



“VASILE ALECSANDRI” UNIVERSITY OF BACĂU
FACULTY OF ENGINEERING



MODULE 2

NEW VISION WITH REGARD TO THE SPECIFIC ECONOMIC ACTIVITIES OF THE RURAL ENVIRONMENT: BY-PRODUCTS VALORISATION AND WASTE REDUCTION

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MULTITRACES

Module 2

SKILLS

Knowledge:

- Description and use of basic theories, concepts and methods on agri-food technologies.
- Explaining and interpreting the principles and methods used in the technological processes in the food chain.
- Management of technologies for valorisation of by-products and waste in the food industry and ensuring environmental protection.

Abilities:

- Monitoring and control of the technological processes in the food industry, application of basic principles and methods in the field for identifying risk situations and proposing solutions.
- Knowledge of the problems regarding the valorisation of the by-products that result in the technological processes of obtaining food products and the proposal of measures for the most efficient use of the handy substances from the by-products and waste resulted in the food industry

GENERAL OBJECTIVE OF THE COURSE

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Knowledge of the principles and methods for the most efficient valorisation of by-products and waste from the agri-food sector. Their reintroduction into the economic circuit is the basic principle of the circular economy.

INTRODUCTION

Mankind is facing a major crisis of material and energy resources, a context in which the food crisis is at the forefront. Under these circumstances, it is necessary as a measure of maximum necessity to valorise the useful substances from by-products from the food industry.

By-product and waste valorisation with their reintroduction into the economic circuit is the basic principle of a circular economy.

From the processing of raw materials of the different branches of food industry, beside the main products, a number of by-products and wastes are obtained whose share varies according to the nature of the raw materials, the finished products, the technology and the equipment used.

The category of by-products includes those materials which result in parallel with the main product in a manufacturing process and which can be used as such for various purposes.

Waste storage and by-product management of the food industry raise particular problems both in the field of environmental protection and in that of sustainable development. The current methods of valorisation of by-products have been developed along with the traditional production lines, being closely connected to the agricultural origin of raw materials.

There are two traditional methods of by-product valorisation in the food industry: as animal feed or as fertilizer.

The technological processes in the food industry must be oriented towards a maximum valorisation of the raw materials so that the quantities of waste are reduced to the maximum, because they raise numerous economic, hygienic-sanitary and other issues.

Reducing environmental pollution can be achieved through optimal by-product and waste valorisation from various branches of the food industry. In this context, an integral and rational valorisation is pursued, being able to obtain products with a value which can sometimes exceed the original product.

In this respect, the present material describes the main by-products and wastes of the milk, wine, beer, meat, sugar, alcohol, oil, canned vegetable and fruit industry, etc., emphasising the methods of valorisation.

1. VALORISATION OF BY-PRODUCTS AND WASTE IN THE AGRI-FOOD SECTOR BY IMPLEMENTING THE CIRCULAR ECONOMY

The scope of the notion of rural space, rural activity, of rural in general, is wider, more extensive, including within it the notions of agrarian space or agrarian activity or, simply, agrarian (*Dona et al., 2005*).

The final form of the definition of the rural space is found in Recommendation no. 1296/1996 of the Parliamentary Assembly of the Council of Europe on the European Charter for Rural Affairs as follows: the term (notion) of rural area includes an inland or coastal area containing villages and small towns, where most of the land is used for :

- agriculture, forestry, aquaculture and fishing;
- the economic and cultural activities of the inhabitants of these areas (crafts, industry, services, etc.);
- the arrangement of non-urban areas for free time and entertainment (or nature reserves);
- other uses (except residential).

From the point of view of the economic structure, in the rural area the agricultural activities hold the largest share in the rural territory.

Along with agriculture, product processing, forestry with forest exploitation, wood industry, domestic industry, artisanal production, tourism and leisure agrotourism, etc. come to complete the economy of the rural space.

Agriculture has a positive influence on industry in various forms. The strongest influence of agriculture on industry and services is the provision of the necessary labour force, a demand that evolves according to the pace of development of non-agricultural activities.

The development of agricultural processing industries stimulates the growth of agricultural production but, at the same time, has a positive influence on certain branches of the industry producing means of production necessary for the processing of raw materials obtained by farmers (*Dona et al., 2005*).

The agri-food sector is considered to be composed of the sum of two economic “aggregates”:

A. Agriculture, in general, consists in turn of:

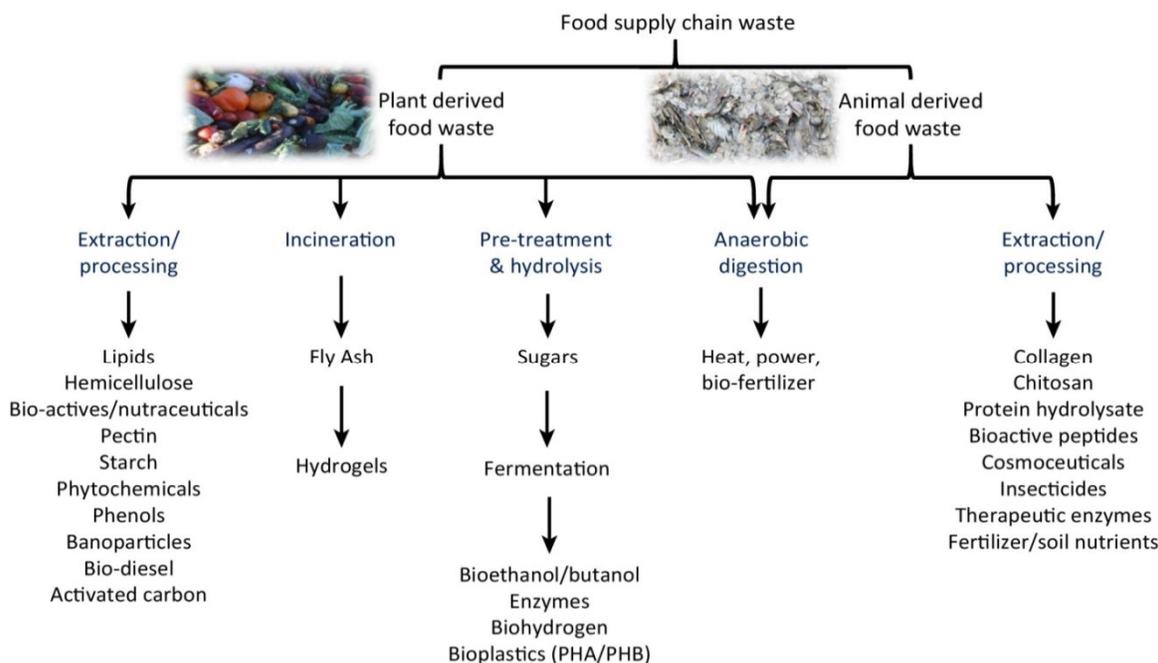
- production of crops (cereals cultivation, sunflower, canola, soybean, sugar beet, vegetables, tobacco, flaxseed, hemp single viticulture, fruit, etc.);
- raising animals (raising cattle, pigs, sheep, goats, birds, rabbits, etc.);
- beekeeping
- forestry and game economy;
- logging;
- fish farming and fishing.

B. The food industry, in general, in turn consists of ten sub-branches:

- meat production and preservation;
- fish processing and preservation;
- processing and preserving fruits and vegetables;
- production of vegetable and animal oils and fats;
- manufacture of dairy products;
- manufacture of milling products, starch and starch products);
- manufacture of other foodstuffs (including sugar);
- manufacture of other food products;
- tobacco industry;
- manufacture of beverages.

From the processing of raw materials of the different branches of agri-food industry, beside the main products, a number of by-products and wastes are obtained whose share varies according to the nature of the raw materials, the finished products, the technology and the equipment used.

Byproducts and wastes from food production can generally be divided into two groups, depending on whether they come from plant or animal origin food (*Yu and Brooks, 2016*).



Trends in Biotechnology

Figure 1.1. Food wastes valorisation (Ravindran and Jaiswal, 2016)

By-product means a substance or object which results from a production process the main objective of which is not to produce it and which satisfies, cumulatively, the following conditions:

- a) the subsequent use of the substance or object is certain;
- b) the substance or object may be used directly, without being subjected to any other processing in addition to that provided by ordinary industrial practice;
- c) the substance or object is produced as an integral part of a production process;
- d) the subsequent use is legal, in the sense that the substance or object meets all relevant requirements related to the product, environmental protection and health protection for the specific use and will not produce overall harmful effects on the environment or public health.

Waste means any substance, preparation or any object from the categories established by the specific legislation on the waste regime, which the holder discards, intends or has the obligation to dispose of;

Valorisation is any operation whose main result is that the waste serves a useful purpose by replacing other materials that have been used for a particular purpose or that the waste is prepared to serve that purpose in businesses or in the economy in general.

Reducing food loss and waste presents unique opportunities to create value, local businesses and jobs, and thus new economic avenues.

To improve the efficiency in the supply chain process and increase the performance of waste management, the implementation of circular economy is perceived as being of significant importance (Nattassha et al., 2020).

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The concept of circular economy - as a model of production and consumption that involves the sharing, reuse, repair, renovation and recycling of existing materials and products as much as possible. In this way, the product life cycle is extended.

The circular economy is different from the traditional economic model, the linear economy, which consists of “buy-consume-throw” (*Figure 1.2a.*) (*Bourguignon, 2016*).

Circular economy (*Figure 1.2b*) is an economy that produces zero waste. When a product reaches the end of its life, its component materials should be kept in the economy as many times as possible. These components can become raw materials, being reused and having a new value.

The circular economy is a technique of rethinking and regeneration through design and aims to preserve products, components and materials at the highest utility and value at all times (*Ellen MacArthur Foundation, 2013*).

The circular economy is a model of production and consumption that involves sharing, reusing, repairing, renovating and recycling existing materials and products as much as possible.

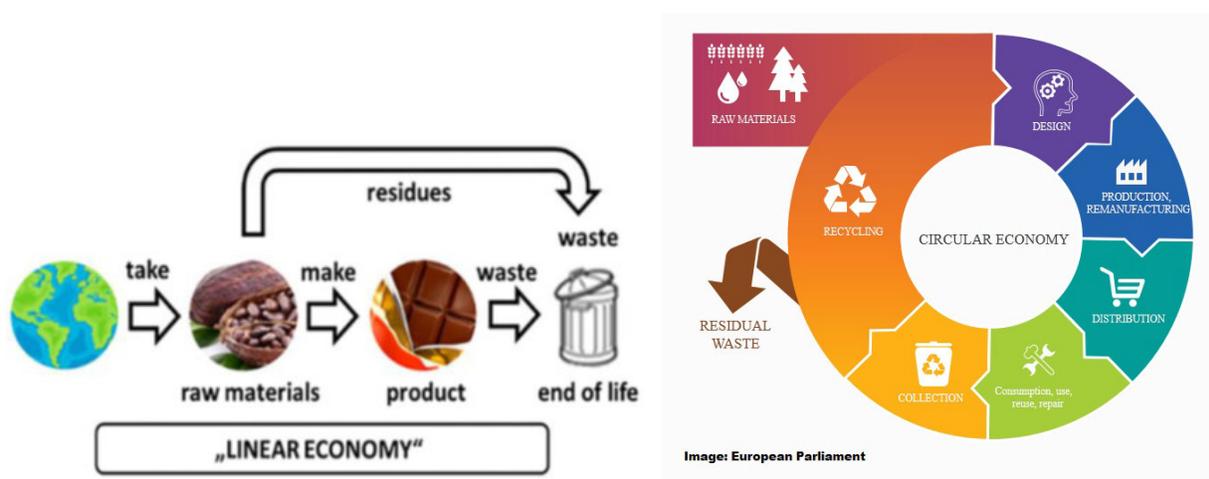


Figure 1.2. a) Linear economy (*Rajković et al., 2020*); b) Circular economy.

The application of the concept of circular economy in rural areas becomes fundamental for the creation of a smart village, given that the circular economy not only contributes to the efficiency of resource consumption but also to the creation of new jobs through new business models.

1.1. Classification and properties of food waste

Food waste is classified into:

- non-specific waste;
- specific waste.

Non-specific waste

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The quantity and quality of non-specific waste is practically independent of the type and quality of the finished product (*Botiș Nistoran, 2014*).

E.g.: containers for chemicals used in the cleaning and disinfection of installations.

Specific waste

The quantity generated by the specific waste reported at the production level can only be modified by technical means (*Botiș Nistoran, 2014*).

E.g.: barley grains depleted from brewing, slaughter by-products from meat production, potato or citrus peels, stale bread, etc.

Specific waste inevitably accumulates as a result of the processing of raw materials. They are produced in various stages of the technological process, stages in which the desired products are extracted from the raw material. After their extraction, potentially useful components often remain in the waste.

Food waste is characterised by a high value of the ratio between specific waste and the quantities of finished products.

The use and storage of specific waste is difficult due to the following factors:

- biological instability;
- potentially pathogenic nature;
- high water content;
- rapid self-oxidation potential;
- high level of enzymatic activity.

Waste storage and by-product management of the food industry raise particular problems both in the field of environmental protection and in that of sustainable development.

The traditional methods of using waste are agricultural solutions:

- as animal feed: exhausted cereal grains, beet leaves and packages;
- as a fertilizer: sludge from filtration or carbonation in the sugar industry (*Gavrilă, 2011*).

Most agricultural solutions for waste disposal are a balance between legislative regulations and the best ecological and economic solutions.

In addition to solid waste, the food industry also produces airborne pollutants (gases, solid or liquid particles) and wastewater, respectively.

These pollutants cause serious pollution problems, being the subject of increasingly stringent legal regulations in most countries.

Wastewater is the most common food industry waste as many unitary operations of ecological product technologies (washing, evaporation, filtration, extraction, etc.) take place in aqueous environment or require significant amounts of water.

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Wastewater from these processes usually contains significant amounts of suspended solids and dissolved organic compounds (carbohydrates, proteins, lipids) causing problems in discharge (*Botiș Nistoran, 2014*).

1.2. General methods of valorisation of food industry waste

The agri-food sector can be considered an organisation comprising the primary production, post-harvest, product manufacture and packaging.

Solid waste can be recycled by recovery processes in agriculture or animal husbandry, incineration, composting, treatment by other anaerobic fermentation processes, treatment by activated sludge process, treatment by membrane processes, treatment by chemical processes, treatment in biomembrane filters and respectively biologically rotating.

Liquid waste can be recirculated by applying untreated or partially treated waste to the ground, sedimentation, decantation and chemical precipitation, dissolved air flotation, treatment in stabilization ponds, in aerated or unventilated lagoons (*Botiș Nistoran, 2014*).

In the food industry system the inputs and outputs are shown in Figure 1.3.

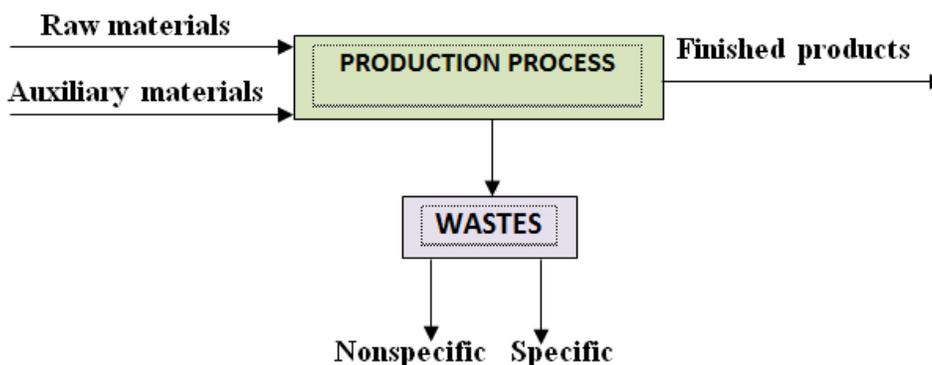


Figure 1.3. Representation of the agri-food sector (*Gavrilă, 2011*).

Waste can occur as emissions to air or water in liquid, aqueous or solid phases. A considerable part of the solid waste used is packaging resulting from food consumption (*Botiș Nistoran, 2014*).

2. VALORISATION OF DAIRY INDUSTRY BY-PRODUCTS

The first food a human body needs ever since birth is milk. This food, rightfully considered complete for the harmonious development of a human body, comes exclusively from mammals (Aruş, 2016).

Milk is a white-yellow, sweet-tasting liquid which is obtained by the complete and uninterrupted milking of healthy, properly fed and cared for animals (Figure 2.1).



Figure 2.1. Cow's milk [73]

The multitude and richness of the elements composing it make this food a raw material of great importance in the elaboration of many food derivatives, such as, for example, cream, butter, lactic acid products, cheeses and many others (Figure 2.2).

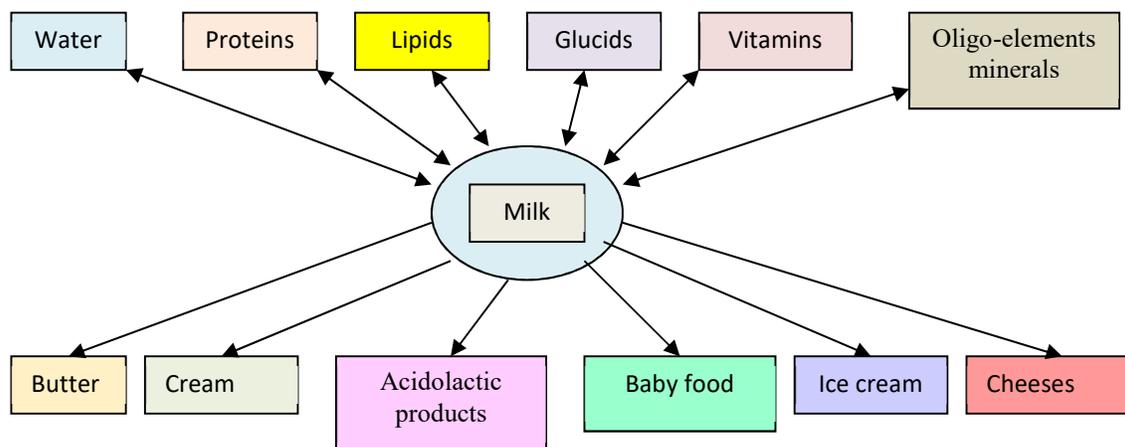


Figure 2.2. Milk elements and milk derivatives (Azzouz, 2002).

There is a wide variety of types of milk, of which only a few have found applications on an industrial scale, namely: cow's milk, buffalo's milk, sheep's milk and goat's milk.

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Milk can be subjected to certain technological processes in order to be used. Its composition determines the type of processing and therefore the range of derived products. Therefore, the chemical composition is the decisive factor in the adoption of the recovery technology.

Milk has a complex composition, with a heterogeneous structure, the main chemical components being presented in Figure 2.3:

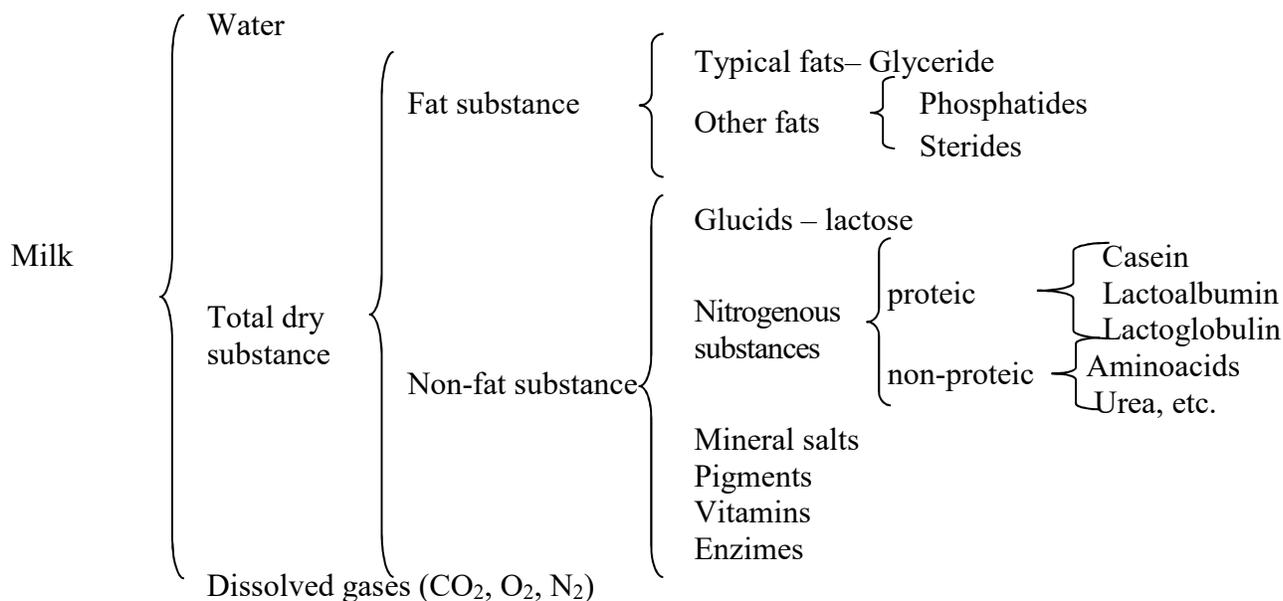


Figure 2.3. The main chemical components of milk (Aruş, 2016).

