TABLE III

Characteristic Rendering Processes

Process		Product Yield 1. Tallow 2. Protein	Quality 1. Tallow 2. Protein	Process Flexibility		Waste Volume Cleanliness Nuisances	Process Costs		Simplicity and Special Features
				Raw Material	Variable Load		1. Labor 2. Energy	3. Maintenance 4. Investment	
Wet rendering		1. Poor 2. Poor	1. Good 2. Fair	Flexible	Versatile	Waste high not contained	1. Fair Steam high	3. High 4. High	Complex Low efficiency
Dry Rendering	Hydraulic press	1. Poor 2. Good	Good	Flexible	Versatile	Waste low not contained	1. Fair 2. Low	3. Fair 4. Low	Simple
	Expeller	1. Fair 2. Good	Good	Fairly Flexible	Versatile	Waste low not contained	1. Good Power high	3. Fair 4. Low	Simple
	Solvent extraction	Good	Good	Flexible	Needs high capacity Versatile	Well contained and clean waste low	1. Good Steam high Solvent loss	3. High 4. High	Complex Solvent hazard
Circulating rendering		Same as dry rendering	Good	Not equal dry rendering	Versatile	Clean but not contained	1. Good 2. Fair	3. Fair to good 4. High	Complex
Impulse rendering		Lower than dry rendering	1. Very good Bone very good	Best suited to bone	Lacks some versatility	Waste high not contained	1. Good 2. High	3. High 4. High	Very complex Large water usage
Kingan continuous process		1. Fair 2. Protein not recovered	1. Very good 2. Poor if recovered	Fats only; not bone or meat	Versatile	Waste high well contained	1. Good 2. High for protein recovery	High if protein is recovered	Complex Intended for edibles
Azeotropic rendering		Good	Good	Limited to fine grinding	Versatile	Waste low well contained and clean	1. Good Steam high Solvent loss	3. High 4. High	Complex Solvent hazard
Melter—Steam tube dryer		Same as dry rendering	1. Fair to good 2. Good	Flexible	Needs high capacity Versatile	Waste low very poorly contained	1. Good 2. Fair	3. Fair 4. Fair	Complex Semi-continuous
Enzyme rendering		Inherently lower than dehydration	Determined by process control	Limited to fine grinding	Versatile	Can be clean and contained	1. Good 2. High enzyme cost	High-added step retains drying to get products	Complex

the greater care and control required, and the added processing step with its attendant cost have apparently stopped any further work in this direction. The method shows a process energy loss rather than gain because of the fine grinding required and the fact that the products still have to be dehydrated and the fat and protein separated.

The foregoing descriptions do not conclude the list of rendering processes available for the processor of animal fat raw materials, but they cover the basic types. Some of the others are the Laab Pressure System, the Titan Expulsion System developed in Denmark, and the Pavia Heated Roller process, which was patented in March of this year. These others are substantially modifications of the unit operations involved in the processes described or are based on similar principles.

Table III is an attempt to present in abbreviated form the principal features of the processes discussed as they relate to the seven factors described earlier as criteria for rendering process evaluation. Their very briefness makes difference of opinion about their relative evaluation probable. No attempt to determine the best or better of the processes is intended. Such an evaluation must be left up to each individual processor to determine for his own needs. This follows because such a selection must weigh the factors of raw material to be handled, utilities available, specific or special purpose intended, and local economic factors and personal opinion factors on items subject to such judgment. Table III merely is a summation of such information as was available or seemed inherent or apparent to the processes.

Application of the fundamental and natural principles of animal fat recovery which have been outlined should serve to guide the processor in the process selection best suited for his particular conditions. The observance of physico-chemical factors occurring during the operation and intelligent care in the control and use of these variables will chart the way to maximum product value at lowest unit cost. This is the pattern not only for survival but for success.

Marine Oils. Production, General Chemistry, and Utilization[1]

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THE fish oils of industrial importance in the United States come from three different varieties of fish, pilchard, herring, and menhaden. All are frequently called sardines.

Pilchard were formerly found in the Pacific Ocean all along the American coast, but in recent years the catch has been decreasing drastically, first in the northern waters, and now in the southern waters as well. The reasons for this are not known, but obviously the effect on the marine oil industry is very serious. The annual catch has dropped from a maximum of 1,500,000,000 lbs. to about 7,770,000 lbs. in 1952.

