

Natalia *DOLGANOVA*

Fish processing

**COMPREHENSIVE PROCESSING OF KRILL AND FISH PRESS WATERS
AND OTHER LIQUID BY-PRODUCTS**

**KOMPLEKSOWA OBRÓBKA BULIONÓW POPRASOWYCH I INNYCH
PŁYNNYCH ODPADÓW Z KRYLA I RYB**

Astrakhan Technical Institute of Fisheries, Astrakhan, Russia

Chemical composition and processing techniques of krill and fish press waters are analysed. Ultrafiltration was found to be of use, but only when an efficient removal of protein suspension could be effected. Besides, ultrafiltration requires a complicated set of apparatus.

Biological transformation of proteins and lipids with the use of enzymatic preparations and microorganisms is suggested as a possible alternative. Application of microorganisms is more efficient due to the well-known potential of their cells.

Future studies on press water technology should focus on developing improved biotechnological methods involving microorganisms.

Press waters are a by-product obtained during fish meal production. When discharged to the sewage system, a total of 30% protein and 5% fat is lost.

Fish press-waters were found to contain 73 - 80% water, 1.5 - 3.1% lipids, and 3.0 - 4.0% total nitrogen (Tab. 1) (Dolganova and Kapitonienko 1981; Vinnov and Dolganova 1989).

When processing krill protein isolate, a similar water-protein-lipid ratios are obtained in the resultant press water (French Patent No. 2373972).

The array of methods used at present for press water processing includes coagulation and flotation, centrifugal separation of protein suspension, separation of free lipids, and hydrolysis. The latter is effected either via autolysis or aided by commercially available enzymatic preparations. As the aquatic organisms' own enzymes are not very active, hydrolysis takes a long time, whereby microbial spoilage is enhanced. Application of chemical conservants (formaldehyde, formic, acetic and hydrochloric acids, sodium pyrrsulphate) reduces the resultant product's utility and inhibits protein decomposition (Černogorcev 1973).

Table 1

Chemical composition of fish and krill press water and krill water-protein-lipid system

Compound name	Fish press water	Krill press water	Krill water-protein-lipid system
Total nitrogen, %	2.50	3.71	2.0 ÷ 5.0
Non-protein nitrogen, %	0.90	1.42	1.0 ÷ 2.5
Water-soluble protein, %	0.13	1.29	0.8 ÷ 1.8
Total lipids, %	1.25	2.50	1.0
Free lipids, %	0.90	2.23	0.8

Table 2

Optimal conditions of krill press water proteolysis

Parameter	With Proteline	With Protosubtiline
Temperature, °C	46 - 52	55 - 62
pH	7.0 - 8.5	6.5 - 7.5
Amount of enzyme as % of protein content	2.5	5.0
Content of solids, %	not less 13.5	not less 13.5

Application of commercially available enzymatic preparations shortens the duration of hydrolysis, but the high costs involved render the comprehensive processing expensive. Nonetheless, enzymatic hydrolysis is regarded as being a more acceptable technological treatment in processing press waters. For that reason, the research presented in this paper focuses on intensification of enzyme-aided hydrolysis.

Initially a method was developed to extract and hydrolyse lipids in krill press

waters and water-protein-lipid system. Krill by-products are characteristic in having a low lipid content, the total lipids being dominated (80 - 20%) by free fatty acids, for which reason extraction is difficult. Lipid yield during extraction by physical methods under optimal conditions is 10 - 20% (Rogozin et al. 1979). Ultrafiltration through cellulose acetate membrane reduces the press water volume by a factor of 5 and helps to concentrate the lipids. Enzymatic hydrolysis is used to decompose protein-lipid complexes and release lipids (Tab. 2).

Comprehensive processing of lipids and hydrolysate obtained from krill press waters and water-protein-lipid system has been a subject of several publications (AS No. 1061311; Ržavskaja and Dolganova 1982; Dolganova and Ržavskaja 1979; Ržavskaja et al. 1988) and is summarised in Fig. 1. Lipid yield is 50 - 80%, depending on the original content in the by-products. The qualitative composition of lipids obtained from krill press waters and water protein-lipid system during concentration and extraction is presented in Table 3, while Table 4 summarises the quantitative composition. The extracted lipids are dominated by triglycerides and contain much less phospholipids, sterols and esters than the natural krill (Tab. 4). Fatty acids in the extracted lipids are the same as in krill (Tab. 5). Spectroscopic examination confirms the results of chemical analyses.

