The quality of fish oil and its potential use in Chemical Industry

Aquarel project Final Seminar
18th September
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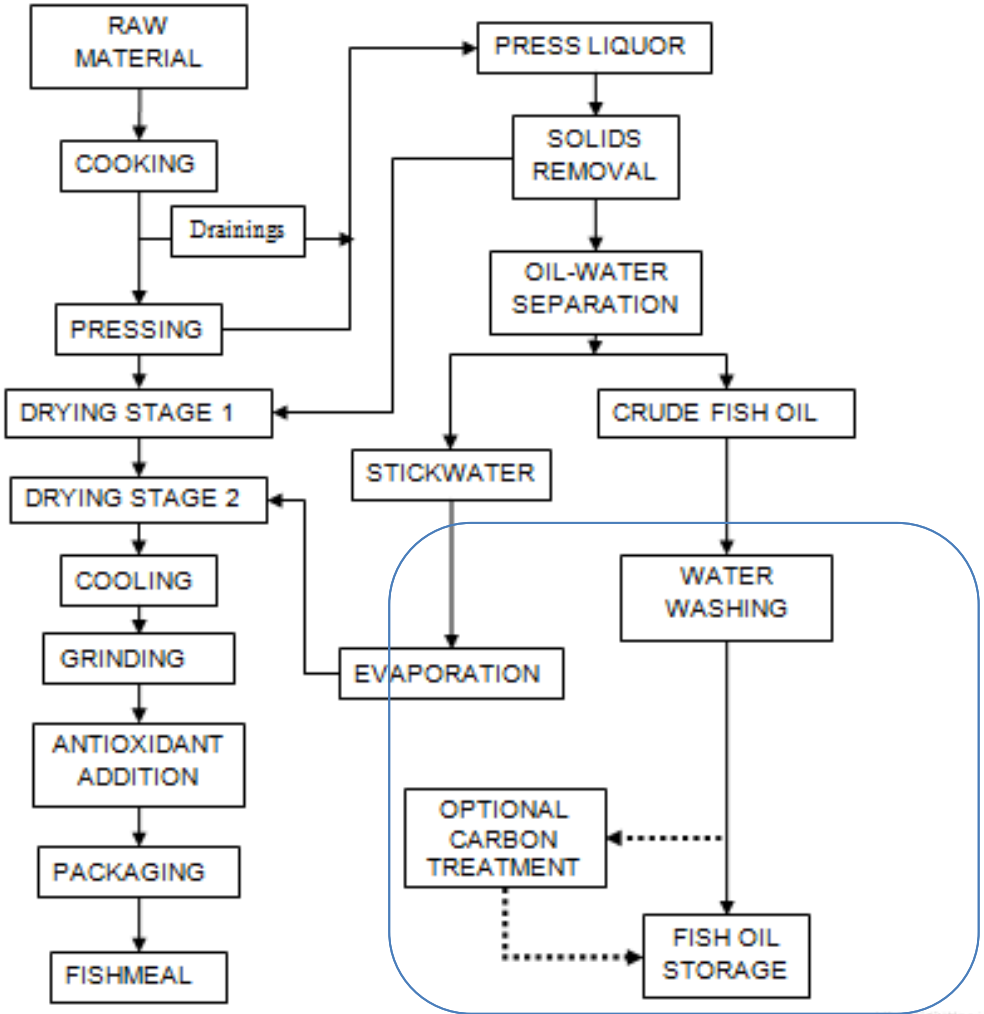
THE PRODUCTION AND PROCESSING OF FISH OILS TO CHEMICAL INDUSTRY