Pilchard spawn in the open sea as far as 300 miles

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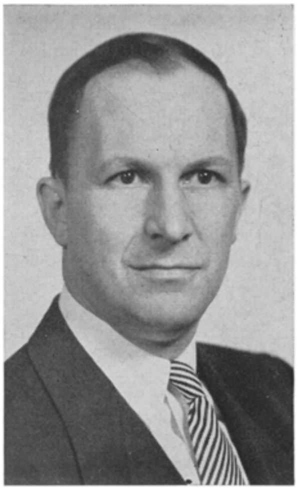
[1] Technical Paper No. 131 from the Archer-Daniels-Midland Company.



J. D. Hetchler

off-shore, and the eggs hatch in about three days. The fish feed on minute sea organisms called plankton. When they are 3 to 5 in. long, they gather in schools and migrate toward shore. When full-grown, they are about 7 in. long and leave the shore waters for the open sea again.

Sea herring are somewhat like the pilchard and belong to the same family. They are found along the Pacific coast from California to Alaska and also along the North Atlantic coast, but the most important catches are off the shores of British Columbia. They spawn from winter in the south to late June in the north, laying their eggs on kelp and other marine vegetation. The young are hatched in 10 to 20 days, depending on the temperature, and most of the fish mature in the third, fourth, or fifth year. When mature, they spawn each year.

Menhaden consist of several species of related fish and are found all along the Atlantic and Gulf coasts. Since the decline of the pilchard catch, beginning about 1946, the menhaden have become the most important sources of fish oil for industrial uses. The catch in 1952 was about 1,300,000,000 lbs.

Menhaden are migratory and travel in large schools. During the first year they attain a length of 5 to 6 in. and at full growth, reached in three to four years, they attain a length of 8 to 10 in.

Whale oils are important marine oils also. Whales are not fish; they are mammals which breathe air, suckle their young, and have other animal-like characterisctics. Whales are the largest mammals known, some attain a length of 100 ft. and a weight of 100 tons. Some types of whales feed on plankton and other small plants and creatures of the sea, but the

TABLE I

Fish Oil and Scrap Production

Production of Fish Oil in Gallons

	Menhaden Oil	Herring Oil	Pilchard Oil	Tuna and Mackerel Oil	Whale and Sperm Oil
1943	5,734,668	1,727,441	13,947,295	219,044	37,964
1944	6,067,111	2,389,287	18,098,982	317,236	7,185
1945	8,335,094	2,663,546	11,852,994	304,143	....
1946	9,758,648	3,532,454	4,866,567	359,437	....
1947	8,473,371	3,875,024	2,103,965	748,017	66,374
1948	8,763,939	3,643,537	2,328,572	660,515	120,089
1949	8,293,911	723,350	6,123,140	597,935	74,950
1950	10,209,958	3,309,457	6,188,607	884,434	....
1951	12,537,115	1,512,814	1,942,586	712,620	68,500
1952[a]	12,888,646	1,081,963	20,881	744,827	....
1953[b]	18,024,061	615,832	11,378	770,191	....

Values of Fish Oil Production in Dollars

	Menhaden Oil	Herring Oil	Pilchard Oil	Tuna and Mackerel Oil	Whale and Sperm Oil
1943	3,892,142	1,129,446	9,301,593	131,906	30,405
1944	3,725,498	1,603,078	11,722,950	177,774	5,135
1945	5,656,550	1,785,040	7,926,147	173,452	....
1946	9,033,032	4,292,776	6,843,376	395,475	....
1947	11,425,497	4,144,643	2,677,453	958,998	70,007
1948	10,132,179	4,004,250	2,457,858	622,110	130,217
1949	3,407,510	394,297	2,872,532	265,736	52,475
1950	5,866,554	2,366,005	4,693,550	553,231	....
1951	9,771,154	1,205,384	1,545,937	525,552	50,200
1952	5,785,395	517,384	10,815	367,585	....

