Manufacture of Levulose from Jerusalem Artichoke

By Junzo YAMAZAKI

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In eight years since 1941, the Japan Levulose Company manufactured 127 tons of pure crystalline levulose (D-fructose) from 6000 tons of tuber of Jerusalem artichoke.

Here will be shown, together with a diagram, the details of the operation performed in 1948, the year of complete mastery of the manufacturing technique.

Fig. 1. Cultivation of Jerusalem artichoke in the end of June at Eniwa, Hokkaido.

Cultivation and Drying of Artichoke Tuber

The artichoke used as the raw material for the manufacture of levulose was cultivated mainly in a field (400 acres) of Eniwa, near Sapporo in Hokkaido, using animal power for cultivation and harvesting, as shown in Fig. 1 (photograph). The variety of Jerusalem artichoke used was of a family of white cortex, and the crop was 9 tons per acre. The fresh tuber was washed with water, sliced into cossette, and dried to a water content of 15 percent by the use of a rotary drier. Thus one ton of dried material was obtained from 5 tons of fresh tuber. To this end 800 kg. of coal was required.

TABLE I

ANALYSIS OF JERURALEM ARTICHOKE

(Cultivated in 1947 at Eniwa, Hokkaido)

			After hydrolysis	
	Moisture (%)	Solid matter (%)	Total reducing sugar(%)	Levulose (%)
Fresh tuber*	80.00	20.00	14.80	11.56
Dried tuber**	15.11	84.89	53.35	40.17

* Mean of the analytical values of 11 samples, converted to the basis of moisture content of 80 percent.

** Mean values of 123 tons of the dried cossette.

The dried cossette can well be preserved, is very little damaged by insects, and is suitable for levulose manufacture throughout the year.

The results of analysis of the tubers, both fresh and dried, are shown in Table I.

Manufacture of Levulose

The dried artichoke used for levulose manufacture from 1941 to 1948 amounted to 1142 tons, corresponding to 6000 tons of cultivated fresh artichoke. The average content of levulose in the dried artichoke was 41.3 percent, the maximum content of year average being 44.0, the minimum 38.0 percent. The crystalline levulose manufactured from these material was 127.4 tons in quantity, the average yield being 11.2 percent of the dried artichoke, corresponding to 27.0 percent of the levulose contained in the raw materials.

In order to explain the details of the levulose production we will illustrate the data obtained in 1948. By this year we mastered the technique of manufacture, producing 16.7 tons of crystalline levulose from 123 tons of dried artichoke during the period from January to July.

In Fig. 2 is illustrated each process of manufacture as well as its material balance in the form of a diagram, where the description of water content and thermal data are eliminated. The width of the figure represents the ratio of solid matter, while the content of levulose is shown numerically. All the numerals in Fig. 2 represent those values recalculated from the data totally obtained during this period, so as to correspond to one ton of the material for manufacture.

Diffusion of Dried Cossette

We have used a diffusion apparatus of a type of semi-counter-current diffusion battery which is usually employed for the extraction of beet sugar. This consists of twelve cells, each of 320 l. in capacity, connected with each other in the form of a circle. Each cell is charged with 63 kg. of the material, and hot water is circulated through the cells, so as to extract the contained fructan. Extraction is in general completed when the liquid

