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# INDUSTRIAL PROCESSING OF THE SHRIMP, ESPECIALLY CARNING V

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1/ The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO.

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#### 1. INTRODUCTION

In the world as a whole, and more specifically in this large region of Central America, with coastlines on two oceans, there are few fishing industries as important as that of the shrimp or <u>camarón</u>. In English the names "shrimp" and "prawn" are used without any general distinction, in Spanish the term <u>camarón</u> means the broad group of <u>Peneides</u>, although other species too can legally and commercially be termed <u>camarónes</u>.

The outlook for the shrimp industry is at present a good one, particularly as regards the international market for the product. Of course we must not forget the fluctuations in catches, which are substantial - although they are well known and are understandable from the biological point of view, because we know that the shrimp has a migratory cycle from the shallow coastal waters to the deep sea-bed. Moreover, all shrimps processed industrially are less than two years old, so that there can be no relationship between the catch for one year and the next.

But however great the biological importance of the shrimp's fluctuations and migration, and however great its economic importance, because of the growing market for it (in the United States of America, Japan and Europe consumption and prices are constantly rising and today the shrimp is worth more than the most expensive meat), its technology is no less important, especially if we consider canning. This is undoubtedly the most difficult type of fish processing from the point of view of quality, a fact which is often overlooked, as is shown by frequent economic failures, including some known to have occurred in this region. For us, the important aspect of shrimp canning is that its adverse features cone within the scope of quality control, which clearly brings out the close relationship between technology and the canning industry.

Having explained, then, the reasons - technological and economic - why this topic of the shrimp is important, I will now turn to the shrimp itself. But first, it is my pleasant duty to thank UNIDO and the Central American Research Institute for Industry (ICAITI) and also to confirm that at the end of my talk I should be glad to have a discussion, since the essential aim of the talk is to open up a mutual and friendly exchange of views, which is the only way of getting to know what questions are of interest to you and clarifying our ideas together.

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BIOCHEMISTRY OF THE SHRIMP: ITS EFFECT ON QUALITY AND INDUSTRIAL PROCESSING 2.

# 2.1 - General Aspects

Let us start by recalling that the adult shrimp (and here we wish to bring out its differentiation during the migratory cycle of its life) is caught - by night or day according to species and fishing ground - at varying though increasingly greater depths, but always in muddy areas. In the interests of better quality it is essential that hauling-in should last as short a time as possible - we can say that it varies from about 1 to 3 hours. We need only visualize a muddy bottom and a shrimping net to realize at once that the high initial contamination is going to affect the whole subsequent processing, aggravated in the majority of cases by a hot climate, wooden boats and unfavourable conditions of handling on board and unloading on land.

But the adverse initial conditions after the shrimp is caught are not due solely to its microbiology (today this is mitigated, especially in industrial processing, by the controlled use of chlorinated water), but also to its specific chemical composition. Let me explain this: the shrimp, by virtue of its basic components, is a non-fat (white fish the composition of which is highly consistent. This composition has been thorough studied and may be summarized as follows for the different species and commercial products:

- Water: The proportion of 80 per cent of water which is more or less typical for all non-fat white fish is reduced to about 65 per cent (about 20 per cent less) in cooked shrimps and to 12-15 per cent in dried shrimp.
- The basic proportion of 18-23 per cent of protein in fresh shrimps risestto 27-28 per cent in cooked shrimps and to more than 75 per cent in dehydrated Proteins: shrimps. In canned shrimps the proportion is between 20 per cent and 27 per cent according to methods of packing, cooking, etc.
- Fat: As already stated, this crustacean is not very fat; we can put the average proportion for cooked shrimps at 1.0 per cent, even less for canned shrimps and of course much higher - up to about 5 per cent - for dehydrated shrimps.
- Ash: Negligible compared with what they receive from the proportion of salt added, and this is a variable that depends entirely on the method of processing.