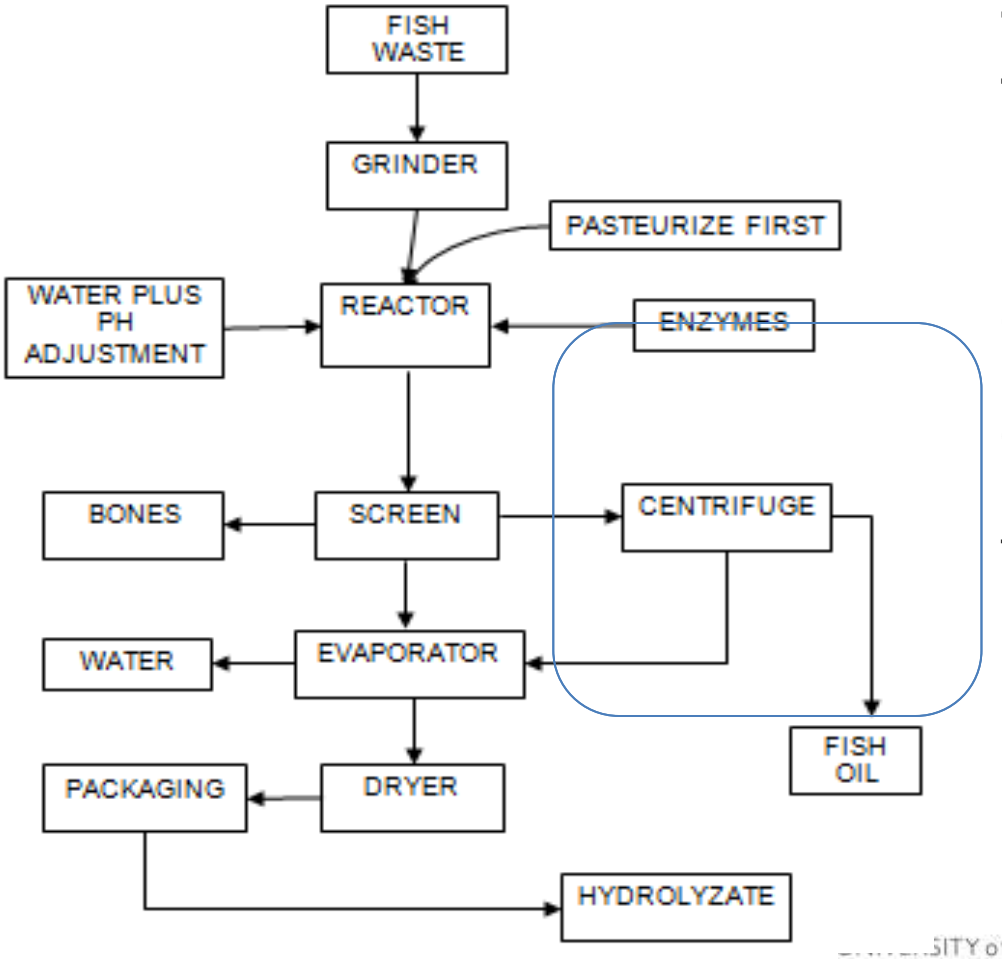
MIKKO AHOKAS

WET REDUCTION



COOKING: Steam cooking ruptures the fat cells,
PRESSING: Mechanically
DECANTER: fine and solids)
OW separator (stickwater)
EVAPORATION from 6 to 40%
DRYING to 10% moisture
GRINDING to reduce particle size
Antioxidant (generally ethoxyquin or some natural)
If animal feed use,
Activate carbon treatment