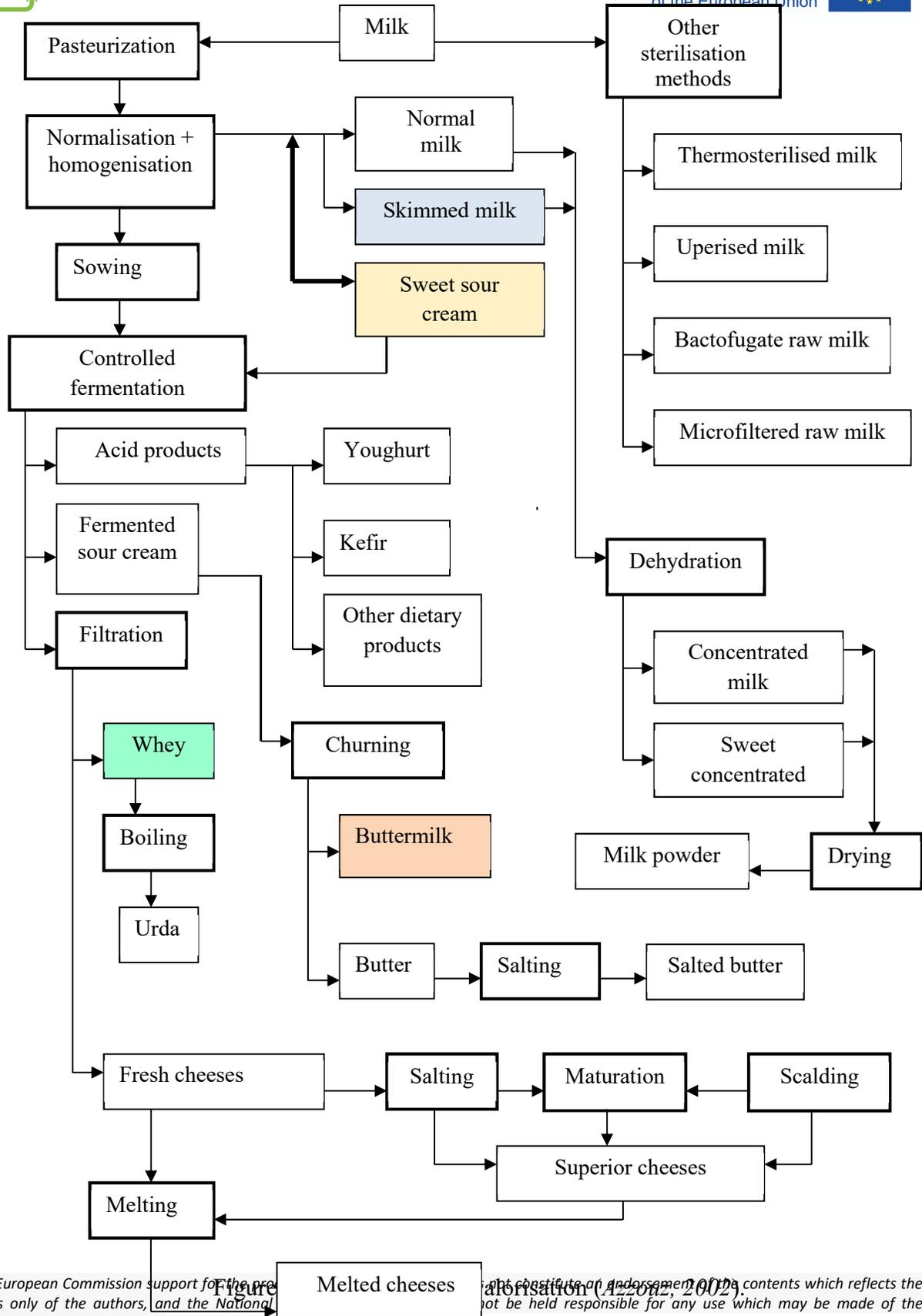
Depending on the nature of the source, the components of whole raw milk are distributed according to the following chemical compositions (Table 2.1.).

Table 2.1. Average chemical composition for different types of milk (Aruş, 2016).

Component	Cow's milk	Buffalo's milk	Sheep's milk	Goat's milk
Water, %	83,7	81,5	82 - 83	86,7
Totally dry substance, %	16,3	18,5	17 - 18	13,3
Fatty substance, %	3,6 - 3,8	4,2	6,8	4 - 8,2
Total proteins, %	4	3,9	5,7	4,3
Casein, %	4	2,8	4,6	2,8
Lactoglobulin + lactoalbumin, %	0,8	1,1	1,1	0,7
Lactose, %	4	4,4	4,5	5
Mineral elements, %	0,8	0,8	0,8-1,1	0,85



The experience gained over time, the technological progress as well as the increase of the standard of living have led to an unprecedented diversification of milk processing and dairy products (Figure 2.4).



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From the main technological processes which take place in the dairy industry result three by-products:

- **skimmed milk** resulting from the separation of cream from milk;
- **buttermilk** resulting from the butter manufacture;
- **whey** resulting from the manufacture of cheeses, casein and protein coprecipitates.

These by-products as well as the products resulting from their industrial processing can be used in human food, for animal feed, as well as for various technical purposes (chemical industry, pharmaceutical industry, paper industry, textile industry, etc.).

Modern, unconventional technological processes have allowed a more rigorous and efficient separation of the components of by-products and, consequently, a better processing, preservation and presentation of them. It is estimated that currently only 70% of milk proteins and lactose are found in finished dairy products, the rest being intended for animal feed, processed into technical products or discharged into wastewater (*Macoveanu et al., 2005a*).

2.1. Valorisation of whey

Whey is the aqueous fraction resulting from the coagulation of milk and the filtration of the obtained curd (Figure 2.5). This phase is a by-product in cheese-making technology, but it can be valorised due to its high nutritional value (*Aruş, 2016*).



Figure 2.5. Whey [74]

The composition of whey varies depending on the characteristics of the milk from which it comes and the manufacturing process of the main product (especially the coagulation process).

Whey generally contains 6-6.5% dry substance, which is more than half of the dry substance of milk (Table 2.2).

Table 2.2. (Average) chemical composition of whey (*Aruş, 2016*)



Type of whey	Water (%)	Proteins (%)	Fat (%)	Lactose (%)	Lactic acid (%)	Ash (%)
Sweet whey	93.5	0.8	0.3	4.7	0.2	0.5
Acid whey	93.5	0.9	0.2	4.2	0.6	0.6

Depending on its origin, there are two types of whey:

- *sweet whey (acidity 10-20°T)*: resulted in the enzymatic coagulation of milk (in the manufacture of fermented cheeses);
- *whey acid (acidity 50-70°T)*: resulted either in the manufacture of fresh or soft cheeses, or in the manufacture of lactic casein.

The acidity of milk and dairy products is expressed in degrees Thörner.

A Thörner degree (°T) represents the acidity of 100 cm³ produced, which is neutralised with 1 cm³ of 0.1 N sodium hydroxide solution (Aruş, 2016).

The whey obtained in the cheese-making processes is characterised by certain organoleptic properties, such as:

- Appearance: Whey is a green-yellow, opalescent liquid.
- Consistency: fluid; a viscous or flowing consistency is not accepted.
- Colour: green-yellow. Other foreign colours are not allowed because they demonstrate the presence of infectious microorganisms or other impurities.
- Odour and taste: sour, specific to lactic fermentation.

The main physico-chemical characteristics of whey are shown in Table 2.3

Table 2.3 Physico-chemical characteristics of whey (Aruş, 2016).

Characteristics	Whey
Relative density, g/cm ³	1.023
Acidity, °T	100
Dry substance, %	6.3

The ways to valorise whey are multiple and largely depend on its chemical composition, as well as the demand-supply ratio of each component in whey.

In Figure 2.5. the main industrial ways of whey valorisation are reviewed.

Dry substance fractionation

Whey is an important source of protein (lactalbumin and lactoglobulin), rich in essential amino acids. Due to the lactose intolerance manifested by a significant number of people, whey as such cannot be used as a source of protein, the only solution being the separation of proteins from whey, in the form of protein concentrates (Azzouz, 2002).

Modern whey recovery processes achieve dry substance fractionation by separating proteins by various methods (precipitation, ultrafiltration, gel filtration) or by demineralization (by ion exchange or electro dialysis)

The separation of whey proteins is of particular interest, due to both their high nutritional value and their various functional properties.

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Separation of proteins by precipitation

The separation of whey proteins is based on the use of physical or chemical agents capable of destabilizing serum proteins and precipitating them out of solution. Under the action of physical or chemical agents, which results in protein denaturation, precipitation is irreversible.

Precipitation is the process of separating and depositing in a solid state a substance dissolved in a liquid; the phenomenon of precipitate formation (Azzouz, 2002).

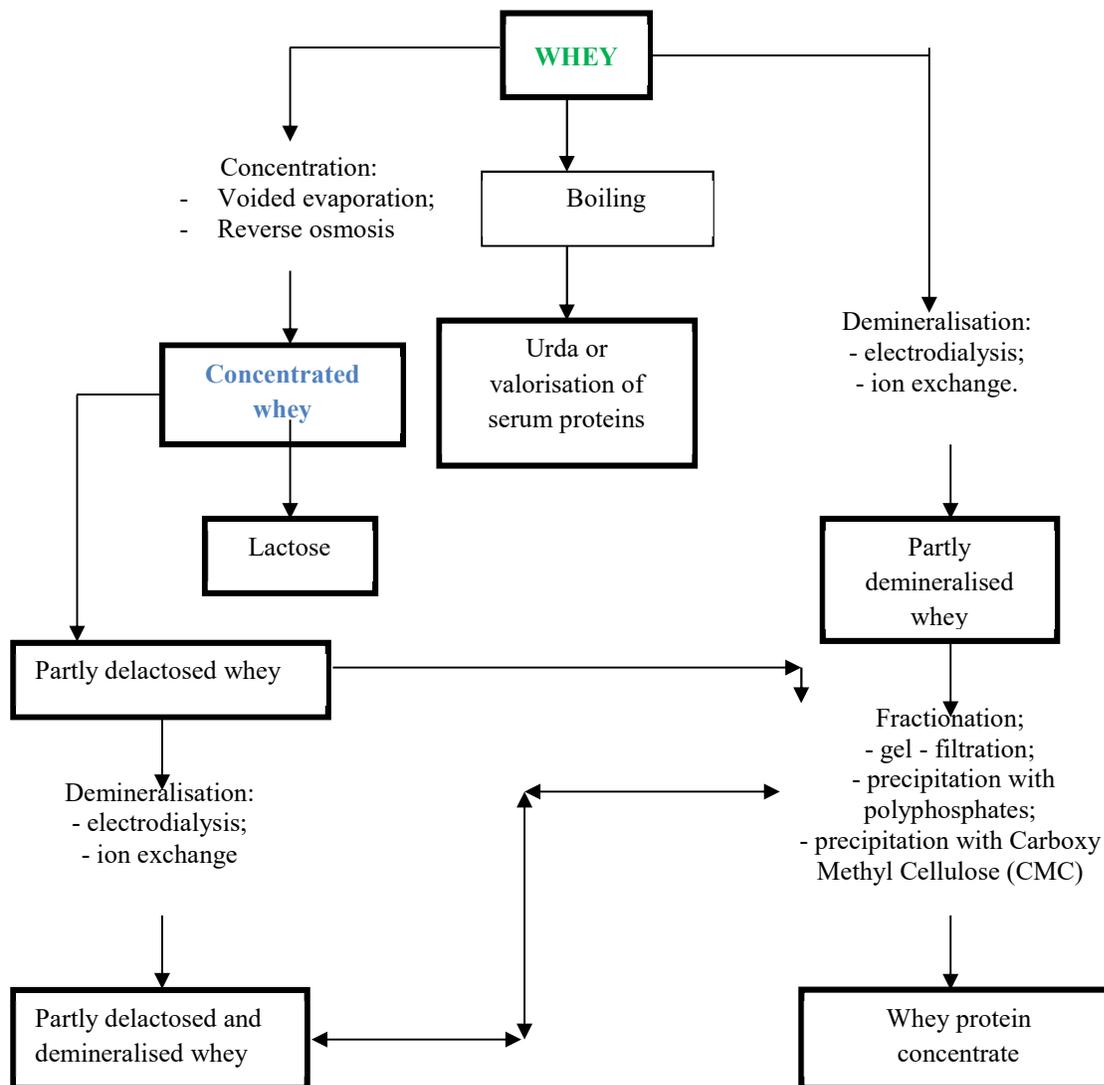


Figure 2.5 Processes for fractionating the dry substance from whey (Azzouz, 2002)

Thus there are the following protein precipitation techniques:

- precipitation by pH and heat treatment,

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- precipitation with alcohol,
- precipitation with metaphosphoric acid salts,
- precipitation with polyacrylic acid.

The protein concentrates obtained, due to their functional properties and high nutritional value, can be used:

- ❑ as substitute agents for egg white: the protein concentrate obtained by precipitation with sodium hexametaphosphate, a precipitate which is used as such or dried and sprayed, used at relatively low temperatures to avoid protein denaturation, is used for this purpose;
- ❑ as a complex product with high beating capacity;
- ❑ as protein textured structures used for the manufacture of meat substitutes
- ❑ in yoghurt – regulating the dry substance content and improving viscosity;
- ❑ as dietary products - in low-calorie diets;
- ❑ in the manufacture of pasta by adding 3% in semolina flour intended for the manufacture of macaroni (2% is added to cake flour).

Protein separation by ultrafiltration

This procedure makes it possible to obtain a protein concentrate in which the proteins are in an intact state, keeping unchanged all the functional properties characteristic of the native state. Injection of whey into an ultrafiltration plant results in a protein concentrate containing about 25% dry substance and 18% protein, as well as an ultrafiltrate containing low molecular weight components (lactose, mineral salts, lactic acid) (*Azzouz, 2002*).

Due to its functional properties and high nutritional value, the protein concentrate is used to obtain a wide range of foods, such as:

- ❑ some products for infants, their composition being close to that of breast milk;
- ❑ certain sugar and pastry products; the protein concentrate obtained by ultrafiltration of the whey, has a high foaming capacity allowing to obtain stable foams for the cream preparation of whipped cream type;
- ❑ some non-alcoholic beverages - protein concentrate can be used either as a nutritional supplement or as a clarifying agent.

Protein separation by gel filtration (molecular filtration)

Gel filtration is a procedure for separating whey proteins using molecularly sized pores. Basically, the process consists in passing the liquid, containing the dissolved substances to be separated, through a tank in which a cross-linked dextran gel is deposited, having the structure of a three-dimensional network (*Azzouz, 2002*).

Making whey cheese

Whey cheeses have a high content of protein, mineral salts, vitamins and varying proportions of lactose and fat (*Azzouz, 2002*).

Ricotta cheese

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This type of cheese originates from southern Italy, from where it has spread to many other parts of the globe and is produced from whey, milk, buttermilk or a mixture thereof. In some countries, Ricotta cheese is obtained from acidified whey heated to high temperatures, and in others, from whole or partially skimmed milk. The product is characterised by a soft paste with a fine structure and a slight caramel flavour (Azzouz, 2002).

Concentrated whey cheeses

These cheeses are made mainly in Norway from whey from cow's milk (Mysost), sheep's milk (Gjetost) and whey with added milk fat (Primost). A widespread product in Norway is **Gudbransdalsost cheese**, made from 88% sheep's whey and 12% cow's whey, both concentrated. Primost has a light brown colour, a sweet caramelised taste, a structure and a creamy consistency. Mysost and Gjetost are darker in colour and have a rougher structure (Azzouz, 2002).

Albuminoid cheese (urda)

This assortment is obtained after a similar standard procedure in the initial phase. After removing and boiling the whey, the mixture of protein and whey (20% of the initial whey) is cooled to 25-28°C and seeded with a culture of lactic acid bacteria (2.7% streptococci and 0.3% lactobacilli) (Azzouz, 2002).

The product is mixed vigorously, then introduced into molds and pressed with a force applied progressively for 12-14 hours at 15-18°C. The finished product, with a maximum of 74% water, is packaged and stored at a temperature of 3-5°C. It can be consumed as such, mixed with butter, sugar and flavourings or with cottage cheese (Azzouz, 2002).

Whey demineralization

The use of whey in the food industry is often limited by its relatively high mineral content as well as its excessive acidity (especially if it comes from the manufacture of fresh cottage cheese). In order to remove this shortcoming, it is necessary to partially or completely demineralise whey, an operation performed by ion exchange (passing the whey through two columns filled with ion exchange resins) or by electrodialysis (dialysis process produced under the action of an electric potential difference, electrodes being placed on either side of a membrane) (Azzouz, 2002).

By demineralisation, the nutritional value of whey increases. The main ions removed by demineralisation are sodium, potassium, chlorine, calcium and magnesium; phosphates and citrates are eliminated to a lesser extent because they are found in the form of soluble complexes and their removal by ion exchange or electrodialysis is more difficult.

Demineralised whey can be used as:

- food for infants and children, with a saline concentration as close as possible to that of human milk;
- dietary product for people suffering from various diseases (kidney, high blood pressure, etc.), whey is an important source of lactose and serum protein;
- confectionery product;

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- sugar product.

Whey concentration by reverse osmosis

Reverse osmosis, a method of concentration with the help of very compact membranes, allows the concentration of whey to a dry substance content of approx. 25% (4: 1 concentration ratio). The permeate (hyperfiltrate) that crosses the membrane has low amounts of salts, non-protein nitrogenous substances and simple acids, not raising water pollution problems.

The whey concentration in reverse osmosis systems allows to obtain a concentrate in which the serum proteins are practically intact and a permeate with only traces of protein and lactose.

The concentrated whey by reverse osmosis can be used as a substitute for powdered whey or concentrated whey, as an additive in bakery and pastry technology, in the manufacture of candies and ice cream.

Whey dehydration

Nowadays, the most important way to valorise whole or fractionated whey is to dehydrate it to obtain concentrated whey or powder.

The most widespread and economical form of valorisation is sweet whey powder, followed by acid whey powder.

The whey powder is obtained according to a technology similar to milk powder, the final content of the product in water being about 8%.

Whey powder obtained from whole whey is used:

- ✓ for making pretzels and breadcrumbs, increasing their tender texture;
- ✓ for making croissants and bagels, ensuring good absorption and elasticity of the dough, which facilitates modelling; the finished product has a finer structure, with a fragile core;
- ✓ for producing soup concentrates to intensify flavour, reducing the proportion of spices and increasing their shelf life; the amount used represents 3-30% of the composition of dry soups (expressed in dry substance);
- ✓ for cooked and frozen foods, because it reduces the absorption of fat and the consumption of spices, maintains the freshness and juiciness of the product, ensures the achievement of an attractive colour and prolongs the shelf life by 50%;
- ✓ for preparing food for children;
- ✓ for sugary products (candies, syrups, chocolate);



- ✓ for obtaining frozen puddings and desserts;
- ✓ as animal feed (pigs) mixed with grits (*Nistor and Muntianu, 2016*).

Whey lactose valorisation

Lactose is the main component of the dry substance in whey, and its separation in the purest form is of definite economic interest. For manufacturing lactose there are two basic processes, which depend on the nature of the whey used, namely:

- crystallisation of lactose from untreated whey;
- crystallisation of lactose from whey from which proteins (and possibly salts) have been removed.

To date, lactose is considered the most suitable carbohydrate for the preparation of culture media for the development of molds in the manufacture of antibiotics. This disaccharide ferments more slowly than other carbohydrates, which is an advantage in the process of antibiotic biosynthesis. Cheaper crude lactose can also be used for a series of industrial fermentations (*Azzouz, 2002*).

In the process of obtaining whey lactose, the following by-products are obtained: whey cream, casein granules, molasses and whey protein.

Lactose has multiple uses in the food industry, especially in the manufacture of infant or dietary products.

Lactose is used in the bakery and pastry industry, in the preparation of sugary products whose appearance and structure are improved, in the drying of fruits and vegetables, as well as in the preparation of fruit juices, because it fixes taste and colour.

In the dairy industry, lactose is frequently used in the manufacture of concentrated milk with sugar for sowing for proper crystallization.

Lactose is also a good ingredient in cheese spreads.

The applications of lactose in the preparation of milk-based foods, coffee powder, dry soups and chewing gum are also worth mentioning (*Azzouz, 2002*).

Lactose is also used in many other areas of the food industry, due to its specific properties, such as (*Nistor and Muntianu, 2016*):

- fixing flavours,
- absorption of pigments,
- its contribution in the drying processes (drying support),
- its caramelisation capability,
- its emulsification capability.

Whey is a convenient substrate for the cultivation of yeasts or molds in order to obtain biosynthetic proteins (also called molecular proteins).

Whey lactose can be fermented by specific microorganisms, in order to produce metabolites, such as ethanol, lactic acid and lactates, and other substances with multiple applications and contributes, as a culture medium, in the biosynthesis of vitamins B₂ and B₁₂.

Hydrolysis of lactose into glucose and galactose is another important way to recover whey. The hydrolysis process can be performed by enzymatic pathway or in the presence of acidic species. In this sense, lactose can be hydrolysed by the enzyme lactase. The main products resulting from the reaction are carbohydrates (galactose and glucose) and lactic acid.

Among the chemicals which can be separated from whey, the most important are the lactic acid and the calcium lactate. For this purposes, the pasteurised whey is fermented with thermophilic lactic bacteria resulting in 0.5-0.6% lactic acid, and calcium lactate is obtained by its neutralisation with calcium carbonate.

Lactic acid is used in the manufacture of soft drinks, in some confectionery products, in the processing of leather in the textile industry, in the manufacture of plastics (Azzouz, 2002).

Whey drinks

Whey can also be used in the form of various beverages such as:

Whole whey drinks

For this purpose, sweet whey or pasteurised and possibly bleached and deodorised acid whey can be used, which is then mixed with various ingredients (juices, fruit or vegetable purees, sugar, citric acid, etc.). The whey aroma, especially acid whey, is well associated with the citrus aromas, especially orange. Compared to similar products made from skimmed milk, whey drinks have a lower protein content but a higher vitamin C content (Azzouz, 2002).

Deproteinised whey soft drinks

These drinks can be of two types: unfermented or fermented (before or after protein removal). The processing of whey with proteases causes an increase in the soluble nitrogen content of whey, increasing the nutritional value of beverages.

Whey alcoholic beverages

These drinks are low in alcohol (maximum 1% alcohol), similar to beer or wine. They should be clear and preferably frothy.

Protein drinks

These drinks are characterised by a content of 2.4% fat and 1-1.5% protein, and are obtained by combining whey with vegetable oils, vegetable colloids and sometimes skimmed milk.

2.2. Valorisation of buttermilk

Buttermilk is a fermented dairy drink. Traditionally, it was the by-product liquid left behind after churning butter out of cultured cream.

In the case of sweet cream, buttermilk has a composition similar to skimmed milk which has been heated at high temperatures.

Buttermilk out of sour cream has a lower casein content, which remains partially fixed on the butter granules.

Due to its chemical composition (Table 2.5), buttermilk can be processed into many products for human consumption (*Costin and Lungulescu, 1985*).

Table 2.5. The (average) chemical composition of buttermilk (*Nistor and Muntianu, 2016*)

Components (%)	Types of buttermilk	
	Sweet buttermilk	Acid buttermilk
Water	90.50	90.93
Dry substance	9.50	9.07
Proteic substances	3.20	3.30
Lactose	4.95	4.50
Fat	0.60	0.31
Mineral salts	0.72	0.80

The products that can be obtained from the buttermilk are:

- ❑ buttermilk for consumption;
- ❑ simple buttermilk powder;
- ❑ proteinised buttermilk powder;
- ❑ fermented buttermilk powder;
- ❑ fermented products from buttermilk and soft drinks;
- ❑ buttermilk cheeses (*Nistor and Muntianu, 2016*).

Buttermilk for consumption

Buttermilk is used in human nutrition through direct consumption or in culinary products. This must have special chemical and bacteriological characteristics.

Buttermilk can be used in various culinary preparations in liquid or dehydrated form.

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From buttermilk you can also obtain a series of drinks by mixing it with sugar and flavouring substances (coffee, cocoa) (*Costin and Lungulescu, 1985*).

Buttermilk powder

The buttermilk drying processes have peculiarities depending on the composition and properties of the product subjected to drying and, in particular, on the degree of acidity (*Nistor and Muntianu, 2016*).

a) Dried sweet buttermilk

Buttermilk powder is obtained, in particular, from the by-product resulting from the processing of sweet cream into butter (*Costin and Lungulescu, 1985*).

Buttermilk can be dehydrated both by the film and spraying processes.

The buttermilk obtained by processing the cream into butter is cooled to 4°C and stored in isothermal tanks. In order to be degreased, buttermilk is preheated to 35-45°C, being held for 15 minutes. Buttermilk is then concentrated to 16% dry substance for the film process and to 30-45% in the case of spray drying, then the concentrate reheated to 70-80°C is dried to 3-4% water.