Production of Fish Scrap in Tons

	Menhaden Dried Scrap and Meal	Menhaden Acidulated Scrap	Herring Meal	Pilchard Meal	Tuna and Mackerel Meal	Other Meal, Dried and Green Scrap
1943	66,357	1,555	9,170	75,611	7,766	29,944
1944	69,170	2,922	14,212	86,196	9,648	30,999
1945	77,451	1,557	14,344	60,860	10,273	36,190
1946	94,622	2,022	19,505	36,899	13,584	32,989
1947	98,602	632	18,454	16,715	19,761	32,276
1948	104,058	........[c]	17,686	19,076	21,305	37,419
1949	113,393	........[c]	5,298	39,278	19,139	60,072
1950	103,365	........[c]	17,797	43,009	25,377	50,406
1951	115,464	........[c]	9,631	17,225	23,147	44,298
1952[a]	144,025	........[c]	9,864	390	21,951	45,173
1953[b]	169,043	........[c]	5,140	152	24,146	20,790

Values of Fish Meal and Scrap Production in Dollars

	Menhaden Dried Scrap and Meal	Menhaden Acidulated Scrap	Herring Meal	Pilchard Meal	Tuna and Mackerel Meal	Other Meal, Dried and Green Scrap
1943	4,766,672	58,821	690,280	5,775,932	505,199	1,832,248
1944	4,913,224	11,104	1,044,861	6,582,600	644,458	1,946,775
1945	5,483,377	62,200	1,120,042	4,643,694	705,976	2,390,049
1946	8,605,118	78,475	2,248,942	5,233,075	1,743,189	2,530,624
1947	10,833,852	26,863	2,649,474	2,556,038	2,998,321	3,265,803
1948	11,560,914	........[c]	2,065,042	2,614,616	2,757,778	4,090,384
1949	17,813,339	........[c]	973,445	6,219,717	3,073,742	7,571,899
1950	12,864,751	........[c]	2,138,776	5,269,696	3,268,594	5,711,918
1951	13,879,523	........[c]	1,370,083	2,266,968	3,021,720	4,835,603
1952	17,847,361	........[c]	1,314,361	51,741	2,892,874	5,055,317

[a] Revised.
[b] Preliminary.
[c] Acidulated scrap included with dry scrap and meal since 1948.
Source: U. S. Fish Wildlife Service.

TABLE II

Weight Percentage Distribution of Constituent Fatty Acids in Fish Oils

	Unsap. Matter %	Saturated			Unsaturated [a]					
		C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
Family Clupeidae										
Pilchard, Sardinops Caerulea, (British Columbia)						Pisces (Teleostomi)				
body oil (a)	1.0	5.1	14.4	3.2	0.1(2.0)	11.7(2.0)	17.7(3.3)	17.9(4.1)	13.8(8.5)	15.2(10.9)
Herring, Clupea harengus, (Iceland), body oil (b)	1.3	7.0	11.7	0.8	1.2(2.0)	11.8(2.4)	19.6(3.5)	25.9(5.2)	21.6(4.3)	0.1(3.8)
(Irish sea), visceral oil (i)	0.75	5.8	15.7	2.0	1.4(2.0)	10.5(2.5)	31.8(2.6)	22.4(7.1)	9.3(10.5)	……..
Menhaden, Brevoortia tyrannus, (North Atlantic) body oil (c)	0.6-1.6	6.0	16.0	1.5	….	15.5(2)	30.0(4)	19.0(10)	12.0(10)	……..
Family Salmonidae										
Salmon, Salmo solar (Scotland)										
flesh (d)	0.9	5.0	11.3	1.1	0.5	9.1(2.0)	25.7(2.7)	26.5(4.7)	20.8(6.4)	……..
mesentery (e)	….	3.6	14.4	2.3	0.1	7.1(2.4)	25.3(2.9)	28.4(4.6)	18.8(6.1)	……..
liver (e)	….	2.7	10.9	1.6	0.7	12.3(2.0)	32.8(2.9)	25.8(5.7)	13.2(7.8)	……..
immature ova (f)	8.8	3.1	16.0	0.5	0.1	12.6(2.0)	23.7(4.0)	27.2(8.0)	16.8(10.4)	……..
ripe eggs (f)	7.2	2.3	12.9	2.2		9.6(2.0)	34.8(2.7)	23.2(7.6)	15.0(11.2)	
Family Pleuronectidae										
Halibut, Hippoglossus hippoglossus, (North Sea) flesh (g)	1.3	4.0	14.8	0.7	trace	6.5(2.6)	23.8(3.0)	26.9(5.2)	23.3(6.5)	……..
Turbot, Rhombus maximus, (North Sea), flesh (e)	2.1	3.4	15.1	2.1	0.3	8.9(2.6)	21.7(3.4)	26.6(6.0)	21.9(7.7)	……..
Family Scombridae										
Bluefin tuna, (tunny), Thymnus thymnus, (North Sea),										
flesh (g)	0.7	4.2	18.6	3.5	….	6.2(2.7)	26.0(3.2)	23.5(5.5)	18.0(6.8)	……..
liver (g)	….	0	17.9	8.9	….	3.4(2.5)	23.5(2.8)	28.2(5.5)	18.1(7.4)	……..
pyloric caeca (g)	….	3.4	18.4	2.7	….	6.3(2.7)	21.9(3.7)	25.5(5.5)	21.8(6.2)	……..
spleen (g)	….	0	21.0	7.0	….	7.0(>2.0)	27.0(3.1)	22.0(5.4)	16.0(?)	……..
heart (g)	….	0	25.0	3.0	….	4.0(>2.0)	26.0(3.4)	25.0(5.4)	17.0(7.5)	……..
Family Acipenseridae										
Sturgeon, Acipenser sturio, (Atlantic),										
peritoneum (h)	….	7.1	14.0	0.8	0.6	23.8(2.0)	35.8(2.9)	12.1(7.4)	5.8(8.6)	……..
liver (h)	….	3.0	19.2	0	0	19.5(2.0)	39.6(2.7)	11.8(7.1)	6.9(10.0)	……..