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#### 2.2 - Non-protein components

But for all their uniformity (and high digestibility) the basic components do not indicate the characteristics of the shrimp, much less its industrial behaviour. For example, the nitrogenous non-protein components, the propertion of amino acids, pH variations, the enzymatic action etc. are much more important than the basic analysis given above. Let us look at some details, on the basis of commercial batches of shrimpe caught in the Gulf of Mexico by United States boats (1-fresh, 2-beginning to undergo some change, and 3-with more advanced change):

	Frozen fresh			I	Frozen cooked		
Degree of Tresmess	1	2	3	1	2	3	
Humidity %	81.0	83.5	86.4	73.0	74.5	75.5	
рН	7.0	7.3	7.5	7.3	7.4	7.5	
Indol mg/100g	<b>0.</b> 9	3.6	12.4	0.2	5.6	21.0	
Volatile acidity	12.4	14.0	21,9	14.1	11.0	12.6	
Succinic acid mg/100g	2.3	2.5	4.4	3.0	1.8	3.5	
otal volatile bases	13.1	17.5	29.7	16.0	15.6	19.1	
Ammonia:							
By microdiffusion	12.8	15.3	25.9	15.5	13.8	16.3	
By colorimetry	14.5	16.9	31.1	14.5	11.0	21.8	
Trimethylamine:							
By microdiffusion	0.3	2.2	3.8	0.5	1.8	2.8	
By colorimetry	0.2	3.1	7.0	0.4	2.0	5.3	
Aerobic count	8 <b>4x</b> 10 <sup>3</sup>	2.3x10 <sup>6</sup>	4x10 <sup>6</sup>	<b>%</b> 100	<b>&lt;</b> .100	<100	

Although the information in the above table is much more detailed than the standard nalysis of water, fats and proteins it does not reflect the full facts concerning the hrimp. In fact, for a score of years it has been known that all crustateeans contain high proportion (between 0.3 and 1.0 per cent) of glycine, an amino acid which can be ost in processing (for example while on ice or in water on board, or in cold storage n land). This loss of glycine is more pronounced with decomposition, so much so that he sweetish flavour which is characteristic of fresh shrimps recently caught is largely ue to the proportion of glycine, and this is used as an indication of quality. Proably, glycine fulfils an intracellular osmotic regulating function (this is the case ith marine animals that migrate towards more or less salty waters) like urea (in lasmobranchians) or taurine (in mussels); an indication of its importance, we may ay that more than 60 per cent of the mono-amine nitrogen in the shrimp is glycine. In act, from the point of view of quality and even processing, it is more important to etermine the glycine content during storage than to pursue the traditional analysis f proteins; the same applies to other components.

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# 2.3 Melanosis in the chrimp: its industrial significance

The complex biochemistry of the shrimp is nevertheless not confined to the foregoing chemical analyses. Shrimps contain tyrosinase, an ensyme which reacts upon the tyrosine occurring naturally in their flesh and, in contact with the air (oxygen) and other factors will result in the dark products generally known as melanins. These are of considerable importance in industry.

The "black spot" shrimp has proved troublesome for a long time. We have been aware for some 20 years that this is not a micro-biological phenomenon (althoug there are cases of black coloration in chellfish, even canned, arising from bacterial, i.e. hydrogen sulphide, formations), but that it is of enzymatic origin, caused by an enzyme (protein - copper) in the head and shell of the shrimp. This explains why there is less darkening when the shrimp's head is taken off promptly on board ship. In brief, then, we have an enzyme which acts on the tyrosine occurring naturally in the shrimp's flesh, oxydizing it and converting it to dihydroxythenylaldnine (dopa), which in its turn goes on oxydizing and evolving until it forme orthoguinones, whose final product is the dark melanins.



# The following scheme simplifies and summarizes the process:

Tyrosine (in flesh) + enzyme: tyrosinase (in head) + oxygen (air) + other conditions (pH, temperature, etc.) = Nelanins (dark)

We should not be alarmed by this coloration - the squid's ink contains a great deal more melanin - but the fact that it is harmless does not stop if from being important commercially. Needless to say, the melanotic (black or spotted) shrimp is unpopular in the trade and even more so among importers.

