STUDIES ON THE EXTRACTION OF FISH LIVER OIL.

Ⅱ. THE EXTRACTION OF OIL FROM FISH LIVERS CONTAINING HIGH VITAMIN A UNIT.

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With 5 tables

Introduction

Examining how to operate in order to produce an oil of high unit value and a high yield, the authors find that by using the generally adopted alkaline method and by stressing pH 11, the best result is obtained.(1)

The following is a report of the results of an industrial test with this method which it is hoped may be of some reference value.

I. Internal Organs of Flounder.

METHODS OF EXTRACTION OF OIL:-

A. Method of separating the upper layer.....Weigh out flounder internal organs that were cleared as completely as possible of meat, bones, skins and other. Chop it finely and place it in a tank. After the stirrer is started, add water. The amount of water is determined by the hardness of the material (that is its frozen condition) when it is chopped and just placed into the tank as well as the content of the water used is generally 2 times the volume of the materials used. If it is to be transferred by gear pump into a tank at a higher position, the chopped material is first placed in a small tank with sufficient water to dilute it so that it can be pumped up. When it is too hard, water may be used. Then it can de handled in the same way. During or after chopping, add approximately 2% its weight solid caustic soda in Bé 15° to 25° solution directly to the tank or the small tank while stirring swiftly. This so adjusted that after it is completely transferred into the tank the resulting pH must be 11 to 12. Blow in steam and raise its temperature (preferable to use a double bottom pan) to dissolve it. While the temperature is increasing the material is also being dissolved with a result that its pH value will be lowered. This is to be adjusted by adding frequently a

small quantity of NaOH solution to maintain its pH at 11. At 50°C. take a portion of the solution in a beaker, set it a few minutes and see whether the dissolution is good or not. When it is good, raise its temperature above 50°C. and examine in the same way frequently. If this is not the case, maintain its temperature at 50°C. to 60°C. and stir all the while for half to one hour and then examine it. If the dissolution is still not good, add sufficient quantity of NaOH solution. Temperature is to be raised only after solid matter has been dissolved.

At 80° to 85°C. stir the mixture for about one hour until it is completely dissolved. Add water to lower its temperature to 50° to 60°C., then stop stirring and cover. Take out the emulsion including oil layer. Add 3 times its weight of hot water, separate by Sharpless' centrifugal machine, so crude oil is obtained.

B. Method of separating whole liquor.....When the whole solution is to be centrifugated by a Sharpless' centrifuge, its dissolution is carried in the following manner: a certain amount of raw material is first chopped and placed in a small tank to which water is added at a ratio of 1:1 or less. This is then heated with alkali. The quantity of NaOH is a little larger than in the former case. Several minutes or more after its complete dissolution the whole material is transferred into a large tank from which the crude oil is obtained by using a Sharpless' centrifugal machine. This operation is repeated again and again.

RESULTS:-

In Table I, A shows the results in each month while B shows that on each day. Both tests were carried out in 1950. In Feb., March, April, July and August there was scarcely any flounder to be used for making liver oil, therfore, these columns are blanks. The amount of NaOH that would adjust the pH value at 11 to 12 was nearly 2.5% for each sample. Temperature of dissolution was 85°C. The necessary quantity of NaOH for complete dissolution seems to be dependent somewhat upon the freshness, quantity of water used, and other factors.

Though thermometric experiment was not carried out, it is clear from industrial test in factories that at a high temperature of about 100°C. vitamin A unit will be decreased by about 7%. Dissolution of raw materials will be better when its temperature is high, however 85°C. is the optimum in the authors' opinion. All experiments were therfore carried out at this temperature.

In December both vitamin A unit and oil quantity were high, yet this differed remarkably in accordance with the origin and the factory where the fish were treated. This increase both in units and in quantity in December may be accounted for from the fact that impurities in the organs are very low, the

weights of liver and pylorus are higher and the water content of organs is less than those of fish taken in other months.

The results obtained from the above two methods show no difference from one another. In other points except numerical relations, there may be some difference. For some reasons the total vitamin A quantity per gr. of internal organs show no remarkable change during seasonal changes. However, generally, it seems that the maximun quantity is obtained in December and in January. In the same period oil quantity will be less when higher quantity of NaOH is used, while vitamin A unit becomes high instead; when amount of NaOH used is lower, the contrary is true. The total vitamin A quantity per gr. of internal organs is the same influenced by the quantity of NaOH used. Raw materials in the same period will require different quantities of NaOH for their complete dissolution. This is owing to the difference in stocking usually at 85°C., for during that time these materials will undergo an autolysis. This autolysis, when occurring to a certain degree will lead to a better dissolution of the material and the total vitamin A quantity per gr. of internal organs will be slightly higher. However, fresh material will show good results in regard to odor, color, deterioration and