[a] Numbers in brackets are the unsaturations in terms of —H. References: (a) Brocklesby and Harding (1938); (b) Bjarnson and Meara (1944); (c) Armstrong and Allan (1924); (d) Lovern (1934a); (e) Lovern (1937); (f) Lovern (1936b); (h) Lovern (1932a); (i) Hilditch and Pathak (1949).

TABLE III

Saturated Fatty Acids Found in Marine Oils

Fatty Acid		Formula	Molecular Weight	Melting point (°C.)	Boiling point (°C. at 760 mm.)	Solubilities (gm./100 gm. Solvent at 10°C.)		
Common Name	Geneva System					Water	Ethanol (95%)	Acetone
Iso-valeric	3-methyl-butanoic	$C_5H_{10}O_2$	102.1	—37.6(—51)	176.6		∞	∞
Caprylic	n-octanoic	$C_8H_{16}O_2$	144.2	16.3	239.7	0.056	1035.00	975.00
Capric	n-decanoic	$C_{10}H_{20}O_2$	172.3	31.3	270.0	0.012	93.5	112.00
Lauric	n-dodecanoic	$C_{12}H_{24}O_2$	200.3	44.2	298.9	0.0046	34.0	21.9
Myristic	n-tetradecanoic	$C_{14}H_{28}O_2$	228.4	52.3	326.2	0.0017	7.64	6.50
Palmitic	n-hexadecanoic	$C_{16}H_{32}O_2$	256.4	63.1	351.5	0.0059	2.10	1.94
Stearic	n-octadecanoic	$C_{18}H_{36}O_2$	284.5	69.6	376.1	0.0023	0.65	0.80
Arachidic	n-eicosanoic	$C_{20}H_{40}O_2$	312.5	75.4				
Behenic	n-docosanoic	$C_{22}H_{44}O_2$	340.6	80.0				
Lignoceric	n-tetracosanoic	$C_{24}H_{48}O_2$	368.6	84.2				

