity of water to be used determined respectively for each upper control. If the water used contains 140 percent per glucose, the yield of crystallized glucose is 50 percent. The error variance of observed value in the commercial plant was small than the error variance in laboratory.

### 4. Acknowledgement

The author feels very honored and favored to had the assistance of Mr. Takashi ITO, Kaichi KOBAYASHI and Nobuyuki TAKASHIMA who contributed their experimental skill, sustained the effort and helped to achieve the objectives of this experiment program. The auther appreciates their collaboration sincerlly and acknowledges the important part they took in this research.

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## 純度の低いブドウ糖液から複塩法によるブドウ糖結晶製造

保坂 秀明

従来不可能視されていた不純物質の多い木材加水分解糖液は、糖液のD.E.が90%以上であれば、煎糖方式によって連続的に結晶が可能であり、複塩結晶の収率は80%に達した。工場規模では実験室試験よりも晶出時間を延長した理由もあって更によい結果を示した。

また、従来の複塩分解によるブドウ糖結晶中の食塩残存率は0.6—0.8%と多く、商品価値として難点となっていたが、使用水量、シード粒径、投入方法などの分散分析により、食塩残存率を0.05%以下にする管理方法を決定した。実験室試験における誤差変動は、工業装置では少ないという結果を得ている。複塩法による不純物質の多い糖液の結晶は直接法に比して、その製品性状と収率がかなりよい結果であった。