Spray drying, compared to drum drying, allows to obtain a superior product in terms of colour and reconstitution capacity (*Nistor and Muntianu, 2016*).

b) Dried acid buttermilk

Buttermilk is pasteurised at 82°C for at least 16 seconds and then concentrated to 30% dry substance. The product is then cooled to 46°C, seeded with 1-5% *Lactobacillus bulgaricus* and stirred continuously during thermostating. After the acidity is high enough (reaching about 10-12% lactic acid in the powder product), the butter is spray dried, without being preheated, to 86-86.5% dry substance (*Nistor and Muntianu, 2016*).

Uses of the buttermilk powder:

In recent years, the amount of buttermilk powder used for human consumption has increased progressively. Due to its chemical composition as well as its sensory properties, buttermilk powder has multiple uses in the food industry:

- ❑ for baking - the amount of sweet powdered buttermilk used in baking processes is between 2 and 15%. This addition improves the taste, structure, appearance, nutritional value and freshness of these products.
- ❑ in the dairy industry - it is used in the manufacture of low-fat ice cream, reconstituted milk and cream for the manufacture of cream cheeses.

- in sugar industry - buttermilk powder containing approximately 1.6% lecithin has a good emulsifying effect in the manufacture of milk chocolate and other sugar products. The addition of buttermilk powder improves the aroma and nutritional value of the products, but it delays the crystallisation process (*Macoveanu et al., 2005a*).

Buttermilk fermented products and soft drinks

For the preparation of these products, buttermilk must be free of contamination bacteria (butyric, coliform, putrefactive). It will have a natural taste and a maximum acidity of 21°T, for sweet butter and 35°T, for fermented cream butter (*Costin and Lungulescu, 1985*).

In order to be used it in manufacturing, buttermilk is carefully filtered to retain all suspended particles (fat, protein) and pasteurised at a temperature of at least 85°C maintained for 10-15 minutes.

Soft drinks are prepared from fermented buttermilk to which sugar syrup, flavourings, etc. are added (*Nistor and Muntianu, 2016*).

Buttermilk cheeses

Buttermilk has a milk-like protein content and can be a raw material for cheese-making.

For cheese-making, buttermilk can be used as such or mixed with skimmed milk in a proportion which is determined by their acidity. There can be prepared low-fat cow's cheese, dessert and appetizer cheeses, telemea brined cheese and melting cheese. Attempts have also been made to obtain hard cheeses (*Macoveanu et al., 2005a*).

Zaroproten

The main steps in obtaining *Zaroproten* product are:

- obtaining vegetable puree;
- obtaining the concentrated buttermilk;
- making the mixture;
- dehydration of the mixture.

Zaroproten is intended for use in children and infants over 3 months of age. It is a fine, homogeneous, yellow powder with a pleasant odour and taste. It is an important source of provitamin A and is recommended in the diet of young children (*Costin and Lungulescu, 1985*)

2.3. Valorisation of skimmed milk

Skimmed milk (non-fat milk) is that milk in which the fat content has been reduced without changing the other components.

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Among the milk by-products, skimmed milk has the highest protein content, which represents about 40% of its dry substance content. The composition of skimmed milk is shown in Table 2.6.

Table 2.6. Average composition of skimmed milk (*Costin and Lungulescu, 1985*)

Components of skimmed milk	Concentration, (g/100g)
Dry substance	9.1
Nitrogenous substances	3.5
Lactose	4.9
Fat	0.05
Mineral substances	0.6
Potassium	0.140
Calcium	0.125
Chlorine	0.103
Phosphor	0.096
Sodium	0.056
Magnesium	0.012
Sulfur	0.025

Nitrogenous substances are represented by:

- casein (milk-specific protein) 2.6%;
- serum proteins (whey proteins) 0.7%;
- non-protein nitrogenous substances.

Milk proteins have a high biological value and are ranked only after the proteins in chicken eggs and ahead of proteins in beef (*Costin and Lungulescu, 1985*).

The concentration of carbohydrates (lactose) is very close to that of whole milk, because in the fat separated from whole milk only traces of lactose pass.

The fat concentration is generally below 1%, depending on the technical condition of the centrifugal separator with which the degreasing operation is performed.

The concentration in saline substances is similar to that of whole milk, skimmed milk is an important source of potassium and calcium for food.

The density of skimmed milk has a higher value compared to whole milk which is due to the absence of cream which has a subunit value.

By various processes for processing skimmed milk, from this by-product, dietary milk, sweetened and flavored, skimmed milk powder, fresh and matured diet cheeses, casein and protein derivatives in powder form, acidic dairy products or delactose milk can be obtained.

Skimmed milk for consumption

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Skimmed milk is used worldwide as a dietary food, being recommended especially for patients with stomach problems, those with liver disorders or cardiovascular diseases.

Due to the high nutritional value, especially given by proteins that contain all the essential amino acids and, in varying proportions, all water-soluble vitamins, being also a good source of calcium salts.

Skimmed milk is promoted in the form of pasteurised or sterilised milk. In order to improve the sensory quality, sugar, cocoa, coffee, coffee substitutes, fruit essences and food colouring are added in the skimmed milk obtaining products approved by consumers (*Nistor and Muntianu, 2016*).

Concentrated skimmed milk

This category of skimmed milk products includes:

a) Sugar-free concentrated skimmed milk

It is obtained by simply concentrating skimmed milk in evaporators under vacuum or by reverse osmosis. This product serves as a source of dry substance in the manufacture of ice cream, fermented dairy products, bakery and candy. The product has at least 20% dry substance.

b) Concentrated skimmed milk with sugar

This type of milk is a product obtained by concentrating skimmed milk, when sugar is added. The product contains 30% milk dry substance and 42% sugar

Skimmed milk powder

Skimmed milk powder is the product obtained by drying concentrated skimmed milk. The moisture content of skimmed milk powder is 3-4%. Under these conditions, the product can be stored for about 1 year in airtight packaging at temperatures below 21⁰C.

Skimmed milk powder is most often used in the food industry as a by-product, being used in the manufacture of dairy products (yogurts, ice cream, some cheeses), in the meat industry (it is part of preparations such as salamis, sausages, rolls, cream sausages), in the bakery industry to increase the nutritional value of bread, preservability, but also to the printing of the caramel taste of the shell, to the manufacture of biscuits, wafers and various glazes, to the manufacture of chocolate and candies.

Dietary acid dairy products

These products (yogurt, kefir, acidophilic milk, drinking milk) are obtained according to technologies similar to those obtained from whole or standardised milk, having the same sensory characteristics, the differences being in terms of fat content and total dry substance.

These products are indicated for people with high blood cholesterol, as well as for people with liver disease (*Costin and Lungulescu, 1985*). By adding sugar, fruit juices, gelatin, are

obtained acidic dietary dairy products with higher nutritional value, respectively with superior sensory properties (lactofruit, fruit-flavored yogurt).

Skimmed milk cheeses

The following types of cheese can be obtained from skimmed cow's milk:

a) Light cow's cheese

This product is a dietary one that is recommended for nutritional diseases and especially for liver diseases. Light cow's cheese also serves as a semi-finished product to obtain fat cheese by adding cream (*Costin and Lungulescu, 1985*).

b) Curd cheese

Curd cheese is obtained by coagulating skimmed milk with rennet (an enzyme found in the stomach mucosa of very young calves and lambs, fed exclusively on milk) at 28-30°C for 30 minutes, the curd being processed with the harp and left for half an hour for separating the whey.

After removing whey, curd cheese is washed with lukewarm water to reduce acidity, after which it is drained into a mold under pressure for a maximum of 12 hours. After pressing, the drained curd cheese is dried and can be used immediately as a semi-finished product to obtain various products or further processed for preservation (*Nistor and Muntianu, 2016*).

c) Cottage cheese

It is a cheese of soft consistency, of granular structure, with a content of about 20% dry substance, being consumed as such or mixed with fruits or vegetables (*Nistor and Muntianu, 2016*).

d) Skimmed milk cheese

It is made according to a technology similar to that of ordinary cheese, the product having a fine paste consistency, with a slightly yellowish colour (*Botiș Nistoran, 2014*).

Casein

Casein, a milk-specific protein, can be separated from milk by precipitation with enzymes, acids or calcium chloride.

The following types of caseins can be obtained from the coagulant agent:

- acid casein: which is obtained by precipitating skimmed milk with a mineral acid (hydrochloric acid, sulfuric acid) or organic acid (lactic acid);
- sweet casein: resulting from the action of curd on skimmed milk, called rennet casein;
- modified casein (low viscosity): which is produced by treating skimmed milk with proteolytic enzymes and an acid (*Nistor and Muntianu, 2016*).

Uses of casein in the food industry:

- addition to meat preparations;



- wine and beer clarification;
- protein-rich dairy products;
- obtaining protein hydrolysates;
- addition to bakery and pastry products;
- addition to dietary products and for children;
- paper industry;
- manufacture of water-based paints;
- adhesive production;
- plastics production (*Botiș Nistoran, 2014*).

Caseinates

Caseinates are products obtained from dry casein, treated with neutralizing agents.

Acid casein in alkaline solutions is used in the production of glues, paper, binders in chalk pastes, in the finishing of animal skins, as well as in the preparation of solutions for photographic paper and films (*Costin and Lungulescu, 1985*).

Sodium, potassium and calcium caseinates are mainly used in the food industry .

Use of caseinates in the food industry:

- in the manufacture of ice cream
- obtaining modified dairy products;
- obtaining coffee bleach;
- imitation cream;
- obtaining sauces and soups;
- as an additive in meat preparation;
- for obtaining similar meat products;
- as an addition to the manufacture of biscuits, bread, pastries;
- as an additive for obtaining protein-enriched products (*Botiș Nistoran, 2014*).

Coprecipitates

Coprecipitates are complexes between caseins and serum proteins (between k-casein in the structure of casein mycelium and β -lactoglobulin), which are formed when milk is heated, complexes that precipitate with an acid, chloride (calcium chloride) or both (*Costin and Lungulescu, 1985*).

Coprecipitates have the following uses:

- addition to the manufacture of dietary bakery products;
- obtaining imitation meat products;
- addition to the production of melted cheeses;

- addition to baby foods based on vegetables and fruits (*Botiș Nistoran, 2014*).

3. VALORISATION OF THE WINE INDUSTRY BY-PRODUCTS AND WASTES

Grapes, as a raw material for industrialisation, are used to obtain food products such as fresh grape wine pressing, juice, wines, distillates, etc. (Figure 3.1) (*Dabija, 2002*).



Figure 3.1. Grapes - raw material for obtaining wine [75]

Wine is a drink obtained by partial or total alcoholic fermentation of sugars from crushed grapes or wine pressing (Figure 3.2.).

Wine pressing is the liquid resulting from fresh grapes, by free draining or by authorised physical processes.

Alcoholic fermentation is an anaerobic process by which fermentable carbohydrates are metabolised by redox reactions under the action of yeast enzymatic equipment in the main products, ethyl alcohol and CO₂. Enzymes are chemicals which contribute to the breakdown of sugars (*Dabija, 2002*).



Figure 3.2. Wine [76]

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Depending on the processes and technological operations used for grapes to be turned into wine and their sequence of development, two basic technologies are known, namely:

- technology for obtaining white wines (white vinification);
- technology for obtaining red wines (red vinification).

The essential difference between the two technologies is that, in the case of white wines, the wine pressing is separated from the pomace as quickly as possible and fermented separately, while in the preparation of red wines the wine pressing is fermented on the pomace.

In the wine industry in the technological stages for obtaining wine as a finished product, a series of by-products and wastes results for which the mass weight, the chemical composition and the vegetal structure vary in wide limits (Figure 3.3) .

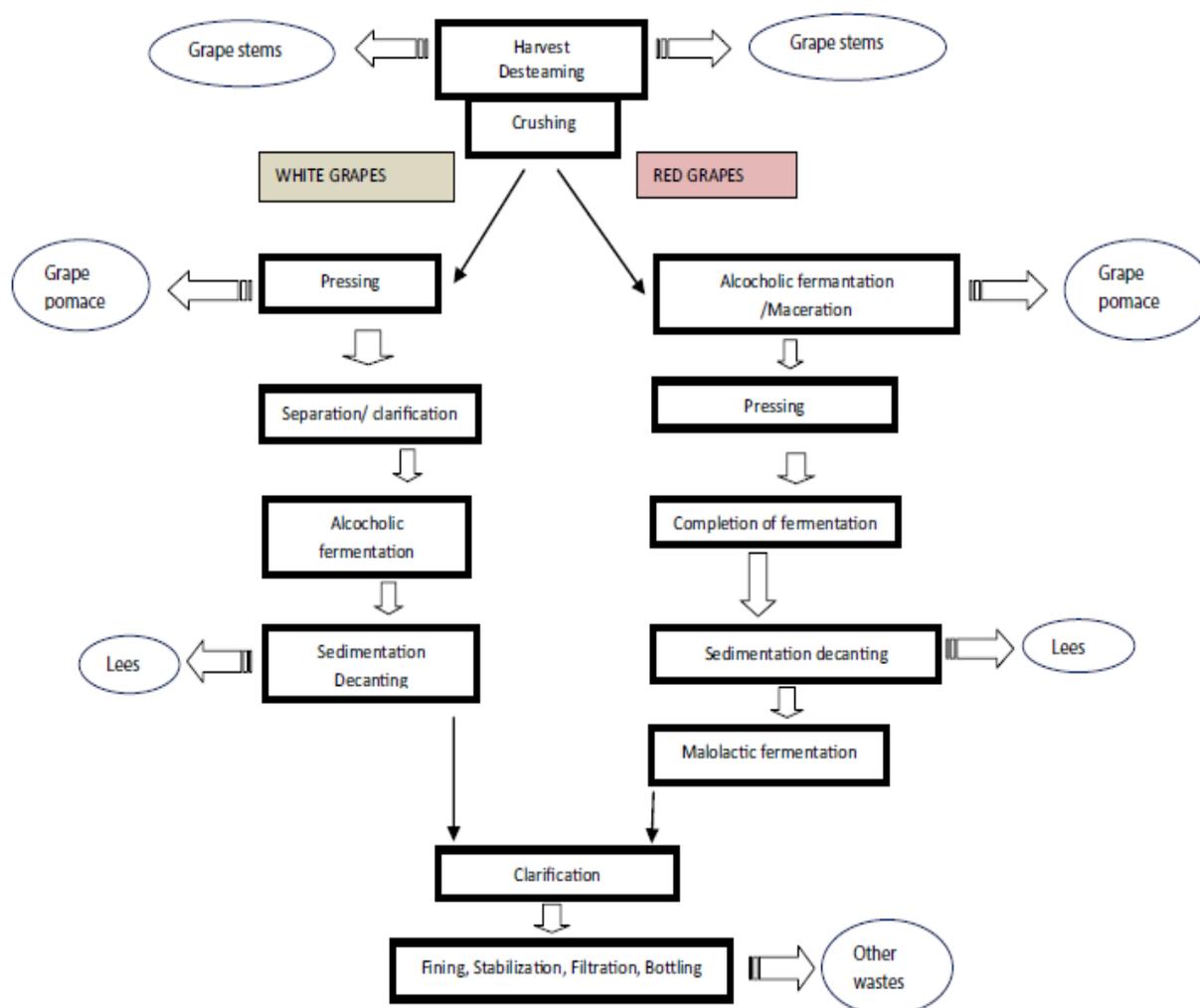


Figure 3.3. Grape by-products generation during wine production process (Kalli et al., 2018)

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The complex valorisation of wine by-products is determined by their large share and substances, the active principles they contain, useful to different industries (*Botiș Nistoran, 2014*).

The wine industry results in a series of by-products and wine waste, such as:

- *bunches (grape cluster)*: form the skeleton of the grape and are separated before pressing;
- *pomace*: represents the solid fraction resulting from pressing marc. *Marc* is the product that results after the separation of the rava wine pressing. The rava wine pressing is the liquid which flows freely by gravity from the crushed grapes or by induced draining.
- *wine yeasts*: represents the deposit which is formed at the bottom of the vessels following the alcoholic fermentation, the clarification of the wine pressing before fermentation, storage and preservation of the wines, the treatments that are applied to the wines; *Yeasts* - are living microorganisms which turn sugars wine pressing into alcohol and carbon dioxide.
- *deposits or sediments*: which are formed after the alcoholisation of wine and wine pressing;
- *deposits from the wine clarifying*: which are formed on the occasion clarification of wine by clarifying; *Clarifying* is the operation of wine clarification by adding substances capable of attracting, binding and entraining in their fall the impurities that cause the wine disorder.
- *tartar (lime stone)*: which is deposited on the walls of the vessels during the fermentation of the wine pressing and the storage of the wine;
- *druff*: resulting from the distillation of cognac wine.
- *ethyl alcohol*: obtained by distilling pomace and wine yeasts, after refining is used in the wine industry or in other industries;
- *tartaric acid and tartrates*: they have a wide use in numerous industrial branches: chemical, pharmaceutical, radiotechnical, food, textile, polygraphic, etc .;
- *seed oil*: it can be used in the chemical industry, and the refined one in the food industry, its nutritional qualities being recognised due to the content of essential fatty acids;
- *tannin*: a compound found naturally in the skin, bunches and seeds of grapes which in large quantities is responsible for the bitterness and astringency of the wine;
- *food colouring*: widely used in the food industry, when colouring acidic foods;

- *grits*: are the result of the extraction of oil and tannin, as well as depleted skins, are used to obtain animal feed (*Nistor and Muntianu, 2016*).

The high value of these products and the current needs to be introduced in the economic circuit have imposed extensive research in all countries with wine production, research which has resulted in studies and technologies for valorisation in advantageous technical and ecological conditions (*Dabija, 2002*).

3.1. Valorisation of pomace

Pomace results from the pressing of white or pink grapes and non-alcoholic products, respectively from the pressing of fermented berries from red grapes (Figure 3.4) (*Dabija, 2002*).

Pomace represents solid residues separated from wine pressing or wine (fermented marc) and composed of skins (55-65%), seeds (18-25%) and liquid residues (wine pressing, wine); pomace sometimes also includes bunches (*Botiș Nistoran, 2014*).



Figure 3.4. Grape pomace [77]

Depending on the technology applied, pomace can be:

- sweet pomace (fresh, unfermented): resulting directly from the pressing of fresh grapes;
- fermented pomace: resulting from pressing the fermented pomace during storage (*Dabija, 2002*).

According to its colour, pomace can be:

- white pomace;
- red pomace.

The chemical and physical composition of pomace is closely related to the nature and quality of grape varieties and the way in which the wine pressing is obtained. Thus, the pomace in warm regions is always richer in sugars, alcohol and sometimes in tartrates (*Nistor and Muntianu, 2016*).



In addition to skins and seeds, sweet pomace also contains a certain amount of wine pressing, and fermented pomace contains a relatively small amount of wine explained by the applied process and precipitates formed from polyphenol tartrates, proteins, mineral salts, pectic substances, microorganisms, etc.

The physical-structural composition of the pomace is presented in Table 3.1.

Table 3.1. Physical-structural composition of pomace (reported to dry substance)
(Nistor and Muntianu, 2016)

Components	Quantity (%)
Skin	37-39.5
Pulp	30.5-32.5
Seeds	28-29.5
Bunch	1-1.5
Different residues	0.2-0.25

The chemical composition of the seeds contains lipids, tannins, cellulose and proteins. The composition is shown in Table 3.2.

Table 3.2. Chemical composition of pomace (Botiș Nistoran, 2014)

Components	Quantity (%)
Water	57.5
Alcohol	3.34
Ash (tartaric salts)	2.55
Nitrogen	0.924
Alcohol-soluble substances	4.51
Cellulose	31.58

Due to the valuable components of pomace (carbohydrates, ethyl alcohol, tartaric salts and seed oil), it can be valorised by obtaining additional products of special value (Figure 3.5.).

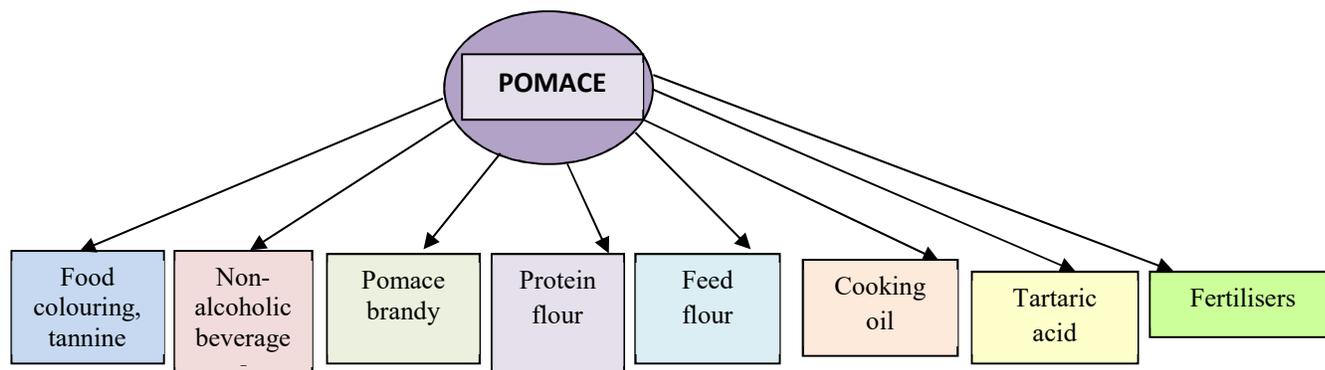


Figure 3.5. Ways of pomace valorisation

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Therefore, about 3 liters of alcohol, 1.5 kg of tannin from 100 kg of pomace can be obtained, and the residue can be a valuable material for animal feed.

From the complete processing of sweet pomace, the following can be obtained:

- *pomace alcohol* (or pomace brandy);
- *seeds*:
 - from which the cooking oil is extracted;
 - tannin is extracted from skimmed cakes and from which protein flour is stored;
- *skins* for feed (*Botiș Nistoran, 2014*).

Pomace brandy

Pomace brandy is an alcoholic beverage obtained by distilling pomace after the fermentation phase (*Dabija, 2002*).

Obtaining pomace brandy comprises the following steps:

- reception of raw material;
- washing;
- pressing on the continuous press;
- filtration and fermentation of the sludge;
- distillation of alcoholic vapours.

Sweet pomace, resulting from the processing of white grapes, consists of solid particles separated from the wine pressing by pressing, being made up of skins, seeds, fractions and remnants of the core tissues (*Botiș Nistoran, 2014*).

Distillation as a method of obtaining ethyl alcohol must be carried out slowly in order to obtain a pure brandy in comparison with that obtained by rapid distillation, which can also lead to the burning of the pomace, to unpleasant tastes and odours of the brandy.

In order to obtain brandy from the pomace, discontinuous installations for direct fire heating (immersed pomace) or indirect (non-submerged pomace) or direct or indirect steam heating are used (*Botiș Nistoran, 2014*).

Cooking oil and tannin

Dried pomace contains on average between 40-65% seeds, whose fat content varies between 12-22%, depending on the grape variety, the degree of maturation and the pedoclimatic conditions of the vine (*Nistor and Muntianu, 2016*).