TABLE IV

Unsaturated Fatty Acids Found in Marine Oils

Acid		Formula	No. of double bonds	Position of double bonds	Iodine Value	Molecular weight	Boiling point (°C.)
Common Name	Geneva System						
Caproleic	Decenoic	$C_{10}H_{18}O_2$	1	9	149.1	170.1	142/15 mm.
Lauroleic	Dodecenoic	$C_{12}H_{22}O_{11}$	1	9	128.0	198.2	
Myristoleic	Tetradecenoic	$C_{14}H_{26}O_2$	1	9	112.2	226.2	
	Tetradecenoic	$C_{14}H_{26}O_2$	1	5	112.2	226.2	
Palmitoleic	Hexadecenoic	$C_{16}H_{30}O_2$	1	9	99.8	254.2	
Hiragonic	Hexadecatrienoic	$C_{16}H_{26}O_2$	3	6, 10, 14	304.2	250.2	180-190/15 mm.
Oleic	Octadecenoic	$C_{18}H_{34}O_2$	1	9	89.9	282.2	286/100 mm. 153/0.1 mm.
Vaccenic	Octadecenoic	$C_{18}H_{34}O_2$	1	11	89.9	282.2	
	Octadecadienoic	$C_{18}H_{32}O_2$	2		181.1	280.2	
	Octadecatrienoic	$C_{18}H_{30}O_2$	3		273.7	278.2	
Moroctic	Octadecatetraenoic	$C_{18}H_{28}O_2$	4	4, 8, 12, 15	367.5	276.2	
Gadoleic	Eicosenoic	$C_{20}H_{38}O_2$	1	9	81.7	310.3	220/6 mm.
Gondoic	Eicosenoic	$C_{20}H_{38}O_2$	1	11	81.7	310.3	
	Eicosadienoic	$C_{20}H_{36}O_2$	2	11, 14	164.6	308.3	
	Eicosatrienoic	$C_{20}H_{34}O_2$	3	8, 11, 14	248.6	306.3	
	Eicosatetraenoic	$C_{20}H_{32}O_2$	4	4, 8, 12, 16	333.7	304.2	
	Eicosatetraenoic	$C_{20}H_{32}O_2$	4	6, 10, 14, 18	333.7	304.2	
	Eicosapentaenoic	$C_{20}H_{30}O_2$	5	4, 8, 12, 15, 18	419.9	302.2	
Cetoleic	Docosenoic	$C_{22}H_{42}O_2$	1	11	75.0	338.3	
	Docosadienoic	$C_{22}H_{40}O_2$	2	11, 14	150.7	336.3	
	Docosatrienoic	$C_{22}H_{38}O_2$	3	8, 11, 14	227.8	334.3	
Clupanodonic	Docosapentaenoic	$C_{22}H_{34}O_2$	5	4, 8, 12, 15, 19	384.2	330.3	236/5 mm.
	Docosahexaenoic	$C_{22}H_{32}O_2$	6		463.8	328.3	
Selacholeic	Tetracosenoic	$C_{24}H_{46}O_2$	1	15	69.2	366.4	
Scoliodonic	Tetracosapentaenoic	$C_{24}H_{38}O_2$	5		354.2	358.3	
Nisinic	Tetracosahexaenoic	$C_{24}H_{36}O_2$	6	4, 8, 12, 15, 18, 21	427.5	356.3	
Bonitonic	Tetracosaheptaenoic	$C_{24}H_{34}O_2$	7		501.4	354.3	
Shibic	Hexacosapentaenoic	$C_{26}H_{42}O_2$	5		328.5	386.3	
Thynnic	Hexacosahexaenoic	$C_{26}H_{40}O_2$	6		396.3	384.3	

TABLE V

Seasonal Changes in Atlantic Herring Oil

Month caught	% Oil	Iodine value of oil	Composition of fatty acids (Wt. %)							
			Saturated			Unsaturated				
			C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
April	8.2	115.5	8.0	15.7	0.2	....	4.6 (2.6)	22.2 (2.9)	22.0 (3.9)	27.3 (4.2)
June	10.7	144.2	7.3	16.7	trace	0.6	7.5 (2.7)	21.1 (3.3)	27.3 (4.8)	19.5 (5.7)
June	15.7	154.3	7.5	12.8	0.1	0.3	7.0 (3.0)	21.1 (4.8)	30.0 (5.2)	21.2 (4.8)
July	20.7	152.5	8.3	12.1	0.3	0.5	6.4 (3.4)	21.0 (4.5)	28.3 (5.5)	23.1 (4.6)
October	18.8	138.6	7.3	13.0	trace	0.8	4.9 (2.7)	20.7 (4.2)	30.1 (4.6)	23.1 (4.3)
October	12.0	129.9	6.6	13.7	0.5	0.2	4.9 (2.8)	16.3 (3.6)	28.7 (4.4)	29.1 (4.1)
April (immature fish)	4.6	147.9	5.8	12.4	0.6	....	4.7 (3.0)	17.8 (3.9)	31.1 (4.3)	27.6 (4.8)

sperm whales have teeth and powerful jaws and feed largely on squid. These whales are fighters and have been known to attack fishing boats when aroused.

Several other marine oils are produced in relatively small amounts and are of minor industrial importance. Among these are salmon oil, tuna oil, cod oil, and mackerel oil. Some of the oils are produced as by-products of the fish canning industry. And, of course, some marine oils are valued for food or medicinal uses, particularly the liver oils for their vitamin content.

Production

Most fish oils are produced by pressing the whole fish after a preliminary cooking or steaming. The crude oil is usually settled and filtered before further processing. The water and other liquids separated from the oil are known as "stick water." This is usually concentrated to a thick syrup-like consistency and used as a feed supplement. The solids, known as fish scrap or fish oil meal, are also used in animal feeds, particularly for hogs and poultry. As a matter of fact, the demand for feed is often the factor which controls the production of fish oil.