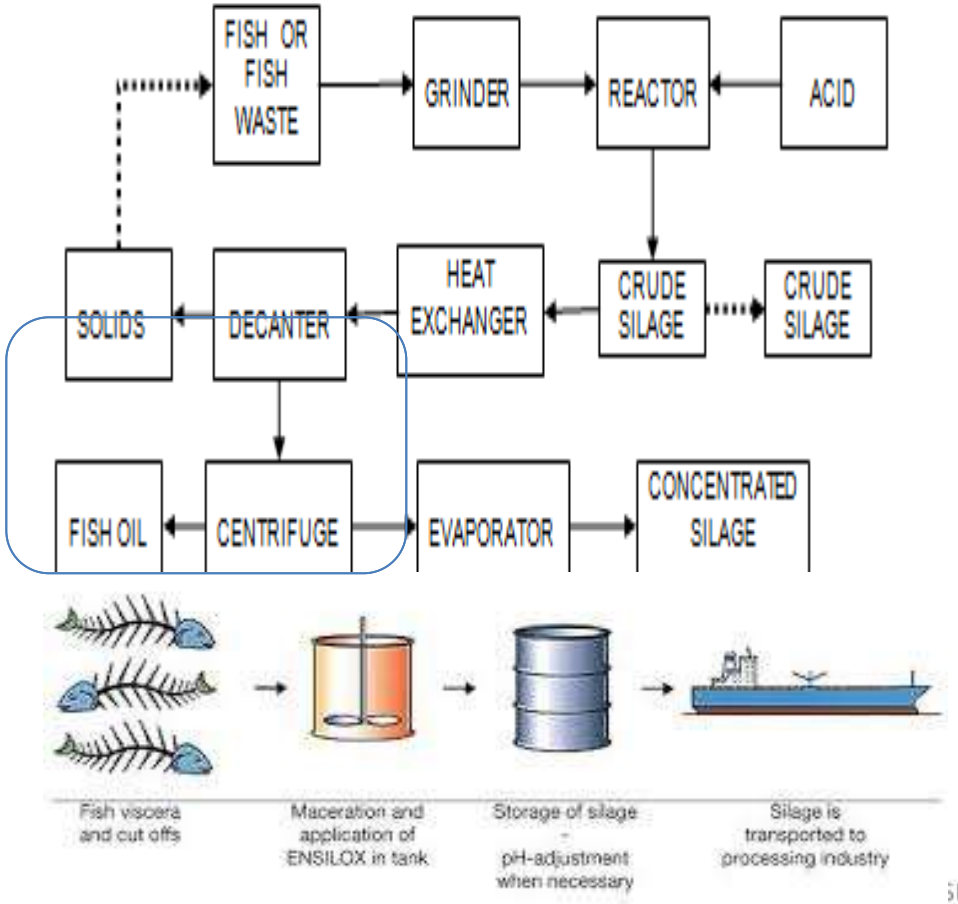
HYDROLYSIS (ENZYMATIC) PROCESS



The enzymes accelerates the breakdown of proteins into smaller units (peptides)

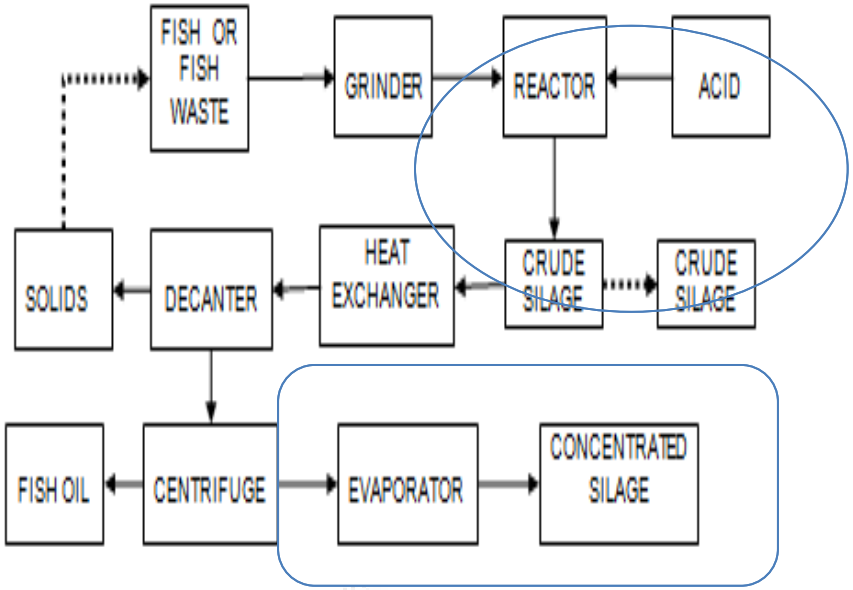
By using some of the newest enzymes available on the market, the process can be developed to recover fish peptides of with specific functionality.

SILAGE PRODUCTION (AUTOLYSIS)



- Fish silage is liquefied fish stabilized against bacterial decomposition by an acid
- Formic, propionic, sulfuric and phosphoric acids have been used. Normally, about 3-4% of acid is added so that the pH remains at or below 4.0.

Autolysis (2 phases)