Table I A

Date	Internal organs quantity kg.	NaOH quantity of addition kg.	NaOH/ Internal organs %	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total Vitamin A quantity per gr. of internal organs G.U.S.P.U.	Method of extraction of oil	Fish market
Jan., 1950	5976.0	135.7	2.27	371.0	6.20	147000	9114.0	By method A	Siogama
Feb., 〃	——	——	——	——	——	——	——	——	——
Mar., 〃	——	——	——	——	——	——	——	——	——
Apr., 〃	——	——	——	——	——	——	——	——	——
May, 〃	7727.0	128.3	1.66	465.0	6.01	124000	7452.4	By method A	Siogama
〃 〃	8431.0	197.4	2.34	524.7	6.22	132000	8210.4	〃	〃
June, 〃	8222.0	288.0	3.50	452.0	5.49	103000	5654.7	〃	〃
July, 〃	——	——	——	——	——	——	——	——	——
Aug., 〃	——	——	——	——	——	——	——	——	——
Sept., 〃	5912.0	178.4	3.01	393.0	6.64	124000	8233.6	By method A	Siogama
Oct., 〃	5925.0	152.2	2.56	390.0	6.58	103000	6777.3	〃	〃
〃 〃	3309.0	89.0	2.68	224.0	6.77	98000	6634.6	〃	〃
〃 〃	2140.0	61.6	2.87	159.0	7.43	99300	7377.9	〃	〃
Nov., 〃	4272.0	159.3	3.72	276.0	6.46	105000	6783.0	〃	〃
Dec., 〃	7518.0	211.0	2.80	549.0	7.30	123000	8979.0	By method B but a part is by method A	Hatinohe
〃 〃	5040.0	125.6	2.49	372.5	7.39	139100	10279.0	〃	〃
〃 〃	10920.0	272.3	2.49	716.0	6.55	150000	9825.0	〃	〃
Total or average value	75392.0	1998.8	2.65	4892.2	6.48	124700	8080.5		

Table I B

Date	Internal organs quantity kg.	NaOH quantity of addition kg.	NaOH/ Internal organs %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Acid value	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of internal organs G.U.S.P.U.
Feb. 27, 1950	1411.0	39.80	2.82	11	85	67.7	4.79	0.24	150000	7185.0
Feb. 28, 〃	1577.0	34.62	2.19	11	85	95.6	6.06	0.55	147000	8908.2
Feb. 29, 〃	1494.0	30.72	2.05	11	85	95.0	6.35	0.80	—	—
Feb. 30, 〃	1494.0	30.61	2.04	11	85	113.0	7.56	1.10	—	—
May 2, 〃	1859.0	22.77	1.22	11	85	125.6	6.75	0.52	109500	7391.2
May 4, 〃	1843.0	24.94	1.35	11	85	117.0	6.35	0.30	—	—
May 5, 〃	1857.0	24.12	1.29	11	85	92.4	4.97	1.80	—	—
May 6, 〃	2168.0	56.55	2.60	11	85	130.0	5.99	0.40	130000	7787.0
May 9, 〃	1762.0	38.62	2.19	11	85	107 0	6.07	—	122000	7405.0
May 10, 〃	1724.0	40.88	2.37	11	85	114.0	6.61	—	—	—
May 11, 〃	1907.0	45.00	2.35	11	85	122.0	6.39	—	—	—
May 12, 〃	1480 0	35.84	2.42	11	85	94.0	6 35	—	—	—
May 13, 〃	1459.0	34.34	2.35	11	85	80.7	5.53	—	—	—
May 15, 〃	99.0	2.75	2.77	11	85	7.0	7.07	—	—	—
June 23, 〃	1936.0	51.88	2.67	11	85	107.2	5.53	—	108700	6011.1
June 24, 〃	1807.0	61.11	3.38	11	85	109.6	6.06	—	97000	5878.2
June 25, 〃	1770.0	68.80	3.88	11	85	99.6	5.62	—	108000	6069.6
Sept. 20, 〃	1679.0	50.40	3.00	11	85	112.0	6.67	0.30	119500	7960.6
Sept. 21, 〃	3307.5	99.20	2.99	11 11	85 100	110.0 106.0	6.53	— —	130100 120900	8201.6
Oct. 13, 〃	3121.0	79.80	2.55	11	85	196.0	6.28	0.46	109000	6845.2
Oct. 14, 〃	1630.0	45.90	2.81	11	85	91.0	5.58	0.66	125000	6975.0
Oct. 19, 〃	3309.0	89.00	2.65	11	85	224.0	6.76	0.40	98000	6624.8
Oct. 31, 〃	2140.0	61.60	2.87	11	85	159.0	7.42	0.32	99300	7368.0

Table II A

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/Liver %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Acid value	Vitamin A unit U.S.P.U.	Total vittamin A quantity per gr. of liver G.U.S.P.U.
Oct. 1, 1949	Swordfish	145.7	2.91	2.00	11	85	11.6	7.96	——	119400	9432.6
〃 〃	Spearfish	29.0	0.75	2.50	11	85	0.6	2.06	——	171100	3422.0
Oct. 13, 1949	〃	164.0	7.00	4.26	11	85	4.3 (0.9)	2.62 (0.54)	——	125000	3375.0 (2781.3)
(Pick up oil of addition. Codfish liver oil Vitamin A unit 23930 U.S.P.U., 3.4 kg.)											
June 24, 1949	Rockfish	992.0	20.83	2.10	11	85	136.0	13.70	——	100000	13700.0
June 4, 1950	〃	533.0	15.51	2.90	11	85	44.0	9.25	1.30	120600	9949.5