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The best way of dealing with this process is through the oxygen in the air. It will be clear why the use of reducing agents (of which the cheapest, most widely usedand most legally acceptable are bisulphite salts of any kind, added in any way), antibiotics, disinfectants, sequestrants, etc., combined with mechanical processes, such as taking off the shrimp's head, cooking it on board ship, reirigeration in the form of refrigerated water or deep freezing, are methods used in industry more or less successfully to combat this process. We shall not go into detail here, because apart from the chemical process itself, other factors such as the feasibility of using the method on board ship, legal authorization by the fishing or importing country, later storage and supply conditions, etc. have to be taken into account. As far as the latest developments in fishing are concerned, the new trawlers equipped with deepfreeze facilities solve the problem completely.

It will be seen that we have been getting deeper and deeper into biochemical problems. But the bacteria count and complex chemical or enzyme composition are not the only factors to be taken into account. Although the flesh of the shrimp is initially neutral, its high nitrogeneous non-protein content means that alkalinity sets in fast (this is even used as a test of freshness). This physico-chemical process is of tremendous importance in canning, as we shall see.

#### 3. INDUSTRIAL PROCESSES

#### 3.1 - Freezing

This is by far the most interesting aspect for this region, and once the microbiological and melanosis problem is overcome, the process is very simple: this is why all the countries and incustries concerned begin with it. Although simple, the process is not without some points of interest, which we shall summarize below:

(a) The practice of preserving shrimps on board ship in refrigerated brine, which is widespared, especially in the Gulf of Mexico and the central Pacific, initially hydrates the shrimp. Prolonged use of this process, however, dissolves some components of importance for quality. For this reason, although the practice is widespread and preferable to other systems, it is not perfect.

(b) In factories chlorine should be used under control, in accordance with emperature, contamination, dissolved organic matter (mainly), destination, etc. There are objections to excess chlorine, although too little would be more serious.

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(c) The United States minimum and maximum freezing speeds and time-limit of six months in cold storage should be generally adopted whatever the market in which the merchandise is sold, because of the deterioration in quality that might otherwise be involved.

(d) The industrialist's best method of conserving the quality of the deep-frozen product is by using additives (polyphosphates, glucose, etc.) to the glazing; the health regulations are fairly lenient in this regard, although less so as regards colorants.

(e) The use of mechanical peelers is very questionable where labour is cheap and shrimp dear. All other forms of mechanization, however, are highly recommended: conveyor belts, size sorters, continuous washing machines, weighing and counting machines etc.

(f) Apart from freezing on board ship, which is used for all species and preparations of fish the most salient industrial developments at the moment are in plastics, tinplate, aluminium, etc. for packaging frozen products. The utilization and price of these are distinctly commercial, given the existing supply situation in the market. From the technical viewpoint, the greatest progress has been in additives and glazings.

#### 3.2 - "Breaded" shrimp preparations

Some years ago this type of preparation appeared - especially in the United States to have a more premising future then it has now. Consumption seems to have levelled off, or at least is not growing as rapidly us in the past. In brief, the processing consists in "breading" the shrimps, either fresh or frozen, with a series of additives (flour of various kinds, eggs, seasonings, etc.) before frying or freezing them. Naturally the microbiological risk is thereby increased, but with strict control (including State control), rapid sale in a limited market of high consumer capacity, a complete refrigeration chain and so on, this risk becomes remote. Although much processing of this kind is done in the United States with frozen shrimps from this region for the moment the product is of secondary interest and there is no local market for it. The variety of seconding and presentation that can be used in such proparations means that the manufacturers' real concern is with finding the best breading mix. Controls notwithstanding, contamination on a large scale, has been reported in the literature, and this danger is constant, despite the conditions laid down for cleanliness of staff (United States basic hygicne law of 1968), the prohibition on re-using one day's

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ingredients the next day, the hygionic design of the machines used and the fact that they are washed down daily, the rapidity of processing and freezing, the supervision of raw materials, cleanliness of utensils, floors, walls, cleakrooms, etc.