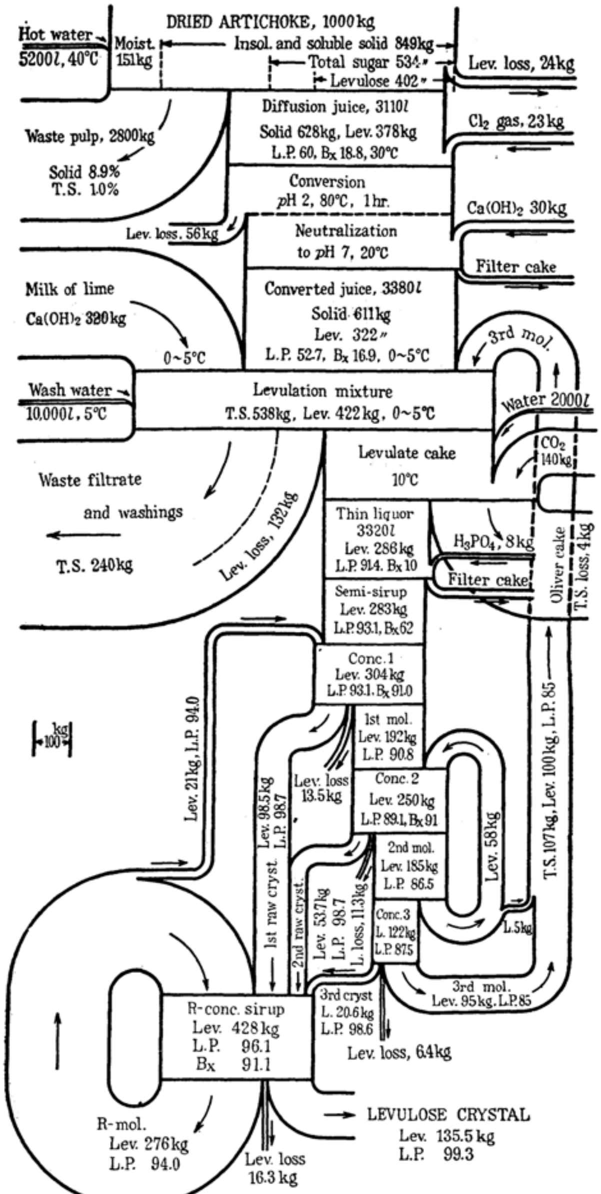

Fig. 2—A process flow diagram of levulose manufacture.

Abbreviations:

T.S.:	Total sugar
L.P.:	Levulose purity
Conc.:	Concentrated sirup
Bx:	Refractometric Brix (% solid)
R:	Refined
Mol.:	Molasses
Lev., L.:	Levulose

passes through ten of the cells, the refractometric solid in the liquid amounting to 18–19 percent. This "diffusion juice" is obtained in a quantity of 200 l. per one charge, is brown in appearance, the total sugar purity (T. S. × 100/solid) being 81, and the levulose purity (Levulose ×100/solid) 60. The yield of levulose of this procedure is 94 percent.

Conversion and Neutralization

A wood tank, 2 m. in height, is filled with this diffusion juice, and chlorine is blown into it at a temperature of 30°C. This is a patented process[1], the characteristic of which is that chlorine destroys any coloring matter, coagulates a part of the impurities, and the hydrochloric acid thereby formed promotes the hydrolysis of polyfructosans. It was once reported[2] that in the oxidation of invert sugar by chlorine, levulose is oxidized at 15°C. to a range of 10 percent, while glucose is destructed by it to the large extent of 80 percent. It is, however, experienced that during the seven months' period the

1) *Japanese Pat.* 92301 (1931).

2) S. Ochi and M. Nakamura, *Repts. Tokyo Imp. Ind. Res. Inst. Lab.*, **24**, No. 5, 46 (1929) (in Japanese).

extent of decomposition or loss in this procedure amount to 14.8 percent for levulose, and to 16.8 percent for other reducing sugars.

It is no doubt possible to prevent the destruction of levulose to a far lesser degree, if hydrochloric acid is used for conversion in place of chlorine, but in this case the filtration of the treated liquor becomes difficult, and, moreover, decolorization as well as clarification can not be carried out with satisfaction. It should be mentioned further that treatment with chlorine has another advantage; this is that in the sugar liquor the growth of moulds is prevented, and thus subsequent operation can easily be performed. The introduction of chlorine is continued until the liquor shows a *p*H between 1.8 and 2.0, and conversion is completed by keeping the liquor at 80°C. for one hour. The liquor is then cooled down to 20°C., and some milk of lime is added to a *p*H 7, when proteinous matters, pectins, etc. are coagulated. On filtering these precipitates a "converted juice" is obtained. The yield of levulose in this process is 85.2 percent.

Precipitation of Levulose ("Levulation Process")