The seeds, depending on the grape variety, have a share of 2-6% of the grain mass, respectively 1-3% of the grape mass and 20-25% of the pomace mass.

The seeds are normally separated from the exhausted pulp after distillation, or after the separation of the tartrates, conditions in which the quality and quantity of the extracted oil are significantly reduced (*Dabija, 2002*).



Figure 3.6. Grape seed oil [78]

The oil content of dried grape seeds is 10-20% and depends on several factors, including: variety and place of production.

In order to obtain cooking oil, characterised as dietary oil due to its high content of essential acids, the known schemes of the vegetable oil industry are applied, with the following particularities:

- crushing the seeds to ensure particles of about 1 mm,
- the extraction temperature should be around 35°C;
- the optimal solvent is the extraction gasoline-acetone mixture (3: 2);
- bleaching and purification are done with activated carbon added right to the extraction (0.25% compared to grinding) to avoid oxidation of fats (*Botiș Nistoran, 2014*).

Uses of pomace seed oil

- in the varnish and paint industry (semi-drying oil);
- in perfumery;
- in the pharmaceutical industry;
- in the soap manufacture.

The cakes resulting from the removal of the solvent are subjected to extraction with ethyl alcohol of 40-60% vol. concentration, at a temperature of 70°C, for a minimum of 3 hours.

The tannin solution is distilled to recover the alcohol, concentrated to a pasty consistency, dried and ground to obtain **enotanin powder** (Figure 3.7.).



Figure 3.7. Tannin [79]

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Cakes depleted in fat and tannins are subjected to frying, grinding and removing fibers, obtaining a feed rich in protein (about 26%) - **protein flour** (Macoveanu *et al.*, 2005b).

Feed flour

After separating the seeds from the dry flour, the remaining skins are shredded and the flour obtained is weighed and packed into bags.



Figure 3.8. Feed flour [80]

The feed flour shows the chemical composition in table 3.3. relative to the dry substance.

Table 3.3. Chemical composition of feed flour (Nistor and Muntianu, 2016)

Components	Quantity (%)
Crude protein	10.56
Digestible protein	1.58
Celulose	18.66
Fats	4.47
Non-nitrogenous extractive substances	59.85
Raw ash	5.89
Calcium	1.06
Phosphor	0.22

In terms of organoleptic properties, feed flour must be free of traces of mold, brownish in colour, with a pleasant smell of pomace (Botiș Nistoran, 2014).

Calcium tartrate obtained from fermented pomace

In order to obtain calcium tartrate, the marc (which remains from the grapes after squeezing their juice) and the solution from the first boil are mixed. Sulfuric acid is used to extract the tartaric compounds.

Tartrates are used as stabilizing agents in meat preparations (sausages), as well as in melted cheeses, in the proportion indicated for citrates (Botiș Nistoran, 2014).

Preparation of food colourants

As a raw material for obtaining the enocolorant, fermented red pomace is used, with a minimum content of 1.5 g/kg anthocyanins, and sweet red pomace, obtained from the vinification of black grapes.

In order to avoid oxidation and polymerization of anthocyanins, the pomace must be processed immediately after pressing, possibly stored not more than 2 months, the pomace being immersed in a solution with a SO₂ concentration of 0.2% (*Botiș Nistoran, 2014*).

Enocolourants are used, replacing synthetic red dyes:

- in the colouring of acidic food products (toffees, marmalade products, carbonated drinks);
- in the pharmaceutical and cosmetics industry (*Nistor and Muntianu, 2016*).

A product similar to raw enocolorant can be obtained from unfermented white grape pomace - **pomace concentrate**.

Pomace concentrate can be used to correct yellow colour and to enhance soft drinks and alcoholic beverages (*Macoveanu et al., 2005b*).

Use of pomace for the preparation of non-alcoholic beverages

The resulting pomace in the preparation of red wine is loosened and pasteurised at a temperature of 90-100°C; after cooling and storage, it is boiled with water and filtered, with sugar and citric acid being added to the filtrate.

The filtration is performed hot, and sugar is introduced into the obtained extract, after removing the acid potassium tartrate (wine stone). The coloured infusion obtained is used directly with the addition of carbonated water (*Nistor and Muntianu, 2016*).

Preparation of pomace and bunch fertilisers

If the pomace, after the extraction of alcohol and tartaric compounds, is not used for the preparation of feed, it must be used together with the bunches for compost.

3.2. Valorisation of wine yeast

Wine yeast is the residue that is deposited after alcoholic fermentation and during storage of wine in containers or resulting from the application of authorised treatments, as well as the filtration or centrifugation of wine (*Botiș Nistoran, 2014*).

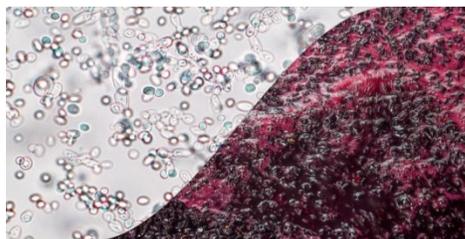


Figure 3.9. Wine yeast [81]

Yeasts separated by decantation contain significant amounts of wine, which are extracted by filtration, in press filters. Decantation consists of pouring the wine from one barrel to another, after fermentation, in order to make it clear (by separating it from the yeast that has deposited at the bottom) (*Dabija, 2001*).

The amount of yeast obtained in winemaking depends on the quality of the grapes and on the manner the wine pressing is obtained by pressing it. Thus, under normal conditions, the yeast represents 5-8% and can reach 12-15% when using the continuous pressing process (*Macoveanu et al., 2005b*).

After fermentation, the yeasts and deposits formed after the alcoholization of the boiling wine pressing are separated from the wines on the occasion of the first decanting, together with the remains of skins and other suspended substances. Wine decantation is the operation of transferring wine from one vessel to another in order to separate it from the yeast deposited at the bottom of the vessel (*Dabija, 2001*).

During the wine clearing process, in winter, substances are deposited, after which wine becomes clear. After clearing, the second process takes place, and the deposits are mixed with yeasts, which are then processed according to the same technology (*Nistor and Muntianu, 2016*).

The chemical composition of yeasts is shown in table 3.4.

Table 3.4. The chemical composition of wine yeasts (*Nistor and Muntianu, 2016*).

Components	Quantity (%)
Water	75
Mineral substances	5-10
Glucids	25-50
Proteic substances	30-75
Fats	2-5

According to the percentage of dry substance content, yeast sediments are divided into the following categories:

- liquid yeast (12%);
- thick yeast (12-30%);
- pressed yeast (30-60%).

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The amount of liquid wine yeasts is variable and depends on the yeast type, the sugar content of the initial wine pressing and the fermentation conditions (*Botiș Nistoran, 2014*).

The resulting wine yeast is diluted with water and pumped to the fermentation and distillation plants to recover the ethyl alcohol from the composition. Distillation separates the **yeast brandy**.

The marc from the distillation can be used to extract calcium tartrate by the following operations: dissolving the tartaric compounds obtained by separating the solution from insoluble mixtures, neutralising the solutions, precipitating the calcium tartrate, washing and drying it.

The yeast left from marc filtration can be used as feed, both wet and dry. For the preparation of dry feed, the yeast draff is washed to a minimum pH of 4.5-5, then pressed and dried in roller dryers or other dryers.

From yeast deposits, in addition to ethyl alcohol and tartaric acid, other by-products can be obtained such as:

- enanthic ester (brandy oil);
- yeast concentrates and autolysates;
- amino acid products;
- vitamin products (*Botiș Nistoran, 2014*). .

Enanthyl ester (brandy oil) is used successfully in the food industry and in perfumery; used to enhance the bouquet of champagne and brandy (*Botiș Nistoran, 2014*).

3.3. Tartar (wine stone)

Tartar (wine stone) consists of potassium acid tartrate crystals (approx. 80%), calcium tartrate crystals (approx. 5%) and impurities (yeasts, bacteria, coloured substances, dyes and tannins).

Tartar is formed on the inner wall of the vessels, being more abundant on rough surfaces (barrels and concrete tanks). Wine stone removal should be performed annually or at most every two years, as the deposit is an outbreak of infection with bacteria and mold.

Tartar can be used as such in the preparation of tartaric acid, the solutions used for chemical extraction are neutralised with calcium chloride and lime milk, obtaining calcium tartrate from which **tartaric acid** can be obtained by acidification.

Uses: Tartaric acid is widely used in the food industry: canned vegetables, sugar products, bakery, soft drinks, winemaking, pharmacy, medicine and chemical industry (*Macoveanu et al., 2005b*).

3.4. Carbon dioxide

The carbon dioxide produced during fermentation is the most important by-product, but with a sporadic or experimental recovery. In order to capture carbon dioxide, it is necessary for the wine pressing to be fermented in closed tanks, from where the gas is stored in gas tanks and then compressed.

Compressed carbon dioxide can be used both in the wine industry, for its preservation under the cushion of carbon dioxide or in the manufacture of sparkling wines (*Macoveanu et al., 2005b*).

3.5. Valorisation of qualitatively altered wines in obtaining vinegar

Food vinegar is an acetic fermentation product obtained by enzymatic oxidation of ethyl alcohol from some liquids with a moderate alcohol content (*Botiș Nistoran, 2014*).

Vinegar is an aqueous solution of acetic acid, which depending on the raw material from which it is obtained also contains: carbohydrates, ethyl alcohol, tannins, dyes, nitrogen compounds, vitamins, mineral salts, etc.

Currently, vinegar is obtained from white and red wines, beer and malt, cider, fruit (apples and pears, bananas, mangoes, citrus fruits, coconuts), and in Asia from rice alcohol.

Both white and red wines can be used to make wine vinegar (Figure 3.10).



Figure 3.10. Wine vinegar [82]

In the manufacture of wine vinegar, qualitatively altered wines are generally used, but not all spoiled wines are suitable for the production of vinegar, wines that have a beginning of vinegaring or that have begun to spread are allowed (*Nistor and Muntianu, 2016*).

In order to obtain vinegar, wines must be clear, filtration is one of the most important operations of vinegar production. Otherwise the acetic bacteria act very hard, and the ferment develops in a viscous form inside without producing a uniform acidification.

For acetic fermentation (aerobic fermentation), the *Acetobacter bacteria* are used, which are differentiated by the alcoholic strength they support (% v/v), the maximum production of acetic acid achieved (% m/v) and the fermentation temperature (*Nistor and Muntianu, 2016*).

4. VALORISATION OF THE BEER INDUSTRY BY-PRODUCTS AND WASTES

Beer is a low-alcohol, non-distilled beverage, obtained by alcoholic fermentation, with the help of yeast, a wort made from malt, water and hops, the malt being able to be partially replaced with unmalted cereals (corn, broken rice, barley) and possibly enzymes (*Figure 4.1*) (*Dabija, 2002*).



Figure 4.1. Beer [83]

The main characteristics of beer are: alcohol content between 1.5-6%, carbon dioxide between 0.2-0.5%, extracts (dextrin, maltose, protein substances, tannin, mineral salts, organic acids) between 4, 5-9%, pH between 4.2-4.4, intense foaming, characteristic taste and smell of malt and hops. In relation to the alcohol content, the energy value of beer is 282-570 cal/l, being known for its physiological and therapeutic properties.

Brewing technology comprises three main phases: malt manufacturing, beer wort production, beer fermentation and conditioning (*Figure 4.2*).

The main raw materials used in the beer industry are barley, water and hops, also adding unmalted cereals and selected yeast crops.

Malt is a product obtained by germinating barley seeds under special conditions, in order to accumulate enzymes and disintegrate macromolecular substances in the grain.

Hops is a plant with yellow-green flowers, whose aromatic and bitter female inflorescences are used in brewing. Due to the compounds it contains in the cones, hops largely influences the taste, aroma, colour, clarity and preservation power of beer.

The by-products obtained in the beer industry are the following:

- cereal waste;
- malt germs (rootlets) ;

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- malt draff;
- protein sediment (trub);
- primary fermentation foam;
- yeast;
- carbon dioxide.

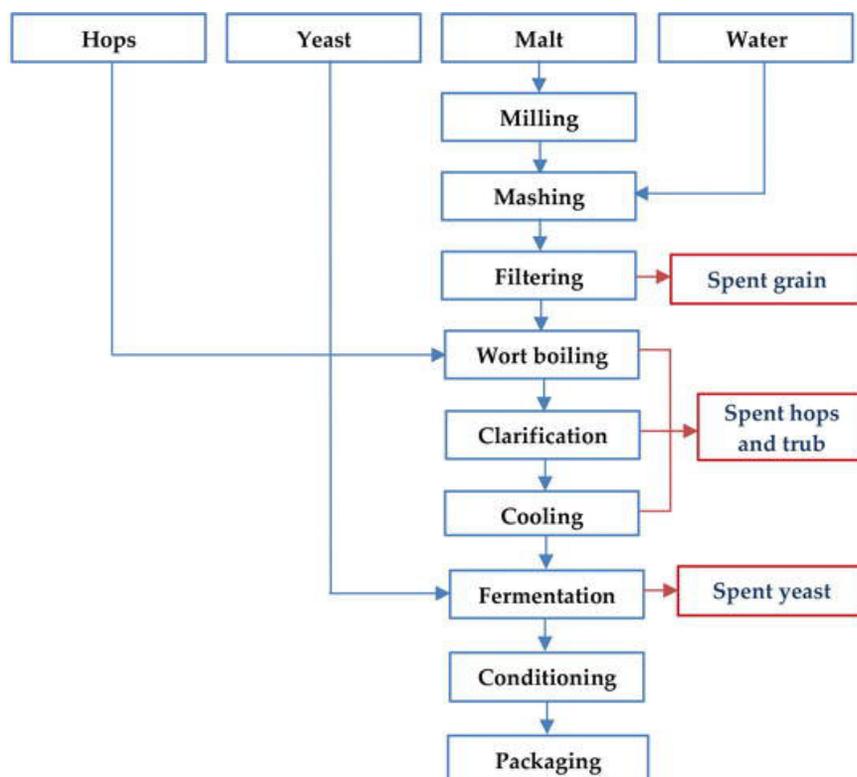


Figure 4.2 Schematic representation of the brewing process and points where the main by-products are generated (Karlović *et al.*, 2020)

4.1. Cereal waste and malt germs

Cereal waste comes from the cleaning, sorting and soaking of barley, as well as from the drying, degermination and polishing of malt.

From the barley cleaning operation, broken grains, vetch, chaff, tares and foreign bodies (dust, sand, earth) are obtained as waste. This waste appears at sorting and represents up to 1.5% of the initial barley. All grain waste is used as feed.

Malt germs (rootlets) are obtained from the germination of malt.

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The malt rootlets are in the form of thin yellow-brown filaments.

Malt germs being high in protein, vitamins, provitamins and other growth stimulants, are used in the preparation of molasses for the manufacture of feed yeast and in the manufacture of lactic acid by fermentation.

Malt germs is also used for feed purposes and for forming culture environments in the compressed yeast industry. Malt feed flour is also used in the bakery industry.

4.2. Malt draff (brewery mash)

Malt draff is the waste which results in large quantities in breweries and is obtained after filtering the beer wort at the boiling section. The draff resulting after boiling has a humidity of approx. 80%, sweet taste and malt smell. The composition of the malt draff is given in table 4.1.

Table 4.1. Composition of the malt draff (*Nistor and Muntianu, 2016*).

Components (%)	Draff		
	Wet	Dry	Reported at dry substance
Water	78.30	9.00	-
Proteic substances	6.63	25.50	28.00
Fat substances	1.70	7.50	8.20
Non-nitrogenous extractive substances	9.72	37.30	41.00
Celulose	5.10	16.00	17.50
Ash	1.20	4.60	5.20

Draff contains a special amount of protein substances and non-nitrogenous extractive substances, having a high feed value.

The degree of assimilation of protein substances reaches 71%, of fatty substances 88%, of non-nitrogenous extractive substances 60%, and that of cellulose 40-80% compared to the draff content (*Nistor and Muntianu, 2016*).

4.3. Protein sediment (trub)

The protein sediment (trub) is a by-product that appears in the beer wort after boiling with hops, obtaining the **hot trub**, continuing in the cooling phase forming the **cold trub** (*Nistor and Muntianu, 2016*).

Its separation begins with the removal of hops cones, where part of it is retained on them, but most of it accompanies the cooling wort. Here, following the cooling process, another part of the protein precipitates and is separated.

The separation of the trub from the wort depends on the machine and the operations in the cooling phase. The amount of trub obtained depends on a number of factors, such as: the quality of the malt, the degree of grinding of the malt, the amount of hops used, the concentration of the wort boiled with hops, the duration and intensity of cooling.

The chemical composition of the trub is varied: it contains albuminoids, tannins, hops resins and minerals (*Botiș Nistoran, 2014*).

a) Warm or hot trub formation

The formation of the warm tube takes place during the boiling of the wort with hops, as a result of the coagulation of proteins under the action of heat and of the polyphenols in hops.

b) Cold trub formation

The formation of the cold trub takes place during the cooling of the wort boiled with hops starting at the temperature of 55 - 70°C and until sowing it with yeast.

The cold trub consists of much finer particles 0.5-1 µm.

Uses of the trub:

The protein sediment as such can be used primarily as feed, but only as a small amount addition to other feed. It is also used to feed fish in ponds and as a fertilizer.

In order to valorise the tube resulting from the cooling of wort, the following are taken into account:

- reuse of protein sediment in a new mold in order to increase the extraction yield, to reduce the hops consumption and to improve the wort quality;
- recovery of the wort from protein sediments and its reuse in the beer brewing, following that the coarse solid part is dried in mixture with the borhot;
- the use of protein sediment for other purposes, such as: obtaining alcoholic distillates for food use (*Nistor and Muntianu, 2016*).

4.4. Yeast

Recovery of yeast from primary and secondary fermentation

Before re-use, the harvested yeast beer wort be washed in order to remove impurities from tubers, hops resins, dead cells and other autolysis products which deteriorate the taste and provide a favorable nutritional environment for beer spoilage bacteria (*Dabija, 2001*).

In most cases, yeast is passed over an oscillating sieve and washed with cold water. Storing the yeast until reuse is usually done under chilled water of 4-5⁰C, in such conditions the yeast can be stored for up to 3 days (*Nistor and Muntianu, 2016*).

The collected brewer's yeast is pressed to recover the beer, and the shelf life in the pressed state is at least 3 times longer than in the suspended state, even after a rigorous washing and disinfection.

Brewer's yeast in the form in which it is harvested has the following chemical composition (Table 4.2).

Table 4.2. Chemical composition of beer yeast (*Dabija, 2001*)

Components	Quantity (%)
Water	85-90
Dry substance	10-15
- proteic substances	51-58
- glucids	9-11
- fat substances	2-3
- nitrogenous substances	25-30
- mineral substances	8-9

In addition to the high protein content, which exceeds half of the dry substance, yeast contains a number of vitamins, especially from group B. Yeast also contains a large number of enzymes from different groups.

Although the composition of yeast is particularly valuable, due to its bitterness and the difficulty of removing it, most of the time the valorisation is limited to drying, obtaining a protein compound used for feed purposes.

The most commonly used process for preserving yeast is drying in roller installations.

When used for feed purposes, drying is carried out at steam temperatures in the roller up to 200⁰C.

The yeast intended for pharmaceutical products and for food purposes is dried in installations which operate on the principle of spraying, 150⁰C air is used.

Brewer's yeast is a type of waste which results from the brewing of both the primary fermentation lines and the secondary and maturing fermentation tanks (*Dabija, 2001*).

The yield of yeast in pressed form (approx. 25% dry substance) varies between 0.2-1 kg / hl beer, depending on the yeast species and the technological process applied.

Due to its complex composition, brewer's yeast is recognized as an important factor for nutrition and is used for this purpose because:

- it is considered one of the most complex vitamin concentrates;

- the protein substances contained occupy an intermediate position between those of vegetal and animal nature. In their composition there are found most of the essential amino acids of which lysine represents 10%;

- it is one of the richest sources of lecithin (3-4.5%), which explains the important proportion of phosphorus it contains and which, in the form of P₂O₅, reaches up to 52% of the total mineral substances contained (*Nistor and Muntianu, 2016*).

Uses of brewer's yeast:

Among the uses of yeast, in addition to its valorisation in the beer industry, we can add the following:

- *for feed purposes;*
- *in human nutrition;*
- *for medicinal purposes;*
- *in veterinary medicine*
- *for obtaining vitamin concentrates;*
- *for obtaining plasmolysates;*
- *obtaining hydrolysates;*
- in the manufacture of medical alcohol;
- for obtaining flavourings enriched in flavour enhancers;
- for obtaining invertase and molasses;
- in cosmetics.

4.5. Fermentation foam layer

The foam layer is formed in the primary fermentation process of the beer wort and is composed of hops resins and precipitated protein substances. Before passing the beer to a secondary fermentation, the foam layer formed on the surface of the beer is carefully removed because the bitter resins it contains would make beer too bitter, having an unpleasant taste (*Nistor and Muntianu, 2016*).

The chemical composition of the foam layer is as follows:

- bitter resins: 0.4%
- total protein: 72.0%;
- assimilable proteins: 71.5%;
- ash: 1.2%.

After removing the bitter resins, the foam layer can be used as feed.



4.6. Carbon dioxide

During the beer wort fermentation, CO₂ is released, which also involves small amounts of alcohol, fermentation by-products as well as water from the wort.

Carbon dioxide results in the fermentation process of beer wort in the amount of 3.7 kg for 1hl of fermented wort. Part of this carbon dioxide dissolves in beer, another part is eliminated with air in the first phase of fermentation and another part, approx. 2.8 kg CO₂ / hl of beer wort, can be taken and valorised.

Carbon dioxide as a by-product of beer fermentation can be recovered, purified and used for various purposes as in the case of the alcohol and wine industry.

Carbon dioxide recovered and purified in the form of gas is also used in various operations in the brewery.

Calcium carbonate is obtained using lime as raw material and CO₂ from fermentation.

Ammonium carbonate is obtained by the reaction between CO₂ and NH₃. It is used as an additive to animal feed, in the case of protein-poor food, with a high assimilation coefficient of about 80% (*Dabija, 2001*)

5. VALORISATION OF THE VEGETABLE CANNING INDUSTRY BY-PRODUCTS AND WASTE

5.1. The main by-products and wastes resulting from the vegetable and fruit processing

When processing fruit and vegetables for preservation as sterilized, dried, concentrated, frozen products, etc., a large range of by-products and waste appear at different stages of the technological process (*Botiș Nistoran, 2014*).

The processing of fruit and vegetables results in significant amounts of waste, residues, leftover, rich in nutrients and which, through further processing, can lead to food or auxiliary raw materials.

By-products from fruit and vegetables are leftover like seed, pulp, skin or pomace, accounting to 10–35% of raw mass. Generally, they are used as animal feed or for production of biomaterials, biofuels, biogas, platform chemicals and bio-fertilisers through biological processes (Dilucia *et al.*, 2020).

In Figure 5.1 and Table 5.1. the main by-products and wastes resulting from the processing of the raw material in the fruit and vegetable canning industry are presented.