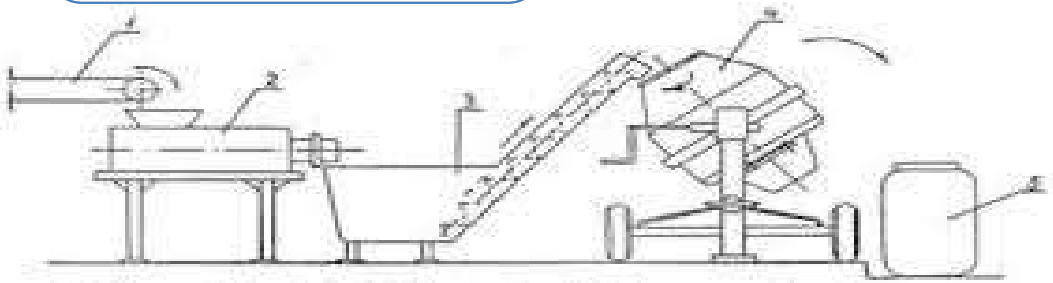
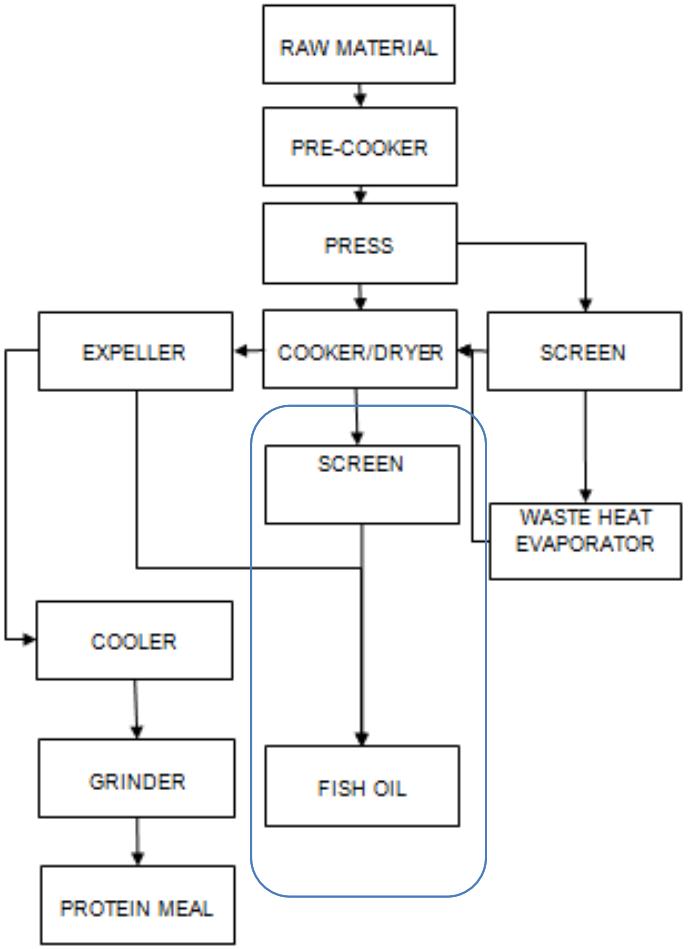


Figure 4.10 Simplified layout of silage production: 1 - feeder, 2 - grinder, 3 - tank with elevator, 4 - mixer, 5 - plastic barrel

Stilage Storing

- The composition of the silage will be very similar to the starting raw material. Fish silage of the correct acidity is stable at room temperature for at least 2 years without decomposition.
- The protein becomes more soluble, and the amount of free fatty acids increases in any fish oil present during storage.
- Silage production offers a solution to the handling of fish waste when the logistics of delivering the waste to a fish reduction plant are not economical.
- Silage can be produced in large or small containers both on the vessel and on shore.
- If the silage is processed quickly to recover the oil, it is possible to make an acceptable fish oil product.

DRY RENDERING

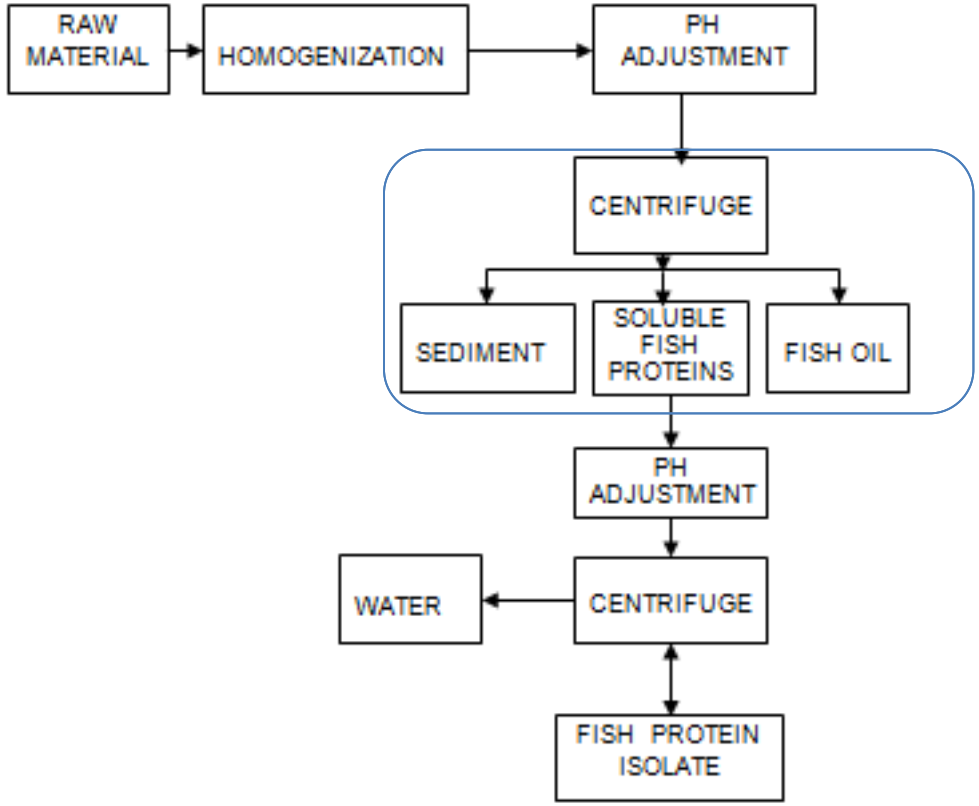


Dry Rendering the oil is extracted from the Dried product while in Wet Rendering a portion of liquid containing the oil is extracted from the raw material.