Table II B

Date	Species of fish and liver quantity kg.	Total liver quantity kg.	NaOH quantity of addition kg.	NaOH/Liver %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Acid value	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.
June 24, 1949	Rockfish 151, Tuna 249, Swordfish 40,	535.0	11.23	2.09	11	85	45.0	8.41	——	130000	10933.0
Oct. 1, 1949	Middle tuna 67.1, Small tuna 274,	341.1	6.70	1.96	11	85	2.6	0.76	——	186500	1417.4
Oct. 5, 1949	Flounder 95, Swordfish 19,	114.0	5.00	4.38	11	85	10.0	8.77	1.68	117900	10257.3
Oct. 18, 1949	Rockfish 153, Middle tuna 50.8, Flounder 22.5, Big-eyedtuna 78.1, Spearfish 1323.1,	1489.8	50.00	3.35	11	85	96.9 (43.7)	6.50 (2.93)	——	120200	7813.0 (6723.5)
(Pick up oil of addition. Codfish liver oil vitamin A unit 23930 U.S.P.U., 44.7kg. and Spearfish liver No.2 oil vitamin A unit 66000 U.S.P.U., 8.5kg.)											
July 10, 1950	Flounder 96, Tuna 27,	123.0	4.80	3.90	11	85	8.0	6.42	——	107000	6869.4
Sept. 22, 1950	Flounder 782, Rockfish 112, Middle tuna 32,	926.0	49.00	5.29	11	85	69.0	7.45	——	127600	9506.2
Oct. 12, 1950	Flounder 738, Swordfish 128, Rockfish 198, Tuna 215,	1174.0	26.50	2.25	11	85	103.0	8.77	0.28	107500	9427.7
Oct. 20, 1950	Flounder 540, Rockfish 111,	651.0	17.60	2.70	11	85	53.0	8.14	0.30	96600	7863.2

Table II C

Date	Species of fish	Acid value	Vitamin A unit U.S.P.U.	Extinction ratio E 300/328
July 2, 1950	Rockfish, Swordfish, Middle tuna, Small tuna,	0.36	202000	——
July 3, 〃	Flounder, Rockfish,	0.44	100000	——
〃 〃	Flounder, tuna,	0.52	107000	——
July 4, 〃	Young tuna	0.41	70300	——
Sept. 10, 〃	Tuna	0.33	221000	65.7
〃 〃	Swordfish	0.40	423600	63.6
〃 〃	Flounder	0.30	132700	62.6
〃 〃	Flounder, Swordfish,	0.32	228000	63.6
〃 〃	Tuna, Swordfish,	0.36	220100	63.6

acid value.

II. Livers of Different Kinds of Fish.

METHOD OF EXTRACTION OF OIL:-

The same as described in I. Since high vitamin A content livers of fish other than flounder are generally hard in quality, they are again finely divided with a micronizer after having been finely chopped. Livers that are likely to have a lesser quantity of liver oil are treted with pick-up oil; the quantity of it has to be used in accordance with the amount of the original raw material to avoid lowering the quantity of vitamin A unit the resultant oil. For cod liver oil and No. 2 oil having a vitamin A units of 20,000 to 30,000 U.S.P.U. it is good to use about 3% of this transfer oil. It is added during stirring after complete dissolution of solid matters. Of course the stirring time must be somewhat prolonged in this case. When the extraction is performed with mixture of livers of different kinds of fish, each kind of liver is chopped in separate tanks and then mixed. Method of dissolution of the mixture is the same as described above.

RESULTS:-

In Table II A shows the oil extraction results with fish livers of different high vitamin A content fish except flounder and B that of mixture of livers of different kinds of fishes. While C shows only their acid values, vitamin A unit and extinction ratio for lacking sufficient livers for weighing purposes.

III. Summary

(1) At pH 11 to 12, though the amount of NaOH used for dissolution is somewhat dependent upon the freshness of raw materials used and the amount of water used in dissolution, it is generally about 2.5% of the weight of the law materials.

(2) In industrial practice in factories, vitamin A unit will be higher while the oil quantity is less when NaOH used is more than that used generally; the contrary is true when less NaOH is used.

(3) In case of flounder, the total vitamin A quantity per gr. of internal organs is highest in December and January. Within the same period, its value is nearly the same without regard to the amount of NaOH used in dissolution of the material.

(4) In the extraction of oil from mixed raw materials, rather a good results were obtained.

IV. Literature

1) K. Murata and M. Suzuki (1951): Bull. Faculty of Fisheries, Hokkaido University, 2, 4, pp. 262-265

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