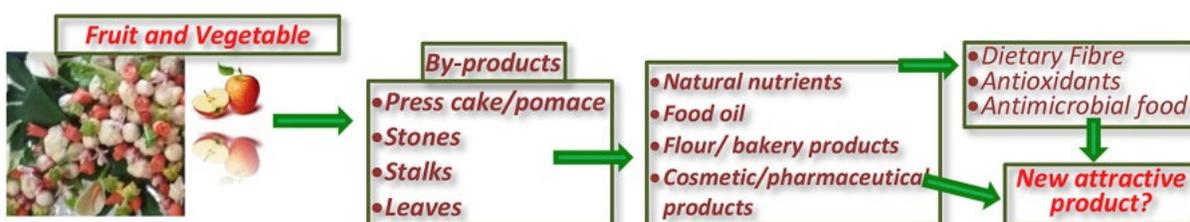


Figure 5.1. Valorisation of fruit and vegetable by-products (Kowalska *et al.*, 2017)

Table 5.1. By-products and wastes resulting from the processing of raw materials in the fruit and vegetable canning industry (Macoveanu *et al.*, 2005a)

Raw material	By-products and wastes	Quantity (%)
Legume		
Green pea	Stalks (mechanised harvesting)	80-85
	Sheaths (manual harvesting)	55-65
Tomatoes	Seeds and peels	7-10
	Seeds, peels and pulp	25-35
	Peels	10-20
Potatoes	Grating (mechanised harvesting)	15-30
	Coji (manual harvesting)	15-25
(Summer) Cabbage	Stalks and external leaves	20-40
(Autumn) White cabbage	Stalks and external leaves	15-25
Green beans	Tips/ends, strings	3-7
Green pepper	Stubs	18-25
Root vegetables	Grating	15-35
Pumpkin root in flowers	Traces of calyx and tails	3-5
Zucchini	Seeds, peels	20-30
Mashrooms	Stems with gills	20-25
Onions	Peels	15-20
Fruit		

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Apples	Kernel and peel Pomace	8-12 25-40
Pears	Kernel and peel Pomace (pressing)	10-17 25-40
Quinces	Kernel and peel Pomace (pressing)	10-20 30-40
Grapes	Bunches Pomace	2-8 15-20
Plums	Stones Skins	5-13 2-10
Appricots	Stones	5-10
Peaches	Stones	7-15
Sour cherries	Stones Tails	1-3 5-10
Cherries	Stones Tails	0,5-2 4-13
Strawberries	Tails	2-4
Raspberries, blueberries	blackberries, Pomace (pressing)	20-30

5.2. Ways to valorise the vegetable canning industry by-products and waste

In the production of canned vegetables, peas, tomatoes, beans and peppers are the raw materials with the highest share (Figure 5.2.).

In the manufacture of canned peas, large quantities of by-products and waste are obtained, in the form of sheaths, when the pea was harvested by hand, or in the form of stalks (including sheaths), in the case of mechanised harvesting (*Banu, 2009; Baisan, 2015*).

Pea pods represent 55-65% of the total sheaths, and 80-85% of stalks in relation to the green mass subjected to the threshing process, when the harvest was mechanized.



Figure 5.2. Vegetables [84]

Pea by-products and waste

The chemical composition of pea pods and stalks is shown in Table 5.2.

Table 5.2. Chemical composition of pea pods and stalks (*Macoveanu et al., 2005*)

Components (%)	Pods	Stalks
Dry substance	12.9	13.4
Non-nitrogenous extractive substances	6.9	6.5
Proteic substances	1.8	1.9
Lipids	0.3	0.37
Celulose	3.0	3.7
Ash	0.9	1.0
Digestible protein	1.0	1.3
Digestible nutrients	9.4	9.6

Valorisation:

The most rational use of pea pods and stalks is their use for feed purposes.

The special technical-economic importance of the valorisation of these by-products and wastes for feed purposes is determined by the high content in protein substances and by the nutritional quality of these products: 74% of the composition of the stalks and pods is nutritional; and 50% of the protein content is animal protein feed (*Macoveanu et al., 2005*).

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Tomato by-products and waste

The industrial tomato waste (seeds and skin) contains a complex range of nutritional compounds, which should be of interest for the proper functioning of the human body, are not maximised, but on the contrary they are used irrationally and incompletely (Botiș Nistoran, 2014).

Tomato seeds contain a significant amount of lipids, proteins and fiber, and the skin is a good source of fiber and antioxidants (lycopene, β -carotene, phenolic substances, phytosterols) which are found in amounts 2-10 times higher than in tomato seeds (Figure 5.3).

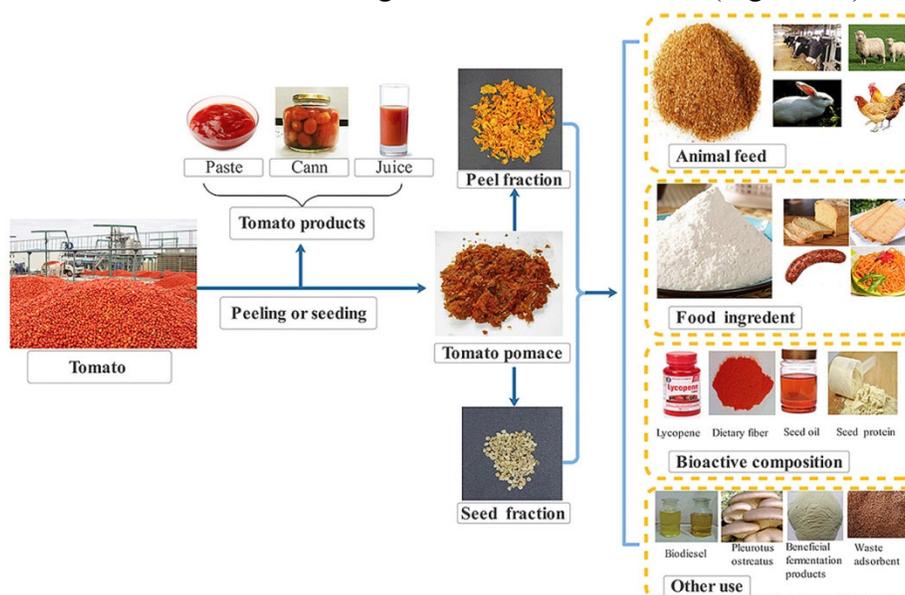


Figure 5.3. Valorisation of tomato by - products and waste (Lu et al., 2019)

When processing tomatoes, the by-products and waste obtained are formed from seeds and skins which differ qualitatively and quantitatively depending on the technological process (Botiș Nistoran, 2014):

- *in the manufacture of tomato paste:* 2-4% seeds are obtained without the pre-boiling phase and 4-6% skins together with pre-boiling seeds;
- *in the manufacture of tomato juice:* a mixture of seeds, skins and a part of the pulp is obtained after boiling, quantitatively it represents 25-35% related to the raw material;
- *in the manufacture of peeled tomato cans:* 10-20% skins are obtained, with a part of the pulp adhering to them; depending on the quality of the raw material and the peeling method, between 10-40% of improperly peeled tomatoes can result in sorting, which can be used in the manufacture of tomato paste;

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- *in the manufacture of canned stuffed tomatoes*: the upper part of the stalk (lid) and the core with seeds are removed, which are used in the manufacture of tomato paste.

Valorisation of seeds for agriculture

Most of the seeds are separated before the crushed material enters the preheater. These are not subjected to heat treatment and can be processed in order to obtain seeds for agriculture. The tomatoes used must be of the same variety.

After separation, the seeds are macerated to remove mucilage, which is done by natural fermentation or acid treatment. After maceration, the seeds are washed with water and dried. Drying can be done naturally by exposing them to the sun or artificially up to 12% humidity (*Botiș Nistoran, 2014*).

Seed valorisation for oil extraction

Tomato seeds contain 25% oil which can be used in food extracted and refined. After drying the seeds, the oil is extracted either by pressing, with a hydraulic press, or by extraction with solvent, obtaining 20% crude oil.

Crude tomato seed oil can be used as such for technical purposes (soap making) or after refining for food purposes.

The cakes obtained after oil extraction, with an appreciable content of protein substances in a concentration of 20-25% are used to feed animals (*Botiș Nistoran, 2014*).

Obtaining colouring extracts

A more rational valorisation is based on the fact that the tomato pulp contains a large amount of natural carotenoid coloring substances, predominantly lycopene.

The lycopene extract from tomato can be used in food supplements, as a food colour in dairy products, non-alcoholic flavoured drinks, cereal and cereal products, bread and baked goods and spreads, to provide colour shades from yellow to red (*Rath, 2009*).

Green beans by-products and waste

The waste resulting from the cleaning of green beans consists mainly of heads and threads, representing 5-10% of the total raw material processed, in the case of mechanical cleaning, and 3-7% in manual cleaning.

Valorisation:

This waste can be recovered for feed purposes either as such or by drying or silage. It is more rational, however, to use them fresh, their quality is maintained after a storage period of 3-5 days without showing changes characteristic of alteration phenomena.

The chemical composition that determines the feed value is represented by: dry substance (10.4-15.2%), total sugar (1.9-3.3%), protein substances (2.4-2.7%), cellulose (1.1-2.4%), vitamin C (5.1-25.4 mg / 100g), ash (0.34-1.27%) (*Botiș Nistoran, 2014*).

Pepper by - products and waste

When cleaning green and red peppers, canned vegetables in the form of vegetable stew, stuffed peppers, rice stuffed peppers, vegetable stew, red peppers in vinegar, etc., waste results in the form of kernels, representing 18-25% of the total raw material.

Their chemical composition is as follows: dry substance (10%), non-nitrogenous extractive substances (3-4%), cellulose (0.9-1.7%), protein substances including seed (2.1%).

Valorisation:

Solid waste from this technological sector is recovered in the form of feed or stored and disposed of in spaces specially designed for non-recoverable waste (*Macoveanu et al., 2005a*).

The bell pepper stubs can be used fresh as feed for cattle, but from it seed is obtained for future crops (*Botiș Nistoran, 2014*).

Potato by-products and waste

In the food strategy, both globally and in our country, potatoes are considered one of the most important crops. It is a complex, dietary food, rich in vitamins and mineral salts (*Botiș Nistoran, 2014*).

Potato is a raw material in the industry for the manufacture of products such as: glucose, dextrin, starch which in turn is either a raw material or auxiliary in the production process in industries such as food, paper, cellulose, chemical, pharmaceutical, building materials, heavy and extractive industry (*Baisan, 2015*).

Potato processing generates waste in the form of peels, pulp and rejects. Potato wastes can be used in the animal feed formulations.

Traditionally, potato peel waste is used for producing animal feed, fertiliser, which causes waste of abundant nutritive materials having the properties of antioxidant, antibacterial, apoptotic, chemopreventive and anti-inflammatory (*Wu, 2016*).

Potato wastes can be managed as components of microbial media in the biotechnological production of cellular biomass of yeasts, microbial polysaccharides, protein and lipids, carotenoids, enzymes and organic acids (*Kot et al., 2020*).

Other by - products and wastes from processing other vegetables

In addition to raw materials with a large share in the production of canned vegetables (peas, tomatoes, beans, peppers), can factories also process, in much smaller quantities, a wide range of vegetables such as: eggplant, zucchini, okra, mushrooms, cabbage, cauliflower, onions.

The cakes resulting from pressing the carrots, in order to obtain juice, contain large amounts of beta-carotene, which make this waste to be used in advantageous conditions for obtaining carotene concentrates or yellow dyes (*Macoveanu et al., 2005*).

5.3. Valorisation of by-products and waste from the fruit canning industry

The main by-products and wastes resulting from the fruit processing process consist of: skins or peels, kernels, seeds, pomace (from pressing), yeast (from juice clarification), bunches, stems and fruit resulting from sorting (Figure 5.4).

The sorting operation eliminates a series of unsuitable fruits in terms of quality, which can be used in the manufacture of alcohol, distilled beverages, vinegar, etc., under the same conditions as waste resulting from fruit cleaning (*Banu, 2000; Banu, 2009*).

The juice is extracted from cherries, raspberries, strawberries, blueberries, which is then used to prepare syrup, jam, etc. (*Botiș Nistoran, 2014; Nour, 2014*).

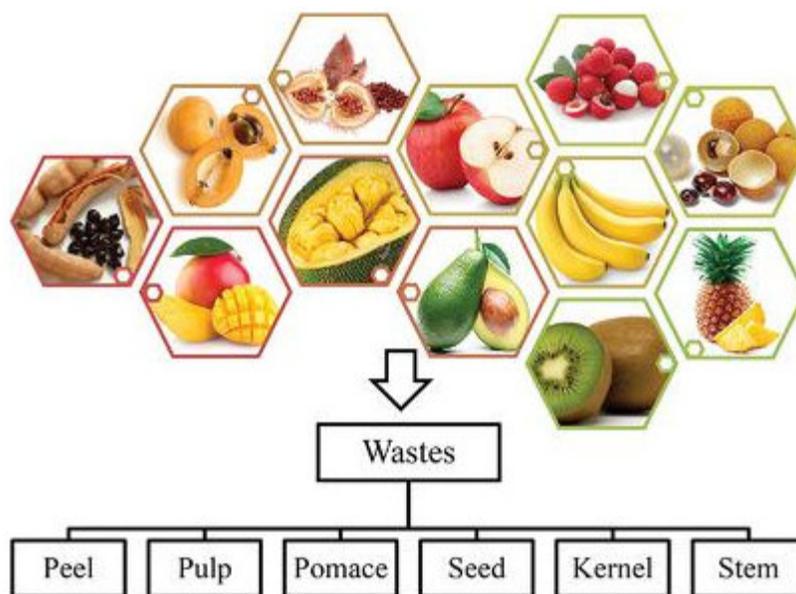


Figure 5.4. Fruit Wastes (*Kringel et al., 2020*)

Fruit wastes are rich in valuable compounds (cellulose, hemicellulose, lignin, moisture, ash, carbon, nitrogen, etc.) which can be utilised in various industries as novel, low-cost, economical and natural sources of dietary fiber, antioxidants, pectin, enzymes, organic acids, food additives, essential oils etc. through different methods of extractions, purifications and fermentations (*Khgk and Rauj, 2017*).

The constituents of fruit wastes have potential to biochemically digested to produce useful products like production of biogas, bio-ethanol, and other commercially useful examples (*Sadh et al., 2018*).

Fruit skin, kernel and seeds

The mechanical or manual cleaning of apples, pears, quinces results in 20-25% of waste formed from the peel and and from the kernel 70-75%. This waste is used in a mixture with fresh fruit or fruit pulp in the manufacture of jam. As the sugar content is over 8%, the skins and the kernel can be used in the manufacture of alcohol and vinegar, being necessary to be crushed and pressed in order to extract the juice.

The waste resulting from the processing of apples and quinces, with a high content of good quality pectic substances, is used in the manufacture of gelling juice for jellies (Botiș Nistoran, 2014).

The most valuable wastes obtained from the processing of apricots, peaches, plums, cherries and sour cherries are kernels, which represent, depending on the fruit, 4-15% of the total processed raw material.

By rational and complex valorisation of these by-products and wastes, crude or refined vegetable oil, bitter almond oil, almond paste, activated charcoal and feed flour rich in protein substances can be obtained (Macoveanu *et al.*, 2005b).

Fruit pomace

When pressing the fruits, in order to obtain the juice, the main waste is pomace, representing depending on the fruit and the pressing conditions 20-40% of the total raw material used (Botiș Nistoran, 2014).

The main means of valorisation of fruit pomace are (Figure 5.5.):

- ✓ obtaining pectin from apple pomace;
- ✓ obtaining tartrate, oil, tannin and other products from grape pomace;
- ✓ use of pomace for fodder purposes;
- ✓ obtaining vinegar;
- ✓ obtaining natural dyes;
- ✓ preparation of pectolytic enzymes.

Obtaining pectin

Pectin is obtained industrially from apple pomace, a by-product of obtaining juices (Nour, 2014).

Pectin, as a finished product, can be obtained in different forms:

- *pectin extract*: which is obtained by extracting hot apple pomace, followed by concentration; the extract contains 10-12% soluble dry substance and 3-4% soluble pectin;
- *pectin powder*: obtained by drying the pectic extracts or by precipitating the aqueous extract, followed by conditioning and then drying;
- *pharmaceutical pectin*: characterized by an advanced purity.

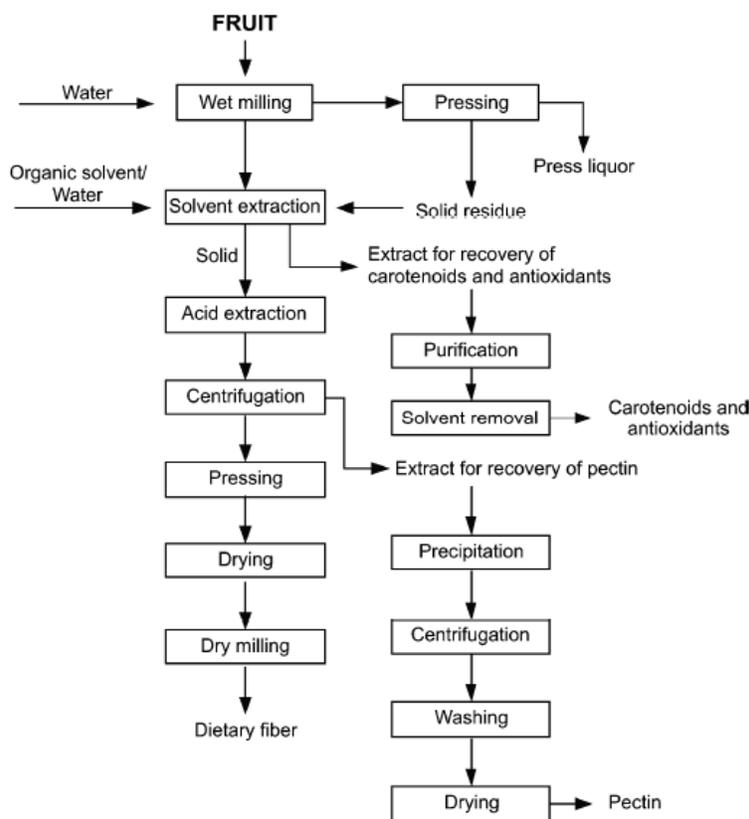


Figure 5.5. Flow diagram for the utilization of fruit pomace (Khgk and Rauj, 2017)

In obtaining pectin, apple cider vinegar is used as raw material, which contains 0.7-1.2% pectic substances and 60-70% water. In order to ensure the functioning of a pectin section for several months, it is necessary to ensure the pomace preservation. Two methods can be used, such as chemical preservation and drying (Banu, 2009).

The pectin obtained has multiple uses:

- in the canning industry;
- in the manufacture of gelled products (jams, jams, jellies);
- in the dairy industry;
- in the manufacture of melted cheeses;
- in the manufacture of ice cream;
- in the meat industry;
- in the manufacture of mayonnaise;
- in medicine;
- in the pharmaceutical industry.

Use of fruit pomace for fodder purposes

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The feed use of pomace resulting from the manufacture of juice for fodder purposes is the simplest means of recovery, being applied on a large scale in most juice-producing countries.

In France, apple pomace is used, mixed with other fodder, in a ratio of 1: 4 in cattle feed (*Botiș Nistoran, 2014*).

Obtaining vinegar

All manufacturing wastes can be used in the manufacture of vinegar (pomace, fruit from sorting, waste from manual or mechanical cleaning of fruit, juice clarification, dried fruit crumbs, etc.) with a content of at least 8% sugar.

Waste which is not processed immediately is preserved by drying or is fermented alcoholically with selected yeasts, avoiding contact with air (*Banu, 2009*).

Obtaining natural dyes

From the pomace of coloured fruits (cherries, sour cherries, raspberries, blueberries, etc.) natural anthocyanin dyes can be obtained, used in the red colouring of sugary products, syrups, juices, alcoholic beverages.

The colorant obtained from the pomace of coloured fruits has not only the advantage of being a natural food colouring, but also a high nutritional value, due to its content in sugars, organic acids, mineral salts and vitamins (*Botiș Nistoran, 2014*).

Preparation of pectolytic enzymes

Dried apple pomace is used as a component part mixed with dried carrots and wheat bran, in the nutrient medium for the surface development of *Aspergillus niger* mycelium, in order to obtain pectolytic enzymatic preparations (*Botiș Nistoran, 2014*).



6. VALORISATION OF INEDIBLE EGGS AND EGG SHELLS

6.1. Egg Degradation

An egg is a complete food with a high nutritional value and is used as a food for both dietary purposes and in the normal diet.

The fully formed egg consists of 10% shell, 59% egg white, 30% yolk and 1% shell membranes (*Banu, 2009*)

Degradation is of three types:

- Egg degradation during oviduct formation;
- Egg degradation during storage;
- Egg degradation by handling and transport.

Egg degradation during formation may occur due to feeding the birds with spoiled or improper feed.

Egg degradation during preservation has as defects: eggs with blood ring, eggs with large embryos, eggs infected with bacteria, moldy eggs. The most common defect of preserved eggs is mold, which occurs due to dirty and damp packaging or keeping eggs in damp rooms.

Egg degradation by handling and transport has defects: broken eggs, scrambled eggs. All these categories of eggs are inedible. They can be used for technical purposes and for feed purposes (*Botiș Nistoran, 2014*).

6.2. Valorisation of degraded eggs for technical purposes

Degraded eggs have a number of technical uses:

- in the leather industry;
- in the dye industry;
- use in painting;
- for obtaining synthetic products;
- for preparing glues and pencils (*Botiș Nistoran, 2014*).

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Valorisation of eggs in the leather industry

In this industry, a significant amount of eggs are used for tanning hides. Liquid tanning yolk consists of eggs well mixed with 12-13% salt for preservation. Tanning yolk due to its pH promotes fat absorption and increases skin resistance.

Sometimes only egg white is used, especially when fixing the varnish and as a colour fixative. A small amount of inedible eggs can be used in the fur industry, namely egg whites to brighten furs.

Egg use in painting

Eggs are used to prepare colours. Although egg oil dries harder than flax glue, yolk or egg white is still used in some painters' recipes.

Egg yolk is added to the primer used to process wood and fabrics to give them strength, impermeability and luster.

Egg white is used in bright paints, especially in molds and anatomical plates which must be seen from a distance.

Valorisation of eggs in the dye industry

Eggs can be used in the dye industry as a fixative. The fastener combines with the fibers it colours, giving very vivid colours, especially for the textile industry.

Synthetic egg products

The egg white paste prepared from calcium oxide and magnesium improves the vulcanization process of the tires. Egg white is used in synthetic formaldehyde resins to increase breaking strength.

Rejected eggs are used to imitate horn, mother-of-pearl and marble. Dried egg whites and egg powder mixed with water and molded are sprinkled. The pressed product is processed with chemicals and all roughness is levelled. If tea powder or Japanese ink is added to the egg white, colours that mimic the colour of the turtle and other colours are obtained.

Another product made from inedible eggs is synthetic fibers. These threads have the properties of natural protein threads; they can be used in surgical sutures because they are resorbed by the tissues.

Using eggs to prepare glues and pencils

Egg whites can be used to obtain highly valued ceramics; they can also be used to prepare greasy pencils made of graphite powder and coagulated egg white with heat.