Whale oils are produced by a rendering process, usually on board the whaling vessel, which is really a floating processing plant. The killer boats tow the dead bodies to the factory ship, where they are pulled aboard through a special chute by means of a power-driven winch. The blubber is cut by large knives into pieces suitable for processing. The most modern ships are equipped to utilize all parts of the whale, including the meal, the concentrated stick water, and even the ground-up bones. Older ships however discard large quantities of valuable by-products, frequently as much as 300 tons a day. Sperm whale oil is usually kept separate from the other marine oils because it is considered unfit for food and is chemically different, containing varying amounts of esters of fatty alcohols and fatty acids together with esters of fatty acids and glycerol.

The annual production of several of the most important marine oils and their by-products for recent years is summarized in Table I (3). The production of oil is shown in gallons and the production of meal in tons; dollar values are also reported.

Characteristics

As mentioned before, most of the marine oils consist of mixed triglycerides of long chain fatty acids although sperm oil is different in that it is composed largely of esters of fatty acids and higher fatty alcohols. The fish oils however are definitely in a class by themselves for they contain substantial percentages of fatty acids of longer chain length and greater degree of unsaturation than is common in the oils of terrestrial animals or plants. Fatty acids with as many as 26 carbon atoms and six double bonds have been identified although chain lengths of 20 or 22 carbon atoms and four or five double bonds are more abundant. Typical fatty acid distribution of several of the common fish oils are indicated in Table II (1) and some of the fatty acid characteristics are listed in Tables III (1) and IV (1).

It should be emphasized that reported characteristics of marine oils indicate broad ranges of properties. This is due to the fact that fish of the same family type caught in different geographical locations or at different seasons of the year may produce oil of quite different properties. This fact is illustrated by the data of Table V (1).

Allowing for these normal variations, some of the most important chemical and physical properties of the three most important commercial fish oils are cited in Table VI (1), and similar data for several different types of whale oil are cited in Table VII (1).

Oil Processing and Uses

As indicated before, crude fish oil is usually settled and filtered before further processing. If the settling period is of short duration, the filtered oil will soon become cloudy and in time considerable additional solid material will separate. These solids, the so-called "stearines," contain the more saturated triglycerides. Their removal, of course, increases the value of the liquid oil for drying oil uses. A large proportion of the stearines can be removed simply by prolonged settling, a process known as "winterizing" or "racking." The separation can be accomplished much more rapidly by chilling to crystallize the solid fats, which

TABLE VI

Range of, the Most Significant Characteristics of the Common Fish Oils

	Menhaden	Herring	Pilchard
Solidifying point	....	....	28–34°C.
Specific gravity at 60°F.	....	.9228–.9265	.9290–.9370
Free fatty acid per cent as oleic	1.0–15.0	0.2–5.0	0.1–13.0
Iodine No.	140–180	118–160	170–200
Saponification No.	189–193	182–189	188–199
Unsaponifiable matter	0.6–1.6	0.5–1.7	1.0

TABLE VII

Characteristics of Oils from Various Species of Whales

Species	Sp. gr. at 15°C.	Iodine value	Sap. value	Unsap mat. (%)	Unsat. fatty acid (%)	Saturated fatty acid (%)
Sei	0.9196–0.9229	136.3–161.5	186.9–193.1	0.56– 1.54	73.6–81.5	18.5–26.4
Fin	0.9137–0.9236	107.4–155.8	190.3–196.5	0.32– 1.98	25	75
Blue or sulphur-bottom	0.9140–0.9307	112.0–131.0	183.0–198.0	0.7 – 3.5	73.7–86.4	13.6–26.3
Humpback	0.9234–0.9154	120.3–159.4	183.5–190.1	0.31– 1.64	87	13
Gray (Calif.)	0.9290	147.0–167.0	191.0–193.0	1.6	83.8–90	10.0–14.2
Bottlenose	0.876 –0.885	79.7– 88.7	121.5–135.9	35.0 –43.2	....	....
Sperm	0.844 –0.881	70.4– 96.4	120.0–150.3	17.5 –44.0	81 –90	10 –19

are then removed by filtration. The "pressed oils" can be made to tolerate various cold tests by varying the temperature to which they are chilled and the time they are held at that temperature prior to filtration.

Stearines can also be removed by selective extraction with solvents. In this way fish oils of 220 iodine value are being produced commercially. The selective extraction process also removes color bodies and some of the odor.