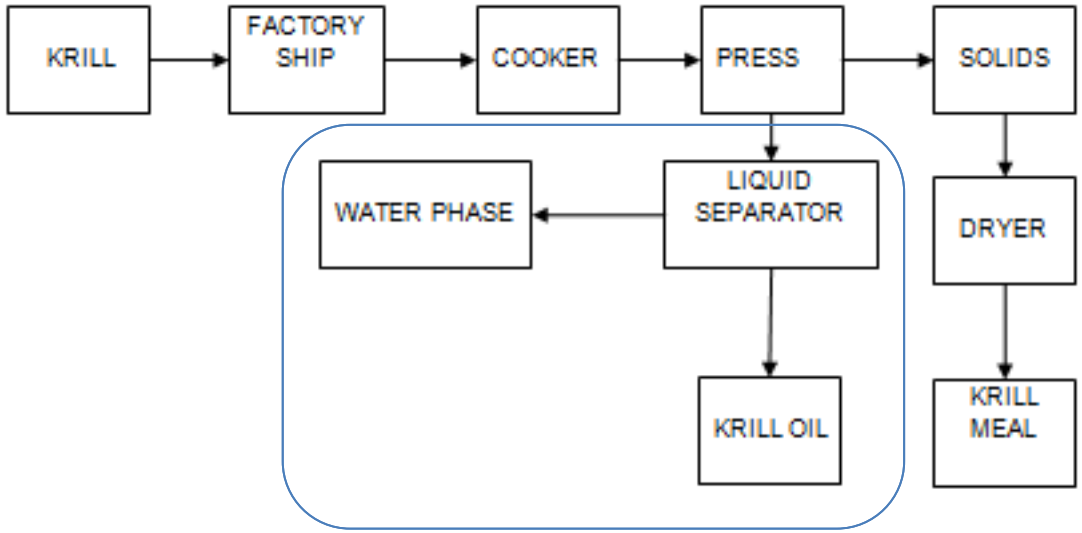
The resultant dry cake is then pressed to remove any oil. Because the water has been removed, the lipid fraction can contain high levels of phospholipids.

The phospholipids normally hydrate in the wet rendering process and are recovered with the water fraction.
Since there is interest in the fish phospholipids, it is possible to produce a PL fraction by hydrating the oil (also called degumming).

ACID-ALKALI AIDED PR(



FAST COOKING (ON THE SHIP)



The Quality of Fish Oil

- All crude oils and fats contain minor amounts of non triglyceride substances.
- Some of these are considered beneficial to the stability of the oil, such as tocopherols and astaxanthin (in salmon and krill oils) which protect the oil from oxidation.

Oil Impurities?

- Th2 impurities are render the oil dark colored, causea foaming problems or smoke. Can beprecipitated when the oil is heated in subsequent processing operations.
- Odors they produce in the fat they reduce stability and shelf life of the foods to which the fats are added. Some impurities are common to all fats regardless of the source or end use:
  - Suspended matter (insoluble impurities).
  - Naturally occurring color bodies.
  - Free fatty acids.
  - Volatile, malodorous compounds dissolved in the fat or oil.

How to purify?

Active Carbon Treatment: Removal of dioxins, furans, and polyaromatic hydrocarbons (PAH).
Gravitation: Insoluble impurities, trace moisture and some phospholipids will precipitate out in the tanks. The combination is known as "foots".
Degummin: Phospholipids, sugars, resins, proteinaceous compounds, trace metals and other materials.
Alkali Refining: Free fatty acids, pigments, phospholipids, oil insoluble material, water soluble material, trace metals
Water Washing/ Silica Treatment: Soaps, oxidation products and trace metals. he magnesium silicate attracts and bonds with polar contaminants, such as soap or glycerin molecules. The mixture was then vacuum filtered to remove the resulting cake. The remaining filtered methyl ester is the finished product.
Drying Moisture
Adsorptive Bleaching & Carbon Treatment:Pigments, oxidation products, trace metals, sulfur compounds, dioxins, furans, PAH and possibly some pcb's.
Winterization : Higher melting triglycerides, waxes. Used to enhance the unsaturated triglycerides

Deodorization Free fatty acids, mono-diglycerides, aldehydes, ketones, chlorinated hydrocarbons and pigment decomposition products.