6.3. Valorisation of defective eggs for feed purposes

Rejected eggs due to breakage by handling, leakage and defects, without the participation of bacterial degradation can be used for feed purposes.

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For this purpose, they are preserved by salting in a proportion of 10% or by drying, under the conditions shown when valorising the eggshells (*Botiș Nistoran, 2014*).

6.4. Eggshell processing

The chemical composition of eggshells is (*Platon, 2015*):

- **sticky egg white:** 88% water, protein (albumin and globulin) 10-13%, glucose 0.5%, salts 0.7%, vitamin B2;
- **shells:** 2% organic substances, 96% Ca carbonate, 1.5% Mg carbonate, 0.25% calcium phosphate and other 0.25% substances.

Eggshells (Figure 6.1.) are used in medicinal supplements, bone graft substitute and denture base (*Mignardi et al., 2020*).



Figure 6.1. Eggshell (*Scattergood, 2017*)

Eggshells can also be employed in constructing floor tiles and in cement to enhance compressive strength (Figure 6.2.). Other applications of eggshell may include, food additives, animal feed, plant fertiliser, batteries, inkjet printers, biodiesel production and removal of heavy metals from soil and water (*Waheed et al., 2020*).

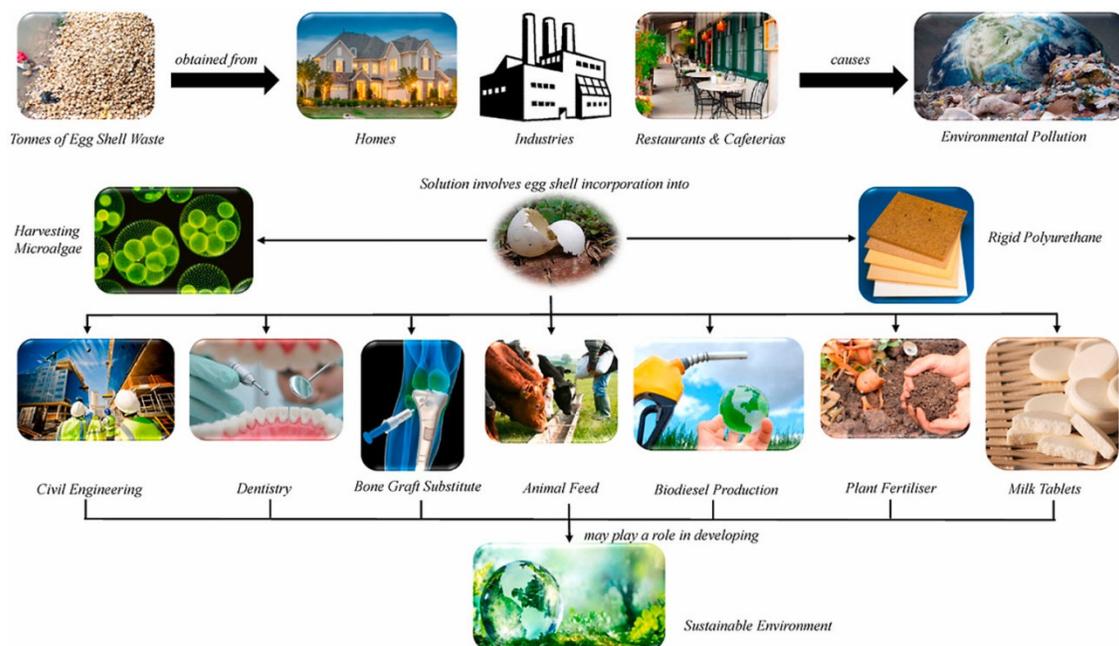


Figure 6.2. Valorisation of eggshell waste (Waheed et al.,2020)

Growing interest is now focused to eggshell powder because can be used as a mineral source for fortification of different food products e.g. yoghurt, biscuits, chocolate cakes, bread (Platon et al. 2020).

Preparation of fodder eggshell flour

The shells with the adhering egg white dry immediately after emptying by evaporation into drying cabinets. Drying is carried out at temperatures of no more than 55°C to preserve the quality of the egg whites. Drying the shells after centrifugation or free draining is more advantageous, because a part of the egg white is obtained, which can be used, after sterilisation by boiling, for fodder or technical purposes (Botiş Nistoran, 2014).

7. VALORISATION OF THE VEGETABLE OIL INDUSTRY BY-PRODUCTS AND WASTE

7.1. Raw materials used in the manufacture of vegetable oils

Vegetable oil is the fat extracted from seeds or other plant parts (Figure 7.1.).

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Figure 7.1. Vegetable oil [85]

Fat consists of lipids, such as fatty acids of different types (*Hammond, 2003*). The proportion of these fatty acids and their different features, give the properties to the different existing vegetable oils.

Chemically, fats and oils are also called “triglycerides.” They are esters of glycerol, with a varying blend of fatty acids.

Vegetable oils are an important component for both food (for feeding, margarine and canned food industry, bakery, confectionery) and for non-food industry (production of detergents, paints, special varnishes, fatty acids, pharmaceuticals and cosmetics products, and painting).

Vegetable oils and fats are found in nature in plant tissue, being concentrated in seeds, pulp, stone fruits, and in the tubers or sprouts. In our country, the main raw material is represented by the oleaginous plants which produce seed (*Ionescu et al., 2013*).

The raw materials used in the manufacture of vegetable oils are as follows:

- seeds of oilseeds cultivated by sunflower, soybean, rapeseed, pumpkin, peanut, sesame, mustard, castor, saffron, poppy, etc.
- textile plant seeds: cotton, hemp;
- seeds of uncultivated neoleave plants: wild rape, hodoban, eruc;
- oily fruits of cultivated trees: olive, coconut, palm, palm, cocoa, walnut, almond;
- oily fruits of uncultivated trees: hazelnut, bechnuts, fir cones, spruce cones, pine cones, allur, chestnut;
- by-products and oil waste: tobacco seeds, rice bran, tomato seeds, peppers, grapes, cherries, sour cherries, plums, green sour apricots, anise;
- corn germs resulting from the milling and starch industry (*Macoveanu et al., 2005b*)

In addition to the main products (edible oils, technical oils and solidified oils), a number of by-products and wastes result in oil plants. Some of them are used even in the factory (e.g. shells), while other by-products (e.g. marcs) are used as raw materials in other industries or in animal husbandry (*Nistor and Muntianu, 2016*).

The by-products and wastes resulting from both the manufacture of crude oils and their further processing are:

- *shells*;
- *groats*;

- *soapstock (obtaining pharmaceutical glycerin);*
- *dregs (obtaining phosphatide concentrate and obtaining sterine concentrate);*

The complex valorisation of the entire range of by-products and waste results in a significant reduction in the cost price of the finished oil and increases the profitability of factories in the branch of vegetable oil industry (*Botiș Nistoran, 2014*).

7.2. Shells

The sunflower seed shells are the first valuable waste for the national economy. This waste appears in the technological process of seed processing in order to obtain vegetable oil, following the peeling operation.

When peeling, not all the shells are removed from the oil core, but depending on the technological process applied in the core, 8-12% of the shell is left (*Botiș Nistoran, 2014*).

Sunflower seed shells are used as follows:

- *fuel;*
- *in the manufacture of furfural;*
- *in animal husbandry;*
- *in the manufacture of chipboard as a construction material;*
- *for obtaining halva.*

Use of sunflower seed shells as fuel

Shells are a good fuel which is used even in oil factories as such. The caloric power of sunflower seed shellshusks is equal to that of wood, 3000-4000 kcal / kg.

The ash resulting from burning sunflower seed shells is rich in potassium salts (10-12%) and used in the chemical industry in the manufacture of potassium carbonate in agriculture as fertiliser on cultivated sunflower fields (*Banu, 2009 ; Botiș Nistoran, 2014*).

Use of sunflower seed shells in the manufacture of furfural

Furfural is obtained by dry distillation or acid hydrolysis of pentosans contained in various vegetable wastes (*Botiș Nistoran, 2014*).

Furfural is an oily, colourless liquid with a specific aromatic odour, slightly soluble in water, slightly soluble in alcohol and ether.

The uses of furfural in the petrochemical industry are the following:

- selective solvent for unsaturated compounds, aromatic substances and resins, under certain conditions being desulfurising;
- selective solvent for refining mineral oils; furfural extracts rich in aromatic products form soluble oils in petroleum products and can be used to obtain fuels by hydrogenation;
- as a raw material for the manufacture of *nylon* plastics ;
- as a tanner in the tannery.

The uses of furfural in the food industry are the following :

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- selective solvent for the separation of vegetable oils into two fractions: one rich in saturated glycerides and the other rich in unsaturated glycerides (the case of soybean oil);
- selective solvent to increase the content of vitamin A and vitamin D of fish oil (*Botiș Nistoran, 2014*).

Use of seed shells in the livestock sector

Lately, sunflower seed shells are in demand in the livestock sector to be used as bedding in large poultry farms.

Birds with the hereditary ability to scratch and peck, consume in this case the last fractions of oilseed core appearing in the form of cracks in the proportion of cracks below 0.5% (*Botiș Nistoran, 2014*).

Use of sunflower seed shells in the manufacture of chipboard as a building material

In this case, gypsum, cement, natural resins, synthetic resins are used as binders.

Sunflower seed shells are purified from core residues to a moisture content of 5% and then mixed with the binder which may be an aqueous solution of phenol-formaldehyde resin.

The mixture is passed to plate presses which are then compressed by means of hydraulic presses.

Sunflower seed shell chipboard can be used as panels, wainscoting, door panels and other non-stress building materials (*Ioancea and Kathrein, 1988*).

Obtaining halva

Halva is a product with a layered fibrous structure, obtained from the core of fried oilseeds, sweeteners and binder, with or without other additives.

Depending on the chemical composition, halva can be: plain, dessert and with additives (cocoa, nuts, fruits, nuts, chocolate in mass or with chocolate coating) (*Botiș Nistoran, 2014*).

Pyrolysis of sunflower seed shells

By pyrolysis of sunflower seed shells are obtained: combustible gases (35%), carbonised residue (35%), tar (approx. 7%), acetic oxide (approx. 5%), methyl alcohol (approx. 1.5%) (*Botiș Nistoran, 2014*).

7.3. Groats

Groats are found as a ground mass, without burnt or moldy particles, without foreign odour and not containing metal residues or other impurities.

The sunflower goroat is classified according to its qualities: with a minimum of 36% protein and a minimum of 39% protein; moisture content of 9%.

The soybean goroat provides: minimum 38% protein and 3.2% moisture.

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Oilseeds contain: proteins, carbohydrates, oil, water, cellulose, mineral salts; are valorised as follows (*Botiș Nistoran, 2014*):

- *in animal husbandry;*
- *for the production of cleirot;*
- *in the manufacture of vegetable casein.*

Use of groats in animal husbandry

Groats are used in animal husbandry as one of the basic components of concentrated animal feed. Some groats contain toxic or unpleasant substances, which require additional hydrothermal treatment when desolventing and toasting.

Sunflower groat

This results from the extraction of fat from sunflower seeds. The quality of these groats depends on the amount of shells they contain, being rich in cellulose and even lignin.

Soybean groat

It has a high crude protein content of 41-48% and 2.6% lysine, but is deficient in methionine, which is why cereal and soybean groat recipes require supplementation with a source of methionine.

Rapeseed and mustard groat

These groats are part of the Cruciferae family, characterised by the presence in their composition of triglycosides, which by enzymatic hydrolysis release a series of spicy active principles.

Hemp groat

Hydrothermally untreated hemp meal is not recommended for pregnant animals, it causes abortions.

Castor groat

This untreated hydrothermal grit is extremely toxic, a toxicity which is mainly due to a protein phytotoxin - called **castor**, due to which it undergoes a detoxification process. Detoxified groats are characterised by 0.68-0.93 nutrient units / kg, being used without problems in animal feed (*Nistor and Muntianu, 2016*).

Use of groats for the production of cleirot

Castor groat contains over 30% protein, substances characterised by their ability to form, under certain conditions, adhesive products called **cleirots** (*Botiș Nistoran, 2014*) .

Cleirot is used in the wood industry to make plywood.

Obtaining the cleirot involves the operations:

- fine grinding of castor groats;

- grinding sieving and cellulosic particle removal as refuse;
- packaging fine grinding in paper bags and delivered to wood processing companies.

Manufacture of vegetable casein from oilseeds

In order to obtain vegetable casein, cakes or groats with a high content of protein substances are used, in order to obtain high yields in casein. The debonding operation must be performed at low pressures, avoiding the irreversible degradation of protein substances.

Vegetable casein serves as a basic material for the manufacture of glues used in the plywood industry. By condensing the vegetable casein with formaldehyde, plastics such as *galalite* are obtained .

Albuminoid substances extracted from oil cakes or groats are used as an additive to improve the mechanical properties of vulcanised rubber products, behaving similarly to synthetic resins (*Botiș Nistoran, 2014*) .

7.4. Soapstock

Soapstock or **refining soap** is a by-product which results from the alkaline oil neutralisation.

The soapstock has got a dark colour and comprises approx. 95% of the total substances, of which 30-60% in the form of free fatty acids.

The fatty acids obtained are stable in terms of colour, oxidation resistance and serve to obtain quality soap.

Soapstock is used to obtain (*Botiș Nistoran, 2014*) :

- *pharmaceutical glycerin*;
- *distillation tars*.

Obtaining glycerin

The resulting soapstock has got a significant amount of neutral oil and can be processed to obtain glycerin.

For this purpose, the fatty substance is separated by treatment with sulfuric acid. Mass purified by washing with water in a proportion of 50% and heating the mixture for 30 minutes. The solution obtained is neutralised with calcium hydroxide, after which an aqueous solution of sodium hydroxide is added, boiled and a solution of aluminum sulphate is added. The aluminum hydroxide precipitate absorbs most of the impurities.

The liquid is filtered by distillation, treatment with activated carbon and thus, *pharmaceutical glycerin* is obtained (*Botiș Nistoran, 2014*) .

Distillation tars

By distilling the fatty acids, resulting from the cleavage of the cotton soapstock with sulfuric acid, the distillation tar is obtained as waste, which comprises significant amounts of gossypol.

This waste has got a series of uses in the form of antifungal, varnishes for painting, binder for making foundry molds, etc.

Tar is used, in combination with zinc chloride, to protect wooden objects from fungal attacks.

Tar as a binder is used to make foundry soil models used in dissolved as *white-spirt form*. The better the binder quality of the product thus obtained is, the richer the tar is in unsaponifiable substances.

By dissolving the tar in an oil fraction, a transparent varnish is obtained, which is used to prepare special paints (*Botiş Nistoran, 2014*).

7.5. Dregs

Crude oil dregs

The filtration of crude oil results, in a proportion of 1%, **dregs**, a dark residue consisting of core particles, shells, seeds, sand comprising 40-65% extractable substances with ethyl ether.

Dregs can be used for the following purposes (*Botiş Nistoran 2014*):

- *oil recovery;*
- *phosphatide extraction, lecithin production.*

Oil recovery

The oil contained in the dregs can be recovered by heating the dregs in a mixture with a solution containing 5% sodium carbonate and 10% sodium chloride at a temperature of 100-105 °C.

Due to the advanced degradation of proteins, the separation by decantation of approx. 80% of the oil contained is produced.

The oil is refined and the residue obtained is used to obtain lower quality soaps.

Phosphatide extraction

Phosphatides obtained from watermelons are used for zootechnical purposes or after further purification for food purposes.

All dissolved vegetable oils contain so-called *accompanying substances*, which in the refining process, following the demucilagination operation, are mostly separated in oil, in the form of a **phosphatide concentrate**, improperly called **lecithin**.

The demucilagination operation is a mandatory step in the refining process of vegetable oils, but only the oils from the second pressing and the extraction oils which have got a higher phosphatide content are demucilaginated in order to obtain commercial lecithin.

Commercial lecithin has the following characteristics:

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- colour: brown or yellow-brown;
- appearance: homogeneous;
- taste and smell: pleasant characteristic, without bitter, sour or altered taste;
- it has got in its composition: phosphatides (65-70%), embedded oil (30-35%), humidity (1-2%), impurities (1-2%), free acidity (12-15%).

Uses of lecithin in the food industry:

- emulsifier in the manufacture of margarine;
- antioxidant for stabilizing vegetable oils, fish and marine oils, fats and soaps;
- agent for dispersing fats in hot syrup in the manufacture of caramels;
- emulsifier and softening agent for the manufacture of chocolate and chocolate products;
- in bakery products;
- in fragile groats;
- in the manufacture of ice cream (*Nistor and Muntianu, 2016*).

Uses of lecithin in the petrochemical industry:

- tetraethylated lead gasoline stabiliser;
- softening and dispersing agent for the manufacture of insecticides;
- lubricated for rubber pressing molds;
- can be incorporated in varnishes and paints;
- can be incorporated into soaps and cosmetics;
- in the manufacture of pharmaceutical products, etc.

Uses of lecithin in light industry:

- softening and polishing agent, textile yarn lubricant, dispersant in dyeing baths;
- softening agent in the leather industry, giving suppleness to the tanned skins.

8. VALORISATION OF THE SUGAR INDUSTRY BY-PRODUCTS AND WASTE

Sugar is one of the most important foods, being a product which the human body fully assimilates, characterised by a high caloric value (*Baisan, 2015*) .

The raw materials for making sugar are sugar beet (Figure 8.1.) and sugar cane (Figure 8.2.). In our country's conditions, the raw material used in the manufacture of sugar is the roots of sugar beet from the first year of vegetation, respectively raw cane sugar.

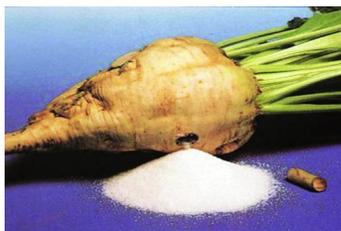


Figure 8.1. Beet sugar [86]



Figure 8.2. Cane sugar [87]

The technological process of sugar manufacturing is a complex one, consisting of various physical, physico-chemical and chemical operations, which ensures the most favourable technical conditions for the extraction and crystallisation of a large part of the sugar contained in sugar beet and sugar cane .

For sugar beet, the main steps of the technological process are the following: preparing the beet, extracting sugar and obtaining broth by diffusion, purifying the broth diffusion and concentrating to broth thick, boiling, crystallisation and refining, conditioning and storing sugar (*Baisan , 2015*) .

The main components of sugar beet are shown in Table 8.1.

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Table 8.1. The main components of sugar beet (*Baisan, 2015*)

Component	Per 100 g of beets (%)	La 100 g S.U. (%)
Dry substance	23.6	-
Sucrose	16.5	69.91
Crude protein	1.05	4.45
Fatty substances	0.12	0.51
Nitrogen-free extract (sucrose-free)	2.92	12.37
Ash	0.75	3.18
Cellulose	1.16	4.91

Sucrose, the main component of beets and the product of the sugar industry, is a solid body that melts at 186-188°C, easily solubilises in water, the solubility increasing with temperature. As a structure, sucrose is a disaccharide, composed of two monosaccharides: d-glucose and d-fructose, linked by their glycosidic groups.

In the complex process of manufacturing sugar from sugar beet (Figure 8.3.) and sugar cane (Figure 8.4.), there results a series of by-products and waste, whose rational valorisation contributes to increasing profitability in this industry.

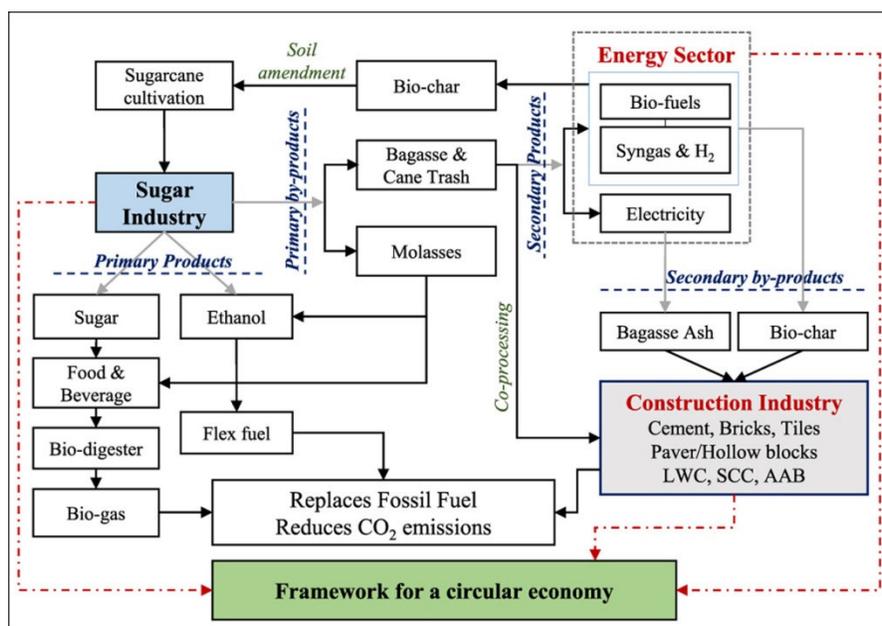


Figure 8.3. Sugar industry by-products (*Athira et al., 2018*)

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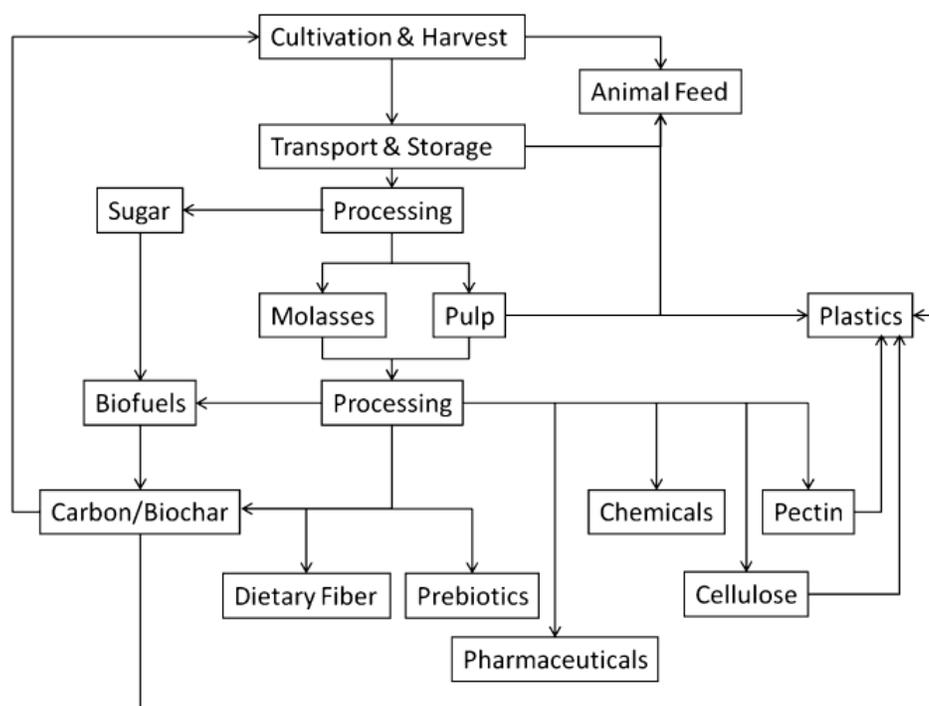


Figure 8.4. Schematic of complete use of sugarbeet into value-added products
(Finkenstadt, 2013)

The by-products resulting from the manufacture of sugar beet sugar are as follows:

- beet leaves;
- beet stalks;
- beet marc;
- molasses;
- filtration sludge.