It is possible to produce fish oil fatty acids of very high iodine values by fractional distillation. This is because most of the saturates are of relatively short chain length, and the most highly unsaturated acids are of long chain length; fractional distillation techniques cannot separate saturated from unsaturated acids of the same chain length. Even though fatty acids of as high as 300 iodine value can be prepared by fractional distillation, and glycerol and pentaerythritol esters of 250 iodine value have been offered commercially, the products have not been widely used, principally because of economics.

Pressed oil is frequently alkali-refined to reduce the acid value and bleached to reduce the color; these treatments are not usually needed for solvent-extracted oils.

For use in protective coatings the fish oils are frequently modified in other ways as well. They may be bodied by blowing with air or by heat-treating. The heat-bodied oils may be solvent-extracted to remove the unpolymerized portions, leaving a high viscosity product of excellent drying properties. But probably the most interesting processes are those involving chemical treatments. For example, fish oils may be co-polymerized with other unsaturated monomeric materials, such as styrene or cyclopentadiene. The cyclopentadiene copolymers are commercially important drying oils, and the degree of improvement for paint and varnish use is truly remarkable. Other chemical modifications applied to other drying oils may be applied to fish oils as well. These include the formation of adducts with maleic anhydride or fumaric acid, followed by esterification with glycerol or pentaerythritol, and the formation of alkyds, either by alcoholysis of the tri-glycerides or directly from fish oil fatty acids.

Fish oils are used extensively in paints and varnishes. They usually have an economic advantage over most other drying oils. Crude oils suffer disadvantages due to the high stearine content, odor, and film yellowing and brittleness, but the chemically modified oils are greatly improved and are often employed in quality products. Fish oil-based coatings are recommended particularly for metal surfaces because they have the ability to penetrate rust to the prime metal; they also have unusual resistance to salt water. The drying properties of fish oils also make them useful in linoleum, caulking compounds, printing inks, and oilcloth. Specialty uses include slushing oils, wood preservatives, leather dressing, metal drawing compounds, and lubricating oil additives.

The stearines removed from the unsaturated portions of fish oils are not without value. Indeed large quantities of fish oil and fish oil fatty acids are hydrogenated to reduce the degree of unsaturation, sometimes almost to zero. Hydrogenated fish oils have been used in the edible field for years, particularly by bakeries and restaurants. The current trend however is toward more industrial uses. The unique properties of hydrogenated fish oil and hydrogenated fish oil fatty acids are probably due to the long carbon chains not present in most other natural oils. These properties make these products of particular value in a number of industrial products, such as lubricants, textile chemicals, buffing compounds, and so forth.

The fish oil is usually alkali-refined before hydrogenation. The hydrogenation process is usually carried out under pressure and in the presence of reduced nickel catalyst. Accurate control is maintained so that a range of products of almost any iodine value and melting point is possible. Fatty acids are usually distilled before hydrogenation; their iodine values may be reduced to as low as 3, and products may have titers from 45 to 55°C.

As may be evident from the differences in composition and characteristics, whale oils are usually handled in a different manner from fish oils and are used for different purposes. This is particularly true of sperm oil, which is by far the most important, at least in this country. The composition of sperm oil varies according to the part of the body from which it was obtained. All sperm oil contains an appreciable percentage of esters of fatty alcohols and fatty acids; that from the head of the sperm whale is particularly high in this ester content, about 74%, with only about 26% triglyceride. Consequently sperm head oil should really be considered a liquid wax instead of an oil. As a matter of fact, the winterizing process applied to sperm oil, instead of producing stearines, results in the crystallization of a solid wax known as "spermaceti." This is used extensively in hand lotions, cosmetics, and for various specialized industrial applications. The sperm oil from which the spermaceti has been removed is called "natural winter sperm oil," and if alkali-refined and bleached, it is known as "bleached winter sperm oil."

Sperm oil is an excellent lubricant and is used for the lubrication of fine machinery, such as clocks, drawing instruments, and automatic controls; hydrogenated sperm oil is used for bi-metal lubrication. Sperm oil is ofen modified by treatment with sulfur, chlorine, phosphorous, and other chemicals and is compounded into crank case oils, automatic transmission oils, hydraulic fluids, and cutting oil bases. Sulfonated sperm oil has long been important for leather fat liquors and for textile wetting agents and detergents.