## 3.3 - Drying: freezo-drying

There is a market for naturally or artificially dried or dehydrated shrimps in the Far East (brought to the United States by people from that region a century ago and to Nicaragua during the last twenty years). However, this is of little interest to us, either in natural form, i.e. just dried, or smoked. Moreover, the cheaptest and smallest qualities ("Chacalin") have traditionally been used for this purpose, and so it is distinctly a product associated with popular taste. No complex technological problems are involved, only those common to all perishable foods (the shrimps are preserved by the addition of salt and intensive dehydration). It goes to popular markets, very often in bulk.

Quite the opposite, technologically speaking, is true of freere-drying, which is of great current interest. Special menus, including those for the first trip to the moon, often include freeze-dried shrimp preparations, but unfortunately a tremendous initial investment in machinery is needed and it is hard to make this pay with shrimps alone. We shall not go into detail on this, but it is interesting to note that vacuumdrying of the frozen product (i.e. freeze-drying) improves the quality of shrimps about to go off because it eliminates gases, smells, etc.

To round off the freeze-drying process, there is the final sealing in a vacuum or inert atmosphere. This process is used for other foods as well, but it does make production more expensive.

# 3.4 - Canning

From the technological though not the quantitative viewpoint, canning is of the createst interest to us, since continuous daily control is the only way of ensuring quality. The Central American region, which has been exporting shrimps since 1953, is nevertheless still importing canned shrimps. Preparations from the United States, Denmark, Nexico, and so on are frequently found on the market, although all these countries, except the last, are net importers - some from this very region.

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Before tackling this subject, let us note that despite the tendency for industry in the United States to be of giant size, none of the score of factories producing canned shrimps exceeds an average daily cutput of 10,000 cans, which would be a totally ridiculous figure for other foods. This is the only remaining family-style industry in United States fishing with an average yearly output per factory of less than 75,000 stendard cases (24 cylindrical 4<sup>±</sup> ounce or 125 c.c. cans).

Simplifying the various processes, it can be said that the first stages in canning - delivery or arrival at the factory, washing in sterilized chlorinated water to rid the shrimps of ice (which floats) and mud, inspection or quality control (almost always by direct organoleptical methods and often under State supervision), weighing and classification by length or size - are common to all processes, and indeed within the continuous production lines that are used a certain uniformity of models and systems is being achieved.

The peeling stage is worth a special mention. The two alternatives, manual and mechanical, with their different possible variations, are not final and it is hard to say categorically which is better: it all depends on the circumstances. The machines which first appeared some 15 years ago, are much faster, but hand peeling produces a greater yield of meat and better appearance. We can summarize the situation by saying that, generally speaking, raw shrimps are machine peeled and cooked ones are hand peeled.

Accordingly, since canned shrimps must be cooked before they are put in the can, all peeling has to be done by hand. The cooking is very important. It should last eight to ten minutes for wet-pack preparations and about two minutes more for dry-pack preparations (we return to this subject below). If the cooking time or the salt concentration (5-8 per cent) is inadequate, the tail of the shrimp will not curve. Out of habit the buyer insists on this, without realizing that in the sea the shrimp is not curved but straight. The cooking method is the same as for dried shrimps.

Once the shrimps are properly cooked, they are allowed to cool and drain naturally on a stainless steel table or conveyor belt, sometimes with a stream of cold air as well. The shrimps are then given a first cleaning (feelers, shell, etc.) and a proliminary selection is made (removal of shrimps of abnormal size, shape, curvature, colcur or appearance, etc.) and a sample taken for the basic pH test.