8.1. Beet leaves and stalks

The aerial part of sugar beet represents 50-70% of the total weight of the plant and consists of vines (60%) and beet leaves (50%) - according to Figure 8.4.



Figure 8.4. Sugar beet

The chemical composition of beet leaves is: moisture (73.5%), crude protein (3.1%), dry substance (0.8%), cellulose (3.2%), non-nitrogenous extractive substances (9.6%), mineral substances (5.8%).

Due to the high content of vitamins, beet leaves are used with good results as fodder, fresh or canned. Beet leaves are preserved either by silage or by drying.

8.2. Beet marc

Beet marc is the product resulting from the processing of depleted beet noodles resulting in the diffusion phase used for sugar extraction (*Macoveanu et al., 2005b*)

The exhausted noodles obtained from the diffusion installation form the wet sludge and represent approx. 90% by weight of processed beets. This marc contains on average 5% dry substance, which consists of: cellulose and hemicellulose (2.3%), pectic substances (2.4%), sugar (0.2%), mineral substances (*Botiș Nistoran, 2014*) .

The beet marc is mainly used as fodder for food, in a wet or dry state.

The marc is also used to obtain food pectin and pectin glue.

Obtaining food pectin

Beet marc is one of the main sources of pectic substances which are found in marc in a wet state up to 1%.

The pectic substances contained in the beet pulp are characterised by a low degree of esterification, which allows gels to be obtained even in the presence of small amounts of sugar.

Pectin can be used in various forms (*Botiș Nistoran, 2014*) :

- in the manufacture of marmelades, jams and jellies;
- as a stabiliser of emulsions in the manufacture of margarine and mayonnaise;
- in the preparation of aspic for meat and fish products;
- as an additive for prolonging the preservation of fresh pastries;
- for increasing the durability of beer foam;
- as a basis for the synthesis of vitamin C.

Obtaining the pectic glue

The pectic substances extracted from marc do not have to correspond to the conditions imposed for the food pectin, the processes of obtaining the pectin glue are carried out under simpler and less expensive conditions.

Pectins are amorphous substances, colloidal in nature, which are strongly soaked in water and give very viscous solid solutions. They have a good adhesive power, behaving similarly to solutions of gum arabic or dextrin.

The use of pectin glue from beet borer in different areas is based on these properties:

- in the textile industry instead of linseed (flaxseed) oil;
- in the printing industry replacing glycerin and gelatin;



- in the wood industry as an adhesive instead of bone glue;
- in the electrical industry as a substitute for dextrin and starch;
- in the manufacture of briquetted feed, as a binder instead of molasses.

The pectic glue obtained has a light yellow color and a good gluing power. The content of pectic substances represents 30-40% of the total dry substance (*Banu, 2003; Botiș Nistoran, 2014*).

8.3. Molasses

Molasses is the main by-product resulting from the technological process of obtaining beet sugar.

Molasses is a product of the general group molasses, known as plant juices with a high sugar content.

Molasses is the intercrystalline syrup resulting from the centrifugation of the thick mass of the final product, therefore, following the separation of the sugar by repeated crystallisations (*Botiș Nistoran, 2014*).

Physically, molasses is a viscous, brownish-black liquid with a specific smell of freshly roasted coffee and a sweet-bitter taste. The amount of molasses is 4-6% compared to sugar beet.

In molasses, in addition to a certain amount of sugar, is concentrated all the soluble non-sugar which was not eliminated in the purification process.

The general chemical composition of molasses is as follows: dry substance (82-85%), water (15-18%), sugar (47-50%).

The purity of molasses is 50-60 % (*Botiș Nistoran, 2014*).

The dry substance is characterised by: sucrose (54-63%), nitrogenous organic substances (14.8-15%), non-nitrogenous organic substances (excluding sugar) 16.7-18%), mineral salts (8.5%).

The dry substance concentration of molasses is expressed in practice in Balling degrees (Bllg) or Brix (Bx), which represent mass percentages of dissolved dry substance.

Until its valorisation, molasses is kept in closed, cylindrical metal tanks, provided with heating coils, supply / discharge pipes, sampling valves.

Due to its composition, molasses is used as a raw material:

- in the manufacture of alcohol,
- for obtaining baking yeast,
- for obtaining citric acid
- for obtaining lactic acid
- for improving feed quality.

Molasses can be valorised by recovering sugar in the form of syrup by demineralisation, using ion exchange resins (*Botiș Nistoran, 2014*).

Molasses sugar can also be recovered chemically by transforming it into insoluble calcium sugars.

The desugarisation of molasses aims to increase the yield of sugar.

The chemical process is based on the property of sucrose to form water-soluble sugars. Ba, Sr, Ca compounds in the form of: barite, strontium hydroxide or lime can be used for this purpose.

By applying the chemical process, by treating the molasses with lime, a reduction of sugar losses can be obtained by increasing the productivity by about 10%.

In the literature, it is mentioned the use, with restrictions of molasses, directly in food.

Molasses contains toxic substances, limiting use to more than 5%; otherwise it leads to delayed animal growth, digestive disorders and even death. Molasses also contains inhibitors with toxic action for the growth of microorganisms, which determines its use as a culture medium to be limited.

In order to valorise molasses, it is necessary to remove non-toxic or toxic substances (*Macoveanu et al, 2005b*)

Obtaining baking yeast

Bakery yeast is a biomass-type product of cells of the genus *Saccharomyces cerevisiae* (higher fermentation yeast), capable of producing the fermentation of sugars from dough with the formation of ethyl alcohol and carbon dioxide, loosening agent and other by-products (*Dabija, 2002*).

The main feature according to which the quality of the baking yeast is appreciated is the power or the leavening capacity (maximum 90 minutes).

Bakery yeast as a finished product, comes in different forms:

- compressed yeast (fresh);
- active dry yeast;
- protected dry yeast;
- instant dry yeast .

The manufacture of baking yeast is carried out according to a complex technological scheme through which it is multiplied successively, on the nutritional support made up of molasses, salts, sterile air, yeast cultures selected from the *Saccharomices cerevisiae* family .

The use of molasses in the manufacture of baking yeast involves the preparation of the raw material, which consists in diluting with drinking water up to 12 ... 14 °Bllg., correcting the pH with sulfuric acid (neutralizing and acidifying the molasses) and adding nutritious salts (ammonium sulphate, superphosphate) and clarification of molasses diluted by filtration or centrifugation. In addition, sterilisation is carried out in order to destroy the present microflora, followed by cooling to the temperature of seeding with culture in the third stage of propagation of the prepared molasses.

In addition to molasses and selected yeast culture, the technological process also uses auxiliary materials in the form of nutrient salts and correction of physico-chemical indicators (ammonium sulfate, ammonia solution, technical diammoniacal phosphate, orthophosphoric acid, potassium chloride , magnesium sulphate, magnesium chloride, calcium superphosphate, dilute sulfuric acid), biostimulating substances for yeasts (maize extract, yeast autolysate, malt roots), low hardness water and antifoams or disperses the formed foam).

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The selected pure yeast culture is multiplied in the laboratory in two stages I and II, after which in stages III and IV the technically pure culture is obtained, which is separated in the yeast milk I. After washing and separation of the washing waters, yeast milk II is obtained, which, purified with sulfuric acid solution, passes to the last multiplication of the yeasts, of the 5th generation. A series of operations of washing and centrifugal separation of yeast milk from washing water follows, finally it is cooled, subjected to a final filtration, kneaded and molded. The last operation is the packaging of the yeast in the form in which it is found in trade.

Obtaining dry baking yeast is performed from yeast milk subjected to the granulation operation, drying the granules with hot air and packaging in materials which do not allow contact with the outside environment (*Băisan, 2015*).

Obtaining feed yeast

Feed yeast is used in a proportion of 2-20% in the preparation of feed mixtures whose composition is determined so that the product obtained contains in sufficient quantities all substances that cannot be synthesized by animals.

Thus, in practice, relatively cheap and highly efficient fodder is obtained by raising animals and birds.

Feed yeast also helps to improve the taste of meat, increases the vitality of animals and decreases mortality, especially of chickens, calves and piglets.

With good results, feed yeast is used in fish and beekeeping farms to supplement the feeding of bees in early spring.

The feed yeast used in the feeding of wild animals raised for fur has led to increased animal resistance to disease and improved fur quality.

At the same time, feed yeast is a valuable raw material from which a wide range of food and pharmaceutical products can be obtained by further processing.

Due to its protein composition, 1 ton of feed yeast is equivalent to the following quantities of feed: 3 tons of oats, 100 tons of straw and 120 tons of fodder beet.

The industrial production of feed yeast is largely made from by-products, waste and industrial residues:

- cellulosic waste: sulfur hydrolysates; wheat straw, corn cobs, sunflower seed shells, wood sawdust, bisulfite lye;
- food industry wastewater;
- whey: waste from the manufacture of cheeses containing lactose as a source of carbon;
- molasses and molasses marc from the manufacture of alcohol;
- kerosene, diesel, methane;
- paraffin wax containing saturated acyclic hydrocarbons;
- methyl alcohol, ethyl alcohol.

These raw materials used as yeast culture media contain, in certain quantities, a series of carbohydrates such as: glucose, xylose, maltose, sucrose, mannose, galactose, arabinose, which yeasts can use as a source of carbon and energy.

Since the production of fodder yeast only aims to accumulate as much biomass as possible, with a high protein content.

Yeasts with weak fermentation power are usually used, but with high multiplication capacity, such as yeasts of the genus: *Torula*, *Candida*, *Rhodotorula*, *Hansenula*.

Of the numerous procedures for obtaining fodder yeast in Romania, only the following are used:

- manufacture of fodder yeast from molasses and molasses marc;
- manufacture of molasses feed yeast;
- manufacture of feed yeast at the same time as obtaining molasses alcohol;
- manufacture of feed yeast from bisulphite lyes.

The technological process of obtaining fodder yeast includes the stages:

- preparation of raw and auxiliary materials;
- preparation of pure yeast cultures (multiplication in the laboratory, multiplication in the pot of pure cultures, multiplication in the prefermentator);
- multiplication of yeast in the production section;
- separation and washing of yeast;
- thermolysis and concentration of yeast milk;
- drying and packaging of yeast.

The packaging of the feed yeast is done in paper bags with the help of a special installation that doses 40-50 kg of product in each bag.

Feed yeast is stored in clean warehouses, in stacks, with a warranty period of about 4 months at temperatures below 18°C and a relative humidity of the air in the storage space of about 70%. If the relative humidity of the air is higher, the yeast absorbs water, being hygroscopic, which allows the development of mold. The hygroscopicity of the yeast increases with the ash content.

According to the internal norm, the humidity of the feed yeast must be of maximum 10%, the protein content of minimum 45% dry substance, and the ash content of maximum 10% (*Macoveanu* , 2005) .

Obtaining alcohol

The valorisation of molasses with the formation of ethyl alcohol is based on the fermentation process of carbohydrate components.

The fermentation process takes place anaerobically, through which fermentable carbohydrates are metabolised by redox reactions, enzymatically catalyzed by yeast, with transformation into the main chemicals: ethyl alcohol and carbon dioxide.

In the process, by-products are also produced: higher alcohols, acids and aldehydes.

The use of molasses in the manufacture of molasses alcohol involves the preparation of the raw material, which is done in the same way as in the manufacture of baking yeast.

Diluted molasses fermentation is made with alcohol yeast (*Saccharomyces cerevisiae*) at the temperature of 30 ... 32°C. Its fermentation takes approximately 72 hours, fermented mash being subjected to distillation, thus obtaining crude alcohol, which is further refined.



Obtaining citric acid

Citric acid consumption for food and technical progress has been made with the application of industrial biosynthetic production process starting from raw materials rich in carbohydrate carbon (*Botiş Nistoran 2014*).

Citric acid is a product obtained by valorising molasses by microbiological fermentation, in surface or submerged cultures.

The citrus fermentation process is an aerobic oxidative process by which the carbohydrate substrate in molasses is metabolized to form intermediate compounds which can accumulate citric acid as the main product in the reaction medium.

Obtaining citric acid is done by using molds of the genus *Aspergillus*, *Citromyces*, *Penicillium*. Among these molds, *Aspergillus niger* strains are the most used, with some strains being able to convert up to 90% of the sugar contained in the fermentation medium.

Uses of citric acid (Botiş Nistoran, 2014) :

- in the food industry as a preservative, colour and flavour protection agent by the chelating activity of the metals which degrade food quality (juices, carbonated soft drinks, sugary products, adjuvant preservative in the freezing process);
- spice stabiliser;
- in the synthesis of fats used to obtain shortening in salad dressings;
- synergistic in the action of antioxidants used in the fat industry, in the synthesis of monostearyl citrate with high fat solubility;
- blood anticoagulant;
- synthesis of sodium citrates, used in the composition of detergents as phosphate substitutes, pollutants by discharge into surface waters favoring the excessive proliferation of algae;
- by aerobic oxidative fermentative processes with the use of *Aspergillus* cultures it forms fumaric acids.

Betaine recovery

Sugar beet contains 0.1-0.4% betaine, quantitatively variable depending on the climate, the nature of the soil, its chemical composition, improving fertility by adding fertilisers with trophic role. Betaine, also known as trimethylglycine, is an amino acid found in sugar beet.

At extraction, the betaine goes through the juice and through the whole technological process without modifications until the molasses component stage.

Molasses contains 3-6.4% betaine and even up to 10%. Nitrogen in the form of betaine is found in the amount of 30-40% of the total nitrogen of molasses (*Botiş Nistoran, 2014*).

Uses of betaine:

Betaine, through its chemical and structural properties can be used:

- as a donor of methyl groups in animal feed with the role of transmitting animal metabolism;
- for obtaining amino acids by assimilating as a methyl group donor in the biosynthesis of methionine from homocysteine;

- in animal feed to reduce the development of animals, with positive consequences in achieving weight gain;
- synthetic raw material for: methionine, trimethionine, vinyl chloride, anticorrosive substances, varnishes, insecticides;
- antioxidant in the oil industry;
- adjuvant in achieving taste properties for food and pharmaceuticals.

Obtaining glutamic acid

Glutamic acid is a component of molasses, known as non-sugar, contains approx. 21% amino acids, of which glutamic acid is found in a proportion of 1.5% with 13% pyrrolidonocarboxylic acid, which by hydrolysis passes into glutamic acid.

The separation of glutamic acid from molasses solution is based on its behaviour as a function of temperature and pH. The pH of 3.2 corresponds to the isoelectric point, sufficient to separate its form from the hydrochloride.

Obtaining glutamic acid from molasses consists mainly in demineralization of molasses and separation of glutamic acid from the starch regeneration effluent (*Botiș Nistoran, 2014*).

Uses of glutamic acid:

- has an important role in nitrogen metabolism, with interventions in detoxifying the body by reducing ammonia in the blood;
- intervenes in the metabolism of the brain by stimulating the ability to concentrate, with uses in medicine for hepatic comas, in the therapy of psychoses;
- used in pharmaceutical synthesis to obtain folic acid;
- as a flavoring in the form of sodium monoglutamate and improves the taste of sauces, soups, vegetables, meat and fish.

Obtaining lactic acid

Obtaining lactic acid from molasses is based on the fermentation of sucrose by lactic bacteria. Fermentation occurs with *Lactobacillus delbruckii subsp. delbruckii*.

As lactic acid accumulates, it is converted into calcium lactate (by the addition of calcium carbonate), because the accumulation of lactic acid would lead to the discontinuation of fermentation lactic acid.

Calcium lactate is finally converted into lactic acid by using the sulphuric acid. The lactic acid is then concentrated under vacuum (*Botiș Nistoran, 2014*).

8.4. Sludge valorization

The sludge obtained by filtering the juice in different purification steps contains about 50% dry substance (when concentrated by vacuum filtration).

The dry substance consists of:

- calcium carbonate, 70-75%;
- organic substances with and without nitrogen;



- other mineral salts other than CaCO₃;
- sucrose, 2%.

Sludge is used as an amendment to correct soil acidity or as a mineral fertiliser (*Băisan, 2015*).

9. VALORISATION OF SLAUGHTERHOUSE BY-PRODUCTS AND WASTE

9.1. Classification of slaughterhouse by-products

Meat and meat products form an important segment of the human diet because they provide essential nutrients which cannot be easily obtained through vegetables and their derived products (*Alao et al. 2017*).

Carrying out the slaughtering process implies the existence of by-products and waste that can contribute to economically or polluting losses if there is no concern to minimise them through valorisation (*Nistor and Muntianu, 2016*).

Animal by-products include all parts of a live animal that are not part of the dressed carcass such as liver, heart, rumen contents, kidney, blood, fats, spleen and meat trimmings (*Alao et al. 2017*).

Animal by-products can be grouped into non-carcass meat (EBPs) and non-meat products (IEBPs) as shown in Figure 9. 1.

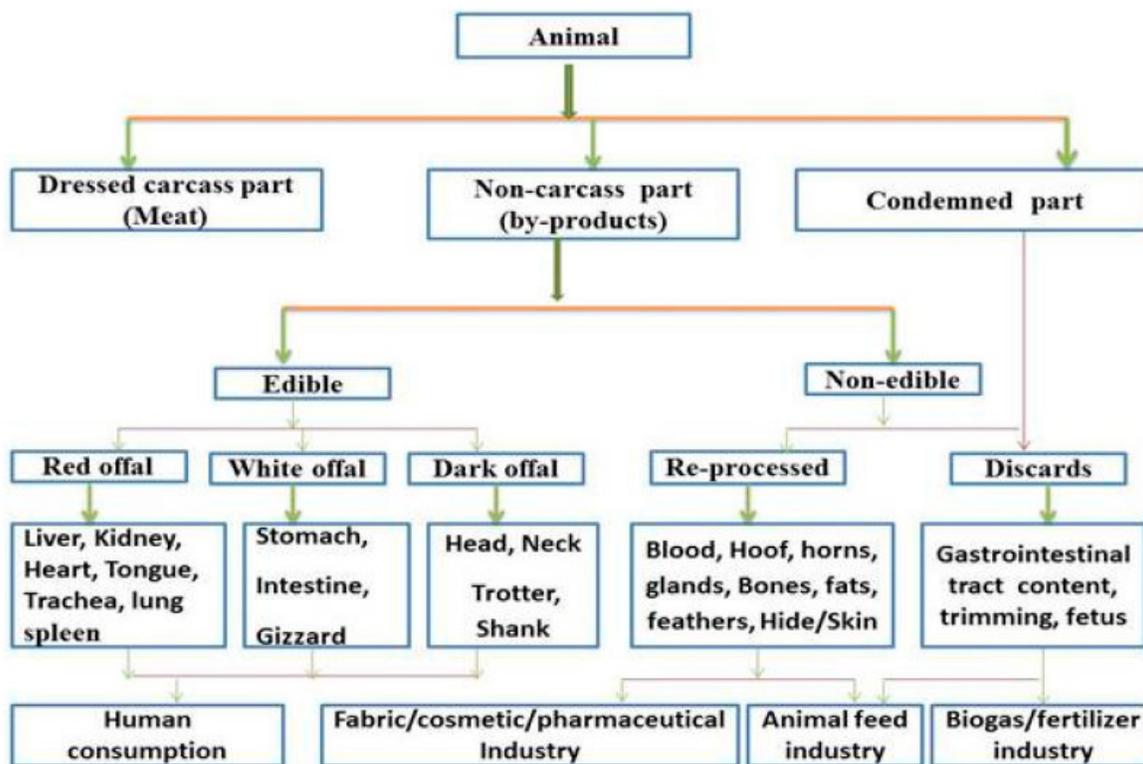


Figure 9.1. Classification of animal by-products (Alao et al. 2017)

Depending on the possibilities of capitalization, the by-products resulting from slaughter (Figure 9.2) are classified into:

- **edible by-products ;**
- **inedible by-products .**

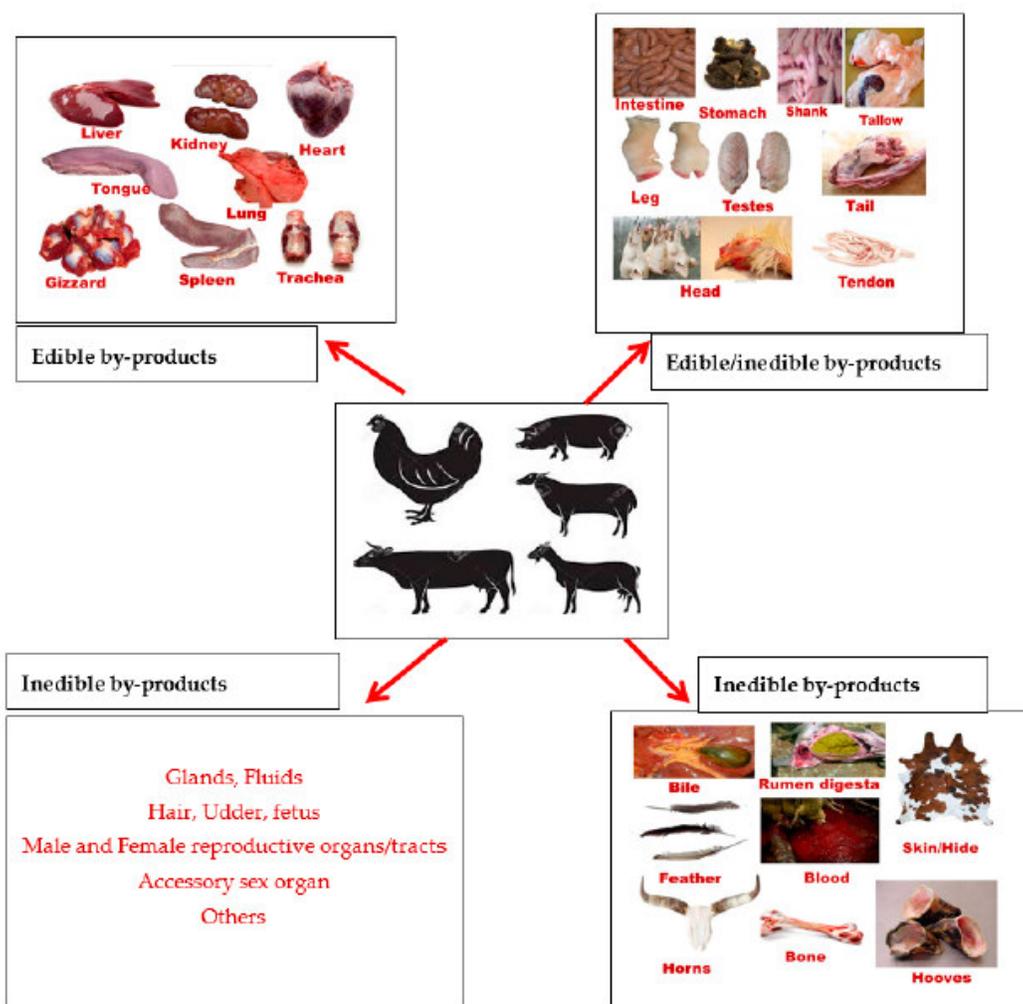


Figure 9.2. General descriptions of edible and inedible by-products (Alao et al. 2017)

9.1.1. Subproduse comestibile de abator

The most important *edible* by-products are:

- organs of cattle, pigs, sheep (tongue, brain, heart, liver, kidneys, spleen, lungs);
- proper slaughterhouse by-products:
- tripe, glands, clumps, lips, legs, ears, ears of cattle;
- stomachs, legs, tails, ears of pigs;
- sheep and pig mouth (the portion at the root of the tongue comprising the hyoid soul, glottis, epiglottis, portions of the submaxillary and parotid glands together with the surrounding muscles);

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- pork rinds from pigs processed by scalding;
- thin braided lamb guts;
- sweetbread (thymus and pancreas), testes, testicles and marrow of pigs, cattle, sheep;
- tubular bones of cattle (femur, tibia, fibula, humerus, radius and ulna);
- pig bones: fork bones, ribs, small bones;
- sheep bones: string bones (thoracic, cervical, lumbar vertebrae) , other bones;
- blood and edible blood by-products (*Nistor and Muntianu , 2016*).