Trends

It seems inevitable that marine oils will be further exploited as raw materials for further chemical modification. They form a unique source of long chain fatty acids and alcohols, and it is quite possible that, by separating the oils from different parts of the fish or animal bodies more carefully, products of greatly increased value will result; certainly this is already true of the liver oils. These marine oil products reacted with various chemicals should form intermediates, such as olefins, amines, nitriles, halogenated compounds, and many others which are not available from other fats and oils or from petroleum. Much research work must be done to accomplish the possibilities that exist in this field.

Additional regulation of the fishing industry may be necessary to prevent the extermination of some important species. These must be accompanied by further studies of marine life to learn how to stem or reverse the migration of some fishes away from the coastal areas of this country. The fishing industry is large and marine oil production is an important phase of it. Continued research is destined to make it even more important in the future.

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Tall Oil

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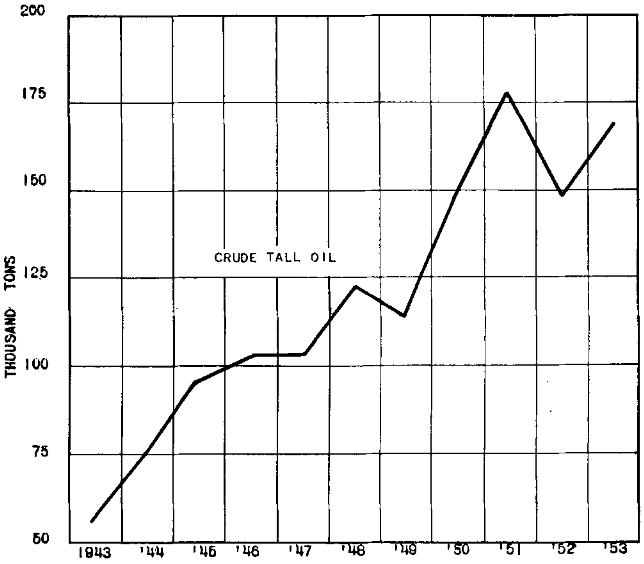
A RELATIVELY new source of inedible fatty acids and of rosin is derived from southern pine. It is tall oil, a mixture of rosin and fatty acids, which is obtained as a by-product in the manufacture of kraft paper by the sulfate process. It is the purpose of this paper to outline the general method used for recovery of tall oil and to review the refining and separation processes which are used in the United States to convert tall oil into more valuable raw materials for the chemical industry. The production of tall oil in America has increased at a rapid rate during the last 10 years, according to figures of the Tall Oil Association (1) shown in Figure 1.

Richard Herrlinger

The fast growth of tall oil production from about 50,000 tons in 1943 to 175,000 tons in 1953 reflects the technological advances achieved during this period by both the producers and the users of tall oil and tall oil products. Processing methods were developed which now allow not only the production of products of higher quality but also the substantially complete separation of tall oil into rosin and fatty acids. The paint and varnish industry, through the use of new polyfunctional alcohols, maleation, and styrenation, has greatly extended the utility of tall oil products in surface coatings. New applications have developed in such fields as detergents and metallic driers.

A major reason for the growth of tall oil production is the economical and stable source of black liquor soap from which tall oil is made. Black liquor soap is derived as a by-product during recovery operations from digester liquors of the sulfate paper process as shown in Figure 2.



PRODUCTION OF CRUDE TALL OIL 1943-53

FIG. 1

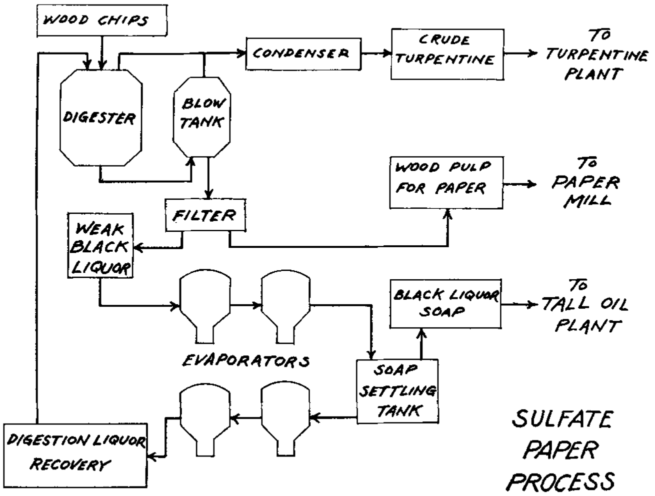


FIG. 2