Chemical processes

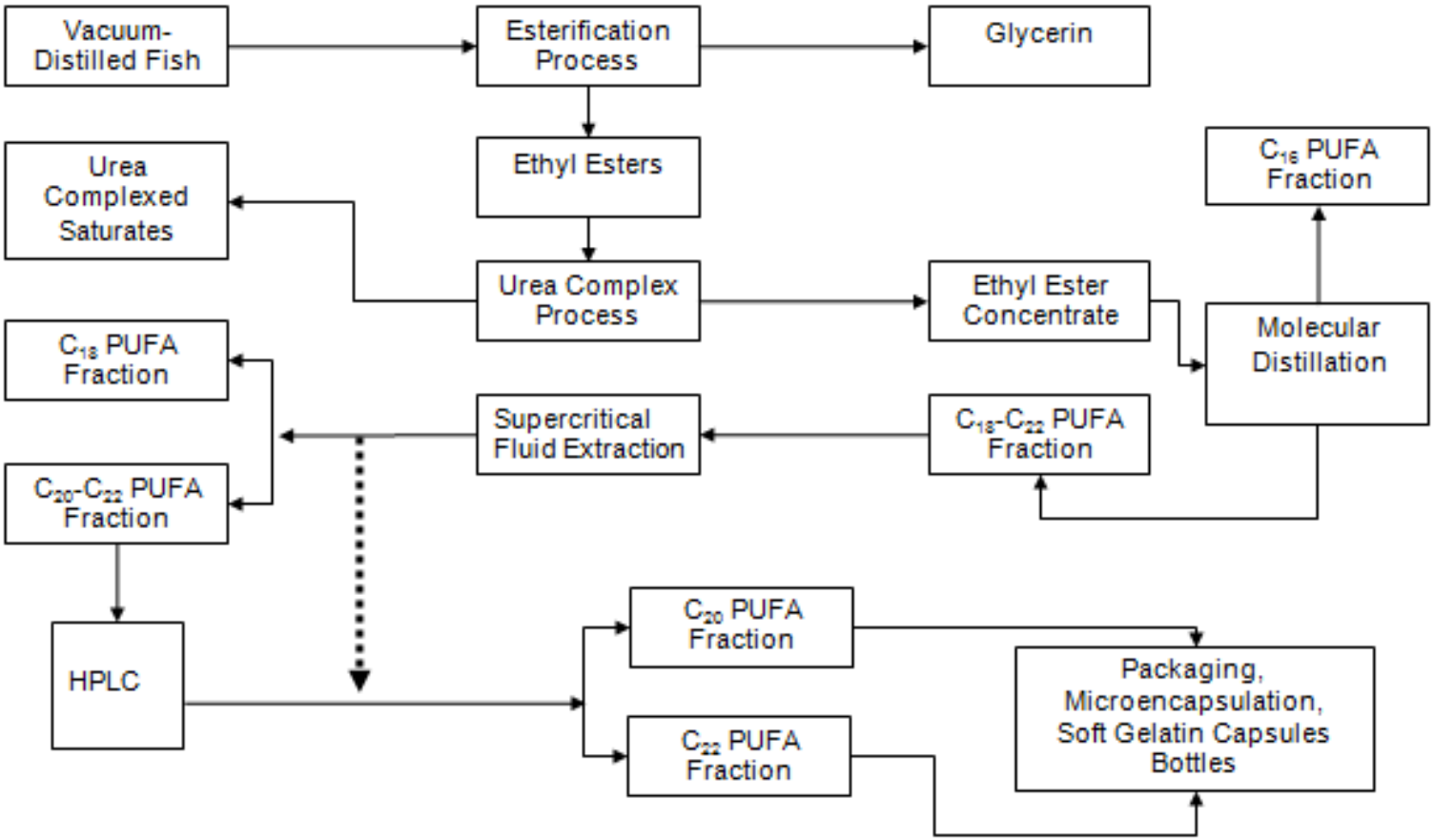
Hydrolysis or Esterification

- Splitting triglycerides, producing fatty acids or esters with glycerin as a by-product. Reaction can be made with potassium methoxide for approximately 16 hours. The solution is allowed to settle and separate for approximately two hours