Krill press water or water-protein-lipid system

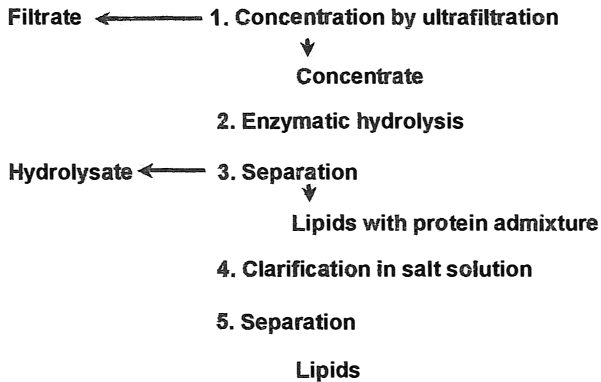


Fig. 1. A schematic of lipid extraction from krill press waters and water-protein-lipid system

Table 3

Change in the extent of lipid oxidation and hydrolysis during extraction

Extent of lipid oxidation and hydrolysis	Lipids in:			
	krill	press water	concentrate	extract
Peroxide value, % iodine	0.05±0.01	0.01±0.005	0.02±0.005	0.02±0.005
Aldehyde value, %	2.5±0.5	3.9±0.5	4.1±0.5	5.2±0.5
Content of oxidised products: non-soluble in ether, %	0.5±0.05	0.1±0.05	0.1±0.05	0.3±0.05
Acid value, mg	6.3±0.7	7.8±0.7	7.9±0.6	8.6±0.6

Table 4

Lipid fractions (%)

Lipid class	Lipids in:			
	krill	press water	concentrate	extract
Phospholipids	18.6±0.8	13.3±0.9	13.8±0.9	4.2±0.3
Triglycerides	57.2±2.4	60.1±2.1	60.8±2.1	77.3±0.1
Diglycerides	0.9±0.1	1.5±0.1	2.0±0.1	1.2±0.1
Monoglycerides	1.8±0.2	4.0±0.1	4.2±0.1	6.3±0.1
Sterols	7.8±0.4	6.1±0.2	5.0±0.2	1.3±0.1
Esters	9.8±1.0	10.5±1.0	10.0±1.0	5.4±0.4
Pigments	0.4±0.1	0.3±0.1	0.3±0.1	0.2±0.1

Table 5

Variability in composition of fatty acid (%)

Fatty acid	Krill	Press water	Concentrate	Extract
14 : 0	21.4±2.0	23.8±2.0	23.3±2.0	23.1±0.0
16 : 0	21.7±2.0	21.8±2.0	21.5±2.0	17.1±1.0
16 : 1	10.0±1.0	15.0±1.1	14.4±1.1	18.3±1.0
18 : 0	1.6±0.1	1.7±0.1	2.3±0.1	3.4±0.1
18 : 1	15.0±1.5	19.1±1.7	20.7±1.7	23.5±1.7
18 : 2	4.9±0.2	4.0±0.1	3.8±0.1	3.2±0.1
20 : 5	18.9±0.3	11.1±0.1	11.1±0.1	5.0±0.2
22 : 6	7.5±0.2	3.5±0.1	3.6±0.1	1.5±0.1
Saturated	44.7±2.0	47.3±2.0	47.0±2.0	44.6±1.5
Monounsaturated	25.0±1.0	34.1±1.5	34.5±2.0	44.0±1.0
Polyunsaturated	31.3±0.2	18.6±0.2	18.5±0.2	11.4±0.2

The treatment discussed produces also a hydrolysate. The hydrolysate was found to contain all the amino acids used as a substrate to obtain some isolated amino acid preparations from (Dolganova et al. 1984).

The technological process discussed contributes to intensification of the comprehensive processing of press waters. The drawbacks of the process lie in an overly complicated apparatus and the need to periodically clean the membranes used.