The quantitative analysis of edible by-products allows their totalisation according to the animal species:

- 27% for cattle;
- 25.6% for pigs;
- 10.1% for sheep.

9.1.2. Processing of edible by-products

The processing of edible by-products is carried out differently as follows:

- *in the case of organs* : removal of blood clots, removal of vascular cords, fringes, coatings, fat deposits and specific shaping, preservation by cold (refrigeration, freezing);
- *in the case of hair-covered by-products* (pig's heads, pig's feet, pig's tails, pig's ears and beef's ears): washing with warm water, scalding at 70 °C and mechanical depilation (consisting of roasting, ash scraping) , cold water washing, cold storage (refrigeration or freezing);
- *in the case of mucosal by-products* (rumen, net, lumps): emptying the contents, washing, degreasing, washing-scalding at 70 °C, manual or mechanical cleaning, curing in water at 100 °C, cooling and preservation by cold (refrigeration, freezing));
- *in the case of cattle feet* : manual cleaning, washing, scalding, thawing, washing in cold water, cold storage (refrigeration or freezing);
- *in the case of blood* : harvesting with a tubular knife, stabilization to prevent coagulation and preservation by refrigeration (*Nistor and Muntianu , 2016*) .

The graphical representation of the by-product preparation process is shown in **figure 9.3**.

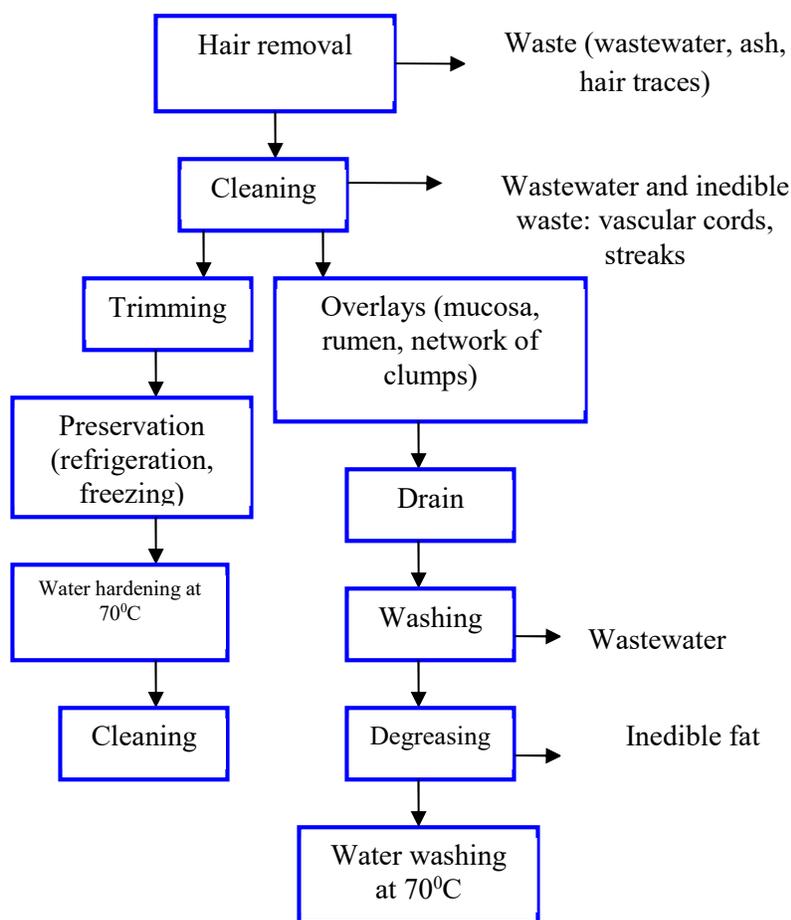


Figure 9.3. Preparation of by-products for the valorisation processes
(Nistor and Muntianu, 2016)

Blood

The blood resulting from the slaughter of animals in slaughterhouses is a valuable product due to its chemical composition and structure and biological properties, which is why it is used as a raw material to obtain various products (Botiș Nistoran, 2014).

The chemical composition of the blood is shown in Table 9.1.

Table 9.1 . Chemical composition of blood (Botiș Nistoran, 2014)

Component parts	Species		
	Cattle (%)	Pigs (%)	Sheep (%)
The water (%)	80.89	79.06	82.16
Dry substance (%)	19.11	20.94	17.84

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- protein	17.11	18.88	16.37
- hemoglobin	10.31	14.22	9.29
Other protein substances (%):	6.8	4.66	7.08
- sugars	0.07	0.07	0.07
- fats	0.48	0.48	0.44
- mineral substances	0.82	0.82	0.73
Other substances (%)	0.63	0.69	0.24

The nutritional value of blood is conditioned by the quality and quantity of proteins and substances with physiological activity. The most valuable proteins are those in blood plasma, which contain essential amino acids for the body.

Hemoglobin is a complex protein, composed of a protein group called *globin*, which represents 95% and a prosthetic group called *heme* in a proportion of 5%. It has a role in maintaining the oxygen reserve and in transporting the oxygen necessary for cell combustion. It forms an easily dissociable combination with oxygen, *oxyhemoglobin*. Iron is extracted from hemoglobin (*Botiș Nistoran, 2014*).

Due to the content of protein substances in quantities close to their content in the meat itself, the blood is used for food purposes. For the same reasons, blood is used on a large scale as a feed product, especially for young animals and birds. Blood is also used for therapeutic and technical purposes.

The preparation of the blood for valorisation consists in establishing the operation which ensures the stopping of the coagulation process and the preservation by refrigeration.

Blood for food purposes has got the following uses:

- blood pigment for food coloring;
- addition for meat preparations, bleeding, Romanian ‘toba’, smoked gypsy ham, colouring when using protein derivatives.

Table 9.2. presents the possibilities of blood valorisation for edible purposes.

Table 9. 2. Solutions for blood valorisation (*Nistor and Muntianu, 2016*)

Technological operation	Name and use of the product obtained
Whole blood centrifuged	- <i>plasma</i> in the amount of 63-67%; composition: 7.9% protein, 0.1% lipids, 1.7% mineral salts, 90.8% water - <i>concentrated with erythrocyte</i> 33-5-37%; composition: 65% water, 33% protein, 1% mineral salts



Whole blood preserved by cooling, defloration and centrifugation	<i>blood serum or fiber</i> : the operation of drying, grinding, aseptic packaging
Whole blood hydrolyzed with HCl ($\rho = 1.18$, temperature 115-120 °C, for 3 hours, filtration purification of HCl. Sterilisation, addition of glucose 20 h / 1 to be hydrolysed.	<i>hydrolysate</i>
Whole blood, at optimum pH sterilised, enzymatically treated	<i>Amino peptides and fatty amino acids</i>

a) Blood processing for feed purposes

This aims to maintain the nutritional value and reduce microorganisms.

These microorganisms are harmful in that they alter the physicochemical properties of the finished product, breaking down proteins making the product unusable.

Blood processing for feed purposes can be done in the form of paste or in the form of flour (*Nistor and Muntianu , 2016*) .

→ Blood processing by coagulation

The simplest form of blood processing is coagulation with heat. By heating to a temperature of 800⁰ C all the protein substances in the blood coagulate, causing their denaturation. At this temperature, some of the microbes in the blood are destroyed.

Blood coagulation is performed in steam-heated boilers or over direct fire. The formed curd is inserted into cloth bags, which are hung in order to drain the serum. After straining, the bags are placed under a press to remove as much serum as possible. Pressing removes approx. 30% water. The curd obtained is used as such for raising pigs within a maximum of 24 hours of production because after this time it begins to decompose.

→ Blood processing in the form of paste

Blood is collected in containers where an anticoagulant has been introduced. The blood thus treated is boiled in open boilers on direct fire or in steam boilers. During boiling, stir continuously to achieve a uniform temperature throughout the blood mass. After boiling, add uncooked lime powder (4 kg per 100 kg of blood). While the lime is cooking, mix well for uniformity.

The paste thus obtained is packed in boxes of 40-50 kg planks lined with paper. The product contains water (69%), crude protein (20%) and ash (11%).

→ Preparation of blood flour

Blood flour, or blood meal, is the most rational form of blood recovery for feed purposes, being the most valuable addition to supplement the need for protein from the food of growing flat animals (pigs and birds). The preparation of blood flour is done by drying in cabinets, processing in Hartmann devices, drying on rollers and spray drying.

b) Use of blood for food purposes

Blood is used for food purposes due to its high biological value and low price (*Nistor and Muntianu, 2016*).

→ Blood kefir

Fresh blood is used to make tonic, low-alcoholic beverages in the form of kefir. It is prepared from fresh blood to which vinegar (5%), sugar (20%) and *Saccharomices* culture are added, then it is thermostated, filtered and bottled.

→ Blood bread crumbs

They are prepared from fresh whey that is added during the preparation of the dough instead of water. Dough prepared with serum has a hydration capacity 1% lower than water.

→ Dry plasma

It is known as food albumin and is used in the meat industry in meat preparations and in confectionery to replace eggs.

→ Dairy hematogen and hematogen for children

The blood can be used in a mixture with milk. Milk and blood proteins form an almost complete food bringing an important intake of iron.

Dairy hematogen is a cocoa-like powdery product. As raw materials are used: defibrinated blood, centrifuged milk and flavour additives. This product is used in the form of cream and pudding.

Hematogen for children is a product in the form of chocolate, with the appearance of nougat, prepared from hematogenous milk, milk powder, cocoa butter, lecithin and sugar.

c) Use of blood for therapeutic purposes

Blood is used in medicine in the form of syrups and other products that are recommended with prescription.

Unspecified plasma is a plasma that has lost its toxic effect and antigen-specific character. The despecification is done by heat treatment associated with the chemical treatment with formalin and ammonia.

Hemoprosthetic serum is a serum from animals which have bled too often consecutively, rich in protein assimilable in tonic and amino acid factors. It is used successfully in asthenia, depression, anemia, after blood loss, in postoperative treatment, etc.

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Peptone prepared from fibrin by alkaline or acid hydrolysis is used in medicine as a desensitizer, in case of anaphylactic accidents or in the preparation of culture media.

Hemoglobin is prepared from either blood clot or fresh blood by centrifugation. It is prepared in powder or glycerin syrup form. It is used in anemia, asthenia.

Amino acids in the blood prepare histidine by hydrolysis. Histidine helps in the formation of globulins and is used in gastrointestinal ulcers.

Thrombin is used in emergency surgery, helping to stop bleeding. It is prepared from plasma with 2% sodium oxalate.

Therapeutic serum from the blood of animals immunized against contagious diseases. It is not prepared from the blood of slaughter animals.

d) Use of blood for technical purposes

Blood is used for technical purposes in the form of plasma or dry.

The technical albumin prepared from pure plasma in which the hemolysis did not take place is called *white technical albumin*, and the one in whole blood is called *black technical albumin*.

White technical albumen is successfully used in the leather industry to pre-polish leather; in the textile industry when fixing colours which require clear contours on the fabric.

Black technical albumen is used to obtain plastics or to manufacture electrical insulating materials; buttons can also be made.

The blood glue is prepared from an aqueous solution of blood flour to which lime milk is added, mixed for 20-30 minutes at a temperature of 28-30 °C after which the glue is obtained. This glue is resistant to moisture and is used in the aerospace and automotive industries.

Coal by burning **blood** flour in refractory brick kilns at 400 °C; it is used to filter juices, syrups, in the wine industry [12].

Bones

Bone tissue

The bones represent the skeleton of vertebrate animals, their mass in relation to the living mass of the animal depends on its species and its mass.

Examples of bone tissue:

- 10-15% cattle of 160- 240 kg ;
- 11.5-12.5% cattle of 240-320 kg ;
- 7-9% in sheep;
- 6-11% in pigs, compared to carcass.

Chemical composition of bone tissue

The chemical composition of bone tissue is known as a variable depending on age, animal species, fattening status and bone structure.

The organic components are:

- **osein** is an existing protein depending on the type of collagen with a proline content of 23.3% and hydroxyproline 14.1%;
- **ostealbuminoid** is an elastin-like protein;
- **osteomuroid** is a mucoprotein that also has mucoitin-sulphuric in its composition.

Mineral composition of bone tissue

The mineral composition of the bone tissue consists of: calcium phosphate 52.26%, calcium fluoride 10%, calcium carbonate 10.21%, magnesium phosphate 1.05%, sodium chloride 1.17%.

Enzymatic content of bone tissue

The enzymatic content is dominant in fresh rolls of which: phosphorylases, phosphatases, olealin, peptidases are found in dominant amounts.

Vitamins A, D, C are found in large tubular bones, which also contain fat, lecithin and iron.

Bone valorisation:

→ *Using bones to prepare glue*

Bones are sorted on a vibrating band, separating the horns, hooves, hard bones, and impurities. The sorted bones are crushed and then placed in an extractor where extraction is performed by using gasoline.

The fat obtained is refined with sulfuric acid and then sent to soap and glycerin factories. The next operation is the degelatinization which consists of the alternative melting of the bones with steam at different pressures and then with boiled water which dissolves the gelatinous mass obtaining a soup with a concentration of 8-12% glue.

The obtained juices are filtered and then concentrated in vacuo at 600 mmcolHg so that the boiling temperature does not exceed 65⁰C. The glue solution is poured into tanks over pipes through which cold water circulates and where it enters within 1-2 hours and gels.

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→ ***Manufacture of bone flour***

The degelatinized flour contains 85% tricalcium phosphate, 11% calcium carbonate, the rest being composed of calcium fluoride, magnesium phosphate and traces of silicon.

Flour degelatinized by treatment with HCl releases phosphoric acid and monocalcium phosphate.

Then, by precipitation with lime milk, dicalcium phosphate known as precipitate is obtained, which is an excellent nutritive factor which favours the rapid growth and development of cattle and poultry.

By treating the melted flour with sulfuric acid, superphosphate is obtained, which is a valuable fertiliser.

→ ***Manufacture of gelatin***

A rational valorisation of the waste resulting from the sausage and meat canning factories and of some slaughterhouse by-products is the manufacture of gelatin.

Gelatin is a product obtained by the partial hydrolysis of collagen contained in bones, connective tissues and skin.

The largest amount of gelatin is used in the meat industry as a gelling agent, the fruit industry to obtain gels and jams, dairy products, etc.

Commercial gelatin comes in the form of light yellow to transparent yellow sheets or powder, sometimes colorless, tasteless and has a foreign smell.

9.1.3. Processing of inedible by-products

Valorisation solutions for inedible by-products

Inedible by-products cannot be considered as polluting waste for environmental factors in the conditions in which recovery technologies are known by obtaining products with uses in non-food industrial sectors.

Table 9.3. presents in summary the technical solutions for valorising inedible by-products.

Table 9.3. Valorisation of inedible by-products (*Nistor and Muntianu , 2016*)

Product	Products resulting from valorisation - characteristics
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blood	Blood flour: moisture 17%, protein 63%, fat 10%, ash max. 8%, carbonized particles 2%
Slaughterhouse waste: organs, heads, confiscated waste, blood vessels, raw blood	Meat flour: moisture 10%, fat 18%, ash 30%, protein 40%; - for fodder use
Endocrine glands	Opotherapeutic products
Raw bovine hair, ears and forehead	- for textile use
Waste: rinds, inedible fats of swine, cattle, sheep, residues of edible fats	Technical twins with min. 70% fat
Kidney, bazaar, mesentery, membrane (prapure), tallow, meat cutting	The only cruel min. 40% fat
Melting of pig fat, bone marrow, fat, bacon from carcass degreasing	Lard for industrial uses - peroxide index - 10; acidity index - 2.5; saponification index expressed in KOH / g - 192-203 - in the manufacture of soap for concentrated fodder
Refrigerated or frozen granulated defatted bovine bones	Gelatin, pharmaceutical, food

Uses for technical purposes:

- leather industry for pre-polishing leather;
- textile industry, agent used for dyeing;
- wood industry for the manufacture of superior glue for varnishing;
- paper industry, manufacture of water-resistant coloured paper;
- chemical synthesis, obtaining plastics, coal, glue.

Horns and hooves

Horns have a very different shape and size in relation to the species, sex and age of the animals.

They contain amino acids of which: leucine 17%, cystine 7%, valine 6%, tyrosine 4.5%, glutamic acid 3%, asparagic acid 2.5%, phenylalanine 3%, alanine 1.5%, serine 1%, glycol 0.4%. The most valuable horns are those of cattle, especially those of light color, transparent and with a glossy surface.

Horn processing involves the following operations: collection, clearing, washing, drying, sorting, storage and processing into consumer objects (*Botiş Nistoran, 2014*).

Uses:

- musical instruments, drinking vessels,

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- furniture and decoration,
- buttons are usually made from deer antlers, not true horn.

Hooves are formations of epidermal origin with a structure similar to that of the horns. The chemical composition is similar to that of horns.

Most hooves are used to prepare hoof flour. Hoof flour, after various heat treatments, is used as nitrogenous agricultural fertilizer and as a raw material in the manufacture of foaming agent.

Foaming is a product used in firefighting, especially petroleum products, and successfully replaces similar imported products.

Hoof flour is also used in the manufacture of prefabricated and porous concrete (*Botiş Nistoran, 2014*).

Fur

Fur is used in reference to the hair of animals, usually mammals, particularly those with extensive body hair coverage. It is used as clothing and / or decoration (*Qahar, 2014*).

Feathers

Feathers are one of the epidermal growths that form the distinctive outer covering, on birds.

Feathers are soft & excellent at trapping heat; thus, they are sometimes used in high-class bedding, especially pillows, blankets, and mattresses. And also used as filling for winter clothing and outdoor bedding, such as quilted coats and sleeping bags etc (*Qahar, 2014*).

Wool

Wool is the textile fiber obtained from sheep and certain other animals, including goats, rabbits, and from camelids etc.

- Uses: in clothing, wool has been used for blankets, horse rugs, saddle cloths, carpeting, felt etc (*Qahar, 2014*).

9.2. Enzymatic preparations obtained from slaughterhouse by-products

Rennet

Rennet (chymosin) is a solid compound obtained from the dry stomachs of veal or lamb and used to coagulate milk.



Rennet powder contains: moisture 5%, NaCl 75%, the total number of germs / g produced is max. 10000.

The product is packed in heat-sealed or clipped polyethylene bags and placed in tin cans of 250-500 g, provided with teaspoons, with a capacity of 1-2 g for measurement. Storage is at 10-18 °C in dry rooms. The warranty period is 2 months from the date of manufacture.

Pepsin

Pepsin is obtained from the red stomach lining of pigs. Pepsin powder is manufactured in two qualities: pepsin type L and pepsin type T; the characteristics are presented in Table 9.4.

Table 9 . 4 . Physico-chemical characteristics of pepsin powder (*Nistor and Muntianu, 2016*)

Characteristics	Admissible conditions		
	Pepsina type L	Pepsin type T	
Water (max.%)	3	3	3
Fat (max.%)	3.5	3.5	3.0
NaCl (% max.)	58	58	28
pH	5.5-6.0	5.5-6.0	4.5-6.0
Coagulation power (in Soxhlet units), min.	1: 50000	1: 120000	1: 120000

The product is packaged in heat-sealed or clipped polyethylene bags and placed in tin cans of 250-500 g, closed with tape-adhesive lids.

In each box of pepsin is inserted a plastic teaspoon for dosing, with a capacity of 2 g. Storage is at a temperature of 10-18°C.

The warranty period for **pepsin L (intended for coagulation of milk)** is 6 months from the date of manufacture and for **pepsin T (intended for digestion of samples used to detect trichina in pigs)** is 12 months.

9.3. Valorisation of slaughterhouse waste and veterinary condemnations.

Waste is classified into:

- **fatty waste:** cleaning of pig skins, greasy sanitary waste (bacon fringes, small pieces of tallow, etc.), industrial scraps, pork guts, confiscated grease.
- **non-fatty waste :** confiscated meat, organs, inedible bellies, cleansing of the belly, skin scraps, guts cleaning (shlaim), stomach contents.

Waste valorisation is carried out in slaughterhouses for the following reasons:

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- the immediate processing of fresh waste ensures a good quality product;
- the hygiene of the slaughterhouses is improved by avoiding the circulation of unhealthy raw materials through the slaughterhouse premises;
- avoid infestation of products from external sources.

Organs and inedible products resulting from cutting such as: glandular stomach from ruminants, large intestines from pigs, ears from ruminants and horses; they are collected in the cutting rooms and then evacuated to the waste recovery section.

Confiscated veterinarians represent approx. 2% of the total raw material that is processed in the slaughterhouse and consists of:

- meat and organs from accidentally dead animals;
- meat unsuitable in terms of veterinary rules.

The composition and structure of this material is to some extent different from the meat and normal organs.

This waste and confiscated are intended for obtaining **fodder flours** in special enterprises, which process them with solvents. These wastes and confiscated are stored in airtight containers for a maximum period of 12-24 hours, depending on the season. They are denatured with creolin or lime chloride (*Nistor and Muntianu , 2016*).

10 . VALORISATION OF THE FISH INDUSTRY BY-PRODUCTS



In the fish industry, as in the meat industry, the processing of the raw material results in a series of by-products and waste (Figure 10.1.) consisting of parts which separate in the processing of the main product, consisting of easily alterable substances, which if not immediately recovered, can form outbreaks of infection within the enterprise (*Botiș Nistoran, 2014*).

The structural composition of some fish species with dominant use in food biotechnologies can lead to definite guidelines regarding how to valorise food by-products and waste.

Thus, it is estimated from the total weight of the fish, meat (45-55%), visceral content (9-16.5%), bones and cartilage (average 7.5%), head (approx. 20%), fins and scales (average 5%). In this context, it should be noted the existence of liver, milk or eggs, bladder fins (*Macoveanu et al. 2005b*).