Urea Complexing

- By dissolving the fatty acids or esters in ethanol or methanol, adding urea and reducing the temperature, it is possible to precipitate a urea complex which traps the saturates and monounsaturates resulting in a concentration of the polyunsaturates. Depending on the starting oil, the losses can be quite high.

via esterification process…



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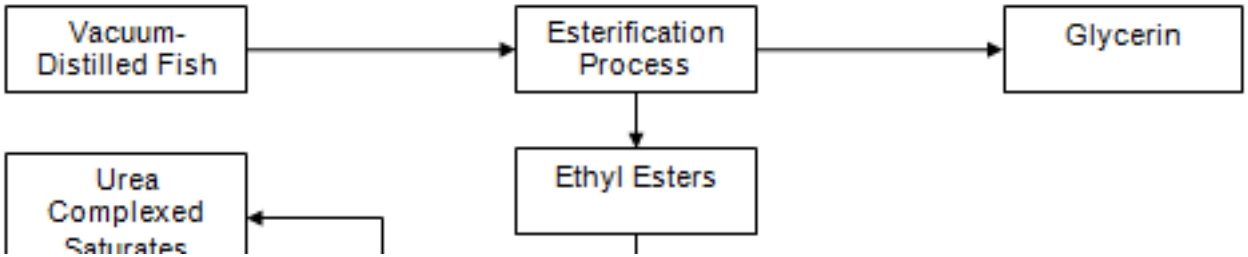


Fatty acids play an important role in the chemical industry
Because they are used as raw material in the production of
Number of very different derivatives.

Methyl /ethyl esters can offer unique benefits

WHY ESTERS?

Generally the esters are easier to fractionate, more stable and
Less corrosive. The main reason is that they have lower boiling point than
Corresbonding acids.

Fatty acid composition

Fatty acid composition (mg/g nominated fatty acids) for various e*
fish oil products

Fatty acid	Cod liver oil	Salmon oil	Fish oil concentrates
14:0	40–50	67	2–117
15:0	3–5	4	Tr
16:0	112–122	156	22–132
16:1	74–91	82	5–113
16:2	2–8	8	Tr–12
16:3	2–3	7	Tr–9
16:4	4–9	19	Tr–37
18:0	20–27	24	24–26
18:1	238–259	140	118–119
18:2 (*n*-6)	23–42	15	9–11
18:3 (*n*-6)	Tr–2	3	Tr–1
18:3 (*n*-3)	12–20	8	3–8
18:4	24–28	28	16–23
20:0	Tr–2	2	3–7
20:1	71–110	18	8–60
20:4	14–15	27	13–42
20:5 (*n*-3)	100–104	194	289–323
22:1	47–66	26	6–41
21:5	4–6	7	8–12
22:5 (*n*-3)	14–26	28	26–45
22:6 (*n*-3)	96–114	140	54–247
Saturates†	179–204	253	63–280
Monoenoic	447–492	266	224–246
Dienoic	27–50	23	11–21
Trienoic	16–23	18	9–12
Tetraenoic	43–62	74	65–66
Pentaenoic	123–132	229	323–380
Hexaenoic	96–114	140	54–247