An alternative to ultrafiltration in the enzyme-aided acceleration of hydrolysis is low-frequency ultrasonic treatment (Fig. 2) (Vinnov et al. 1983, 1985, 1986, AS No. 1224250). The best effects were obtained when using ultrasonic frequencies of 18 - 20 kHz, 1.4 kW acoustic power, and 0.07 kW/kg for 8 - 10 min. The content of water-soluble proteins was found to increase from 0.13 to 0.6%. Duration of enzymatic hydrolysis on sonication decreases somewhat. The final yield of protein decomposition products was found to be independent of power frequency and time of sonication.

The hydrolysate is clarified by heating (100°C) or by coagulation with FeCl₃ (Vinnov and Dolganova 1985, 1986, 1988). Coagulation of press water protein or hydrolysate containing 100 mg N/100 g fluid requires the coagulant in the amount of 6×10^{-4} g. As a result of ultrasonic enhancement of enzymatic hydrolysis, a product containing 8 - 10% non-protein nitrogen compounds and some amino acids is obtained (Vinnov and Dolganova 1990).

Comparison of the two processes showed that, in terms of hydrolysis efficiency, increase in the content of solids is more important than preliminary sonication of the substrate. The research carried out so far makes it possible to draw the following conclusions:

1. Intensive protein hydrolysis is the major obstacle in efficient extraction of proteins from press waters and water-protein-lipid systems. Proteins can be separated out using membranes with very fine pores, the efficiency of the process being thus reduced.

2. Enzymatic hydrolysis is the major operation in processing press waters; however, to render the hydrolysis efficient, the protein content should be no less than 18 - 20%.
3. Ultrafiltration and autolysis can be used to concentrate proteins in the press waters. However, the ultrafiltration apparatus is overly complicated, the filtrate obtained containing excessive amounts of proteins (Kuzniecova 1988). Before discharge to open waters, the filtrate needs biological purification. Application of autolysis calls for chemical conservants which diminish the utility of the products.

Press water

1. Sonication (ultrasonic treatment)

2. Enzymatic hydrolysis

3. Enzyme inactivation

4. Separation → Lipids

↓
Fat-free hydrolysate

5. Coagulation

6. Centrifugation → Protein coagulate

↓
Clean hydrolysate

Fig. 2. A schematic of hydrolysate production from fish press waters

The problems listed above may be overcome by using biotechnological approaches involving microbial cells. Some microorganisms are known to inhibit putrefaction. The use of yeasts is another possibility. Yeasts are known to convert certain soluble nitrogen-containing compounds into non-soluble proteins, thereby considerably simplifying the separation process and contributing to formation of a supernatant devoid of soluble nitrogen compounds.

Future studies on press water technologies should pay attention to biotechnological developments which take advantage of physiological properties of live microorganisms.

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Natalia *DOLGANOVA*

KOMPLEKSOWA OBRÓBKA BULIONÓW POPRASOWYCH Z KRYLA I RYB

STRESZCZENIE

Przeprowadzono analizę składu chemicznego i metod przetwarzania bulionów poprasowych z ryb i kryła. Stwierdzono dużą przydatność metody ultrafiltracyjnej, ale tylko wówczas gdy uda się ją połączyć z efektywnym systemem chemicznego bądź mechanicznego usuwania zawiesiny białkowej. Utrudnieniem w zastosowaniu tej metody jest skomplikowana aparatura.

Sugeruje się zastosowanie tej metody polegającej na procesie biologicznej konwersji białek i lipidów, bądź to za pomocą zwykłych preparatów enzymatycznych, bądź zastosowania mikroorganizmów. Ten drugi sposób jest bardziej skuteczny ze względu na znaczne potencjalne możliwości komórek mikroorganizmów, np. drożdży, stąd dalsze badania nad przetwarzaniem bulionów poprasowych winny być ukierunkowane na stosowanie zabiegów biotechnologicznych w oparciu o mikroorganizmy.

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Authors' address:

Ph.D. Natalia Dolganova
Astrakhan Technical Institute of Fisheries,
Astrakhan
Russia