The converted juice is cooled down to 0°–5°C., and milk of lime of the same temperature is added. The necessary quantity of the lime is 1.45 times the quantity equivalent to the total sugar in the hydrolyzate. It is desirable to employ lime of good quality containing more than 67 percent of available CaO, and especially consisting of fine powder. The quality and the quantity of lime has a remarkable effect on the yield of levulose as well as on the amount of carbon dioxide necessary for neutralization. The most important point of this procedure lies in obtaining a compound between levulose and lime ($C_6H_{12}O_6 \cdot CaO \cdot XH_2O$, "lime levulate") in the form of granular precipitate filtrable as easily as possible. Either when the juice is too thick, or when the mixing of the liquors is too rapid, undesirable blocks or fine precipitates are readily formed. To prevent this it is necessary to mix the juice with milk of lime gradually and alternately, and to keep the mixture constantly in a medium of a little excess of lime by stirring well at the temperature between 0° and 5°C. It is, however, unnecessary to add crystal seeds of lime levulate, as already pointed out by Jackson[3]. After thorough mixing for some time, the precipitate is filtered through a filter press, and washed with cold water of 5°C. Washing is continued till the filtrate becomes colorless. The filter cake ("levulate cake") is mixed with cold water, transferred to a carbonator as a thick suspension, and carbon dioxide is introduced until the liquor shows a *p*H 8, keeping the temperature below 10°C. Here levulose is liberated, and by filtering the precipitate of $CaCO_3$ on an Oliver filter, a "thin liquor" of light yellow coloration is obtained. This liquor has a concentration of 10 percent, and a levulose purity (L.P.) 90 to 99 (av. 91.4). In later operations the final (third) molasses, which is removed from raw crystal, is diluted and subjected to levulation process for recovery of levulose, either solely or in admixture with the converted juice.

The process of levulation must be carefully performed, since the loss of levulose in this process is the greatest in the whole procedure, often becoming equal, in quantity, to the final product. The yield of levulose is 65 percent with respect to the artichoke juice, and 80 percent to the molasses. In this illustration the two are mixed and treated, so the yield becomes 68.7 percent on the average.

Evaporation to "Semi-Sirup"

The thin liquor is, while still cold, neutralized with phosphoric or oxalic acid to a *p*H 5.8. After filtration the liquor is concentrated to 62 percent in a vacuum evaporator, and preserved in a tank. The calcium salt in the solution separates out gradually, and finally the value of L.P. increases to 93 on the average.

Crystallization of Raw Crystals

The sirup which has been blended from a few lots of semi-sirups, so as to make the L.P. value to 94, is again thickened by heating in a vacuum evaporator to a "concentrated sirup" having a concentration of 91 percent as regards to solid. This thick sirup is then introduced into a crystallizer, seeded at 52°C. with a fine powder of crystalline levulose, gradually cooled down with constant gentle stirring, so that the seed can grow up sufficiently. Thus the content will be in the state of massecuite, when the temperature is lowered to 30°C. within 24 hours. Then the molasses is removed by means of a centrifuge, where the first raw crystal is obtained. The former (the first molasses), on concentrating, is subjected to repeated (twice) crystallization. In a similar manner the second and the third crop of levulose crystal is obtained, thereby the value of

3) R. F. Jackson, C. G. Silsbee, and M. J. Proffitt, *Sci. Papers Bur. Standards*, No. 519, **20**, 609 (1926).

L. P. is hardly lowered as to the crystal, but is depressed to 85 with the molasses. This molasses with a low L. P., being unfavorable for crystallization, is returned for recovery of levulose to the above mentioned process of levulation.

In practice, the second molasses is concentrated to obtain a third crop of crystal, in so far as the L. P. value is above 87.5. If below, the molasses is blended to a sirup of L. P. 89 by adding the first molasses, and made to yield the second crystal. With the depression of L. P. value the yield of levulose crystal suddenly falls with respect to massecuite, and also the crystallization process becomes tedious, as shown in Table II.

TABLE II

CRYSTALLIZATION OF LEVULOSE

Crystal	No. of Crystallization	Crystals obtained (kg.)	Crystals per one Cryst'n (kg.)	Av. Purity of "Conc."	Yield of Cryst. as to Massecuite (Solid/solid)(%)	Time required for Cryst'n (day)
1st raw	42	12,290	292.6	93.1	29.6	1
2nd raw	35	6,706	191.6	89.1	19.4	2
3rd raw	17	2,574	151.4	87.5	15.1	6
Refined	57	16,810	294.9	96.1	30.7	0.8—1

Crystallization of Refined Crystal

The raw crystal and the sirup (R-mol. of Fig. 2), which is removed from the refined crystal, are made up to a L. P. of 96, decolorized with active carbon, and subjected to crystallization. The crystals, after centrifugation, are washed with a little distilled water, and dried in vacuum at 40°C.

The refined crystals thus obtained are colorless, tilted cubes of a relatively uniform size (from 0.5 to 1 mm.). The L. P. is 99.3 on an average, well in agreement with the Japanese Pharmacopoeia. By recrystallizing from dilute methanol or ethanol we are able to obtain easily a sample of highest purity[4].