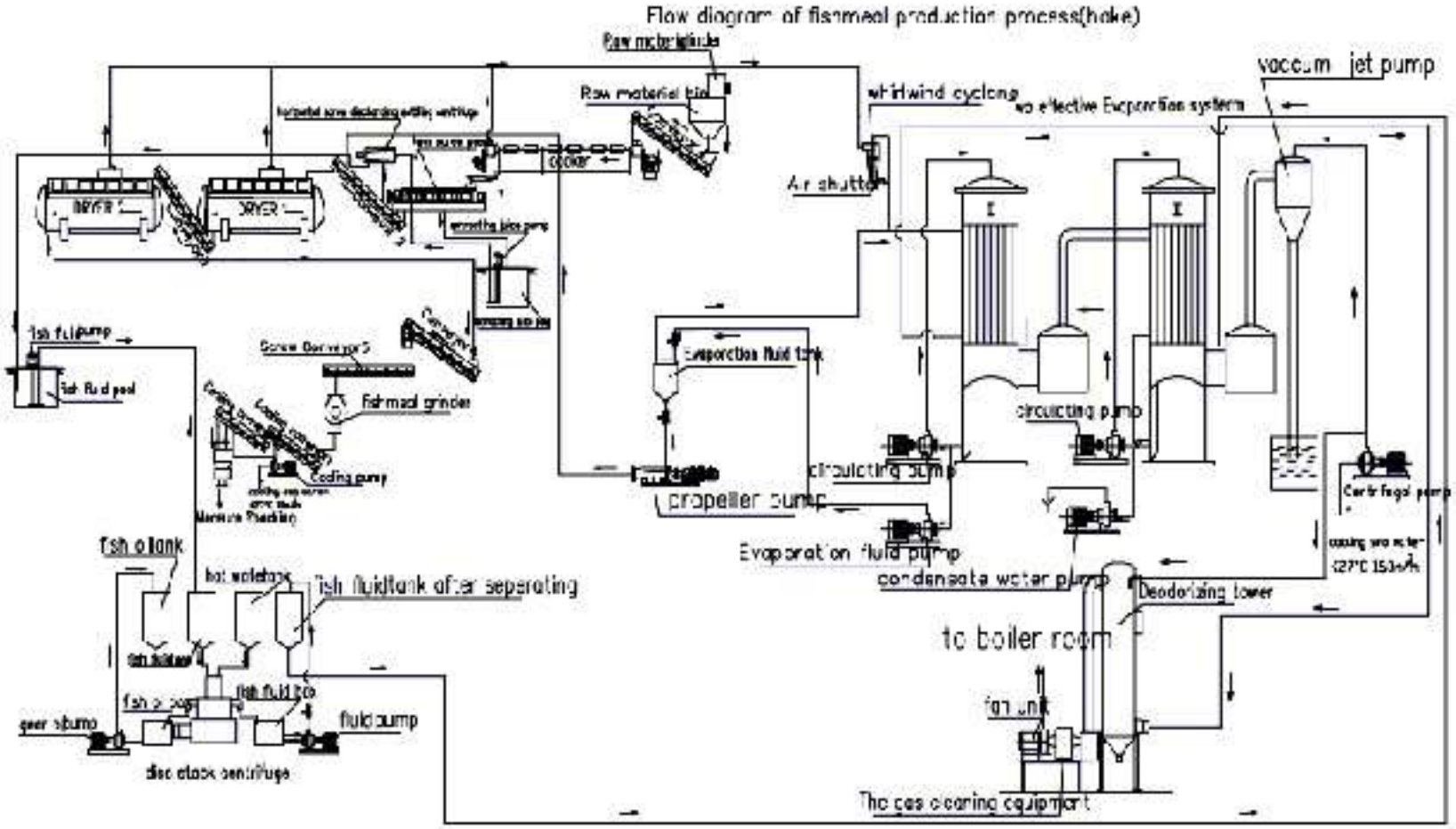
ALA

EPA

DHA

Chemical values

- Iodine value 120-150 (unsaturation value)
- Saponification value 185-195
- Free Fatty acids 0.2-0.3%
- Titer 28-32 C
- Unsaponifiables 0,5-2%


Flow diagram of fishmeal production process(hake)
Raw material bin
whirlwind cyclone
vacuum jet pump
Air shutter
DRYER
DRYER
cooler
fish fluidpump
fish fluid pool
Screw conveyor
fishmeal grinder
coding pump
evaporation fluid tank
circulating pump
circulating pump
propeller pump
Evaporation fluid pump
condensate water pump
Deodorizing tower
to boiler room
fish oil tank
hot water tank
fish fluidtank after separating
fish fluid tank
fish oil pump
gear pump
fluid pump
disc stack centrifuge
fan unit
Tail gas cleaning equipment
Centrifugal pump

Industrial use of Fish Oils

The major industrial uses take advantage either of the unique type of

- high degree of unsaturation
- lubricity
- Detergency and plasticity
- Unique fatty acid composition

Potential Industrial use?

Protective Coatings?

- **Fish** oils can be useed in alkyds, varnishes, and *mixtures* in paints.

Lubricants?

- Sulfurized fish oils are one of the components of extreme pressure paraffin baseoils (Mitacek and Greham 1965; Swensen 1942).
- Lead soaps of menhaden oil are used for the same purpose.

Potential Industrial Use

Variety of Esters

- A lot of commercial products are made by esterification of the acids or interesterification of the oils themselves with alcohols.
- Commonly used Methyl, ethyl, and butyl alcohols, pentaerythritol, propanol, trimetylol propane are used. Butyl esters of saturated acids are recommended as lubricants for rolling aluminum, die-casting plastics, textile spinning, and alloy metal-working. There has been some commercial interest in the esters for conversion to the alcohols by hydogenation.

”Fatty acid ethyl esters in hair as markers of alcohol consumption. Segmental hair analysis of alcoholics, social drinkers, and teetotalers”

Thank You for Your attention1

Any Questions?