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We have already said that because of its composition the shrimp passes from a neutral state to an increasingly alkaline one, depending on its own biochemistry, species, habitat, sex, etc., and on environmental factors (time when caught, temperature, whether the head has been taken off or not, travling conditions, (tc.). This means that each consignment can be and is different from the next. Moreover, the finished canned product has to have a pH between 6.3 and  $\epsilon$ .8 or, to be very demanding, between 6.5 and 6.6. Since this product has a tendency to become alkaling with time, acids have to be addcd: the most often used is citric acid or a proparation containing it. But the concentration must not - for reasons of taste, inter alia - exceed 2.5 per cent (with salt, possibly sugar and other products added). The amount to be added must be enough to keep the pH within the limits mentioned. Too much results in corrosion, a bad taste and excessive acidity, while too little leads to the bluish colour produced in shell-fish by the copper in their blood homocyanine, just as we have iron. Only by strict pH control can the white-pink colour and the sweetish but slightly acid taste expected of canned shrimps be attained and corrosion and gelatinous liquids eliminated (the covering brine must be practically transparent).

The last stages in the process are purely mechanical: the canned weight of the shrimp must be checked (there is less in a wet pack then when paper is used, i.e. in a dry pack), the can must be pre-heated or sealed under heat, and above all sterilized and cooled as quickly as possible, if possible in an autoclave with stirring under pressure.

Obviously, when the finished product is sent off to the warehouse, the troubles are not over, for the abnormal bluish colour can always return. Even if it does not, struvite (an ammonium manganese phosphate crystallizing with six water molecules) is frequently found. This has often been mistaken, especially in war-time, for crystals improperty added to the canned product but in fact it is found in all canned crustaceans kept for long periods. Storage may also produce formaldehyde (in some cases over 100 ppm have been found), which in many countries may be used as a preservative for fresh fish products, but which here is the result of the natural, slow degradation during storage of the trimethylamine oxide which is part of the shrimp's natural composition. The same is true of indol: both are hard to determine, not so far as the substances themselves are concerned but because of the other natural components that accompany them.

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But none of these phonomona are as important for cans in storage as sulphurization, by which we mean the sulphur compounds which attack the tin of the tinplate (lacquered or not) and the iron in the steel underneath. In the first case, the tin sulphide i results in a light grey-bluish tinge, whereas the iron sulphide is much blacker. For over twenty years this problem has been studied and it has been practically solved by the use of the so-called "C" lacquers, which contain zine and hence produce white sulphates which do not show. But the lacquering is never perfect and de-tinning results, (still more so in the case of unlacquered tins), the process being accelerated by the proteins which absorb free tin, so that the iron then comes under attack. The attack is greater when acidity is strong, hence the need not to exceed the dose of citric acid. None the less, to show once again that these processes, which at first sight appear to be limited to pH control, are extremely complicated, we might point out that, although there is no difference from the pH standpoint between using pure citric acid and using it with lemon juice added, the can reacts differently because the latter's flavonoids prevent sulphurization much better. Lemon juice is therefore used in many preparations, although the reason for this improved performance is not quite clear.

All these biochemical considerations and quality requirements are very interesting to us but not at all interesting to the ordinary consumer, whose standards for assessing quality are much simpler and more commercial.

We all know that size is a criterion for classification (ounce or 100-gramme units), and one which is recognized internationally. The natural colour of the shrimp, without any symptoms of spoiling, is used to classify fresh, frozen or canned shrimps (white, pink, red, etc.). Other factors which can enhance or detract from the commercial quality are whether the tail is duly curved, the salt content, the proportion of solids to liquids and whether the liquid is turbid, contains dissolved solids, etc.

All these aspects, together with the use of authorized colorants (EDTA, orthophosphorineid, citric or tartaric acid, sugars, etc.), and now even the absence of pesticides, which the shrimp can pick up when close to agricultural areas, are other factors which make constant control necessary. I have tried to give you a general survey of the subject and to show that shrimp canning is the most technical aspect of the fish canning industry, and hence the ideal one for this group. Simply by attending and taking part in the Seminar, participants have given the best possible proof of their technical interest, for which I am sincerely grateful.

#### NOTE



Although it does not refer to the subject of the conference, a full and varied bibliography of the shrimp will be provided separately, arranged in chapters.

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