In order to obtain further crystals from the mother sirup (L. P. 94) of the refined levulose, some raw crystal is dissolved into it, the excess sirup being returned to the stage of the first raw crystal. Such a somewhat complicated method of preparing refined crystal is, in reality, a most economical process, and favorable for keeping constant the quality of the product.

Steam, Electric Power and Labor

The manufacture of levulose consumed, per one ton of dried artichoke, 6 tons of steam, 1500 KWH of electric power, 345 man hours of labor (in the case of all-night operation) and the chemicals indicated in Fig. 2.

Analytical Procedure

It is of the utmost necessity, for chemical control, to carry out the exact analysis of levulose and the accurate determination of its purity. A number of various analyses were made for each lot of the raw material as well as its intermediates, and finally summed up. The value of refractometric solid was assumed directly as the value of solid in aqueous solutions. The total reducing sugar (T. R. S.) was measured by the titrimetric method of Lane and Eynon[5], after the test liquid was hydrolyzed by hydrochloric acid. The levulose ratio (L. R.) was obtained according to Jackson and Mathews[6] from the titre of T. R. S. and the saccharimetric polarization. It was very fortunate that both of these methods enabled us to perform rapid and accurate determinations. The levulose content (L.) is obtained by means of an equation: L. = T. R. S. × L. R., and likewise the levulose purity (L. P.) by a relation: L. P. = L. × 100/S. All the analytical procedures required considerable skill and precision; nevertheless, after some experiences, accurate and consistent values were constantly obtained. (Here allow us to mention that Messrs. M. Nakamura†, K. Nishiki, and S. Kidooka of this factory helped us to systematize these analytical methods and carry out practical determinations).

Utilization of Waste Liquor

It is possible to collect nearly 90 percent of the total waste sugar in a concentration of 5 percent from the waste filtrate of the levulate, when combined with the first portion of the filtrate obtained by washing.

This liquor, on neutralizing with carbon

4) Y. Tsuzuki, J. Yamazaki, and K. Kagami, *J. Amer. Chem. Soc.*, **72**, 1071 (1950).

5) J. H. Lane and L. Eynon, *J. Soc. Chem. Ind.*, **42**, 32T (1923), **44**, 150T (1925), A. O. A. C., 5th ed. pp. 498~9 (1940).

6) R. F. Jackson and J. A. Mathews, *Bur. Standards J. Res.*, **8**, 435 (1932).

dioxide or with sulfuric acid, proved to be an active culture media for yeasts.

Experiments culturing Fleischmann's yeast by the so-called "Zulaufsverfahren" with a concentrated liquor, to which was added some ammonium sulfate and phosphate showed that sugar consumption is 92.6 percent and the yield of dry yeast is 49.7 percent with respect to the sugar present in the liquor. The effect was even superior to a control experiment done with malt juice, where sugar consumption was 90.2 percent, yield 49.5 percent[7].

It is, therefore, possible to produce even 1200 lb of fresh yeast by utilizing the waste liquor produced from one ton of dried artichoke.

Cost and Mode of Manufacture

In Japan at present, the mill cost of levulose can not be lowered below $3 per kg., owing to the high price of Jerusalem artichoke. Consequently, raw sugar (sucrose) or beet molasses has been used as the raw materials for levulose manufacture since 1949. It is certain that Jerusalem artichoke has no advantage as raw material, unless the price of fresh artichoke is less than 1/20 of that of sucrose. However, if there is any possibility of utilizing fresh artichoke directly the cost will be equal to that of sucrose, even if the artichoke is, in price, as high as 1/7 of sucrose.

Since the price of this tuber is, in general, lower than this, the cost will be considerably decreased, if such a scheme of production is adopted. If it is possible to produce yeast at the same time, further decrease of the cost by 10 to 20 percent will be expected. One of the best schemes to realize this would be to cultivate Jerusalem artichoke in the vicinity of a beet sugar factory with an attached yeast manufacturing factory, to extract fresh artichoke tuber by using a large diffusion battery during the winter, to preserve the concentrated converted juice till the spring of the next year, and by utilizing the season of cessation of beet sugar production to carry on levulose manufacture. This appears to be a most economical form of levulose production, considering the circumstances that direct extraction of fresh artichoke is at some important points more profitable than the use of dried artichoke.

Japan Levulose Co.,
385 Ichinotsubo, Kawasaki

7) T. Asai, H. Arioka, C. Sakurai, and S. Takahashi, *J. Agr. Chem. Soc. Japan*, **22**, 136~9 (1949) (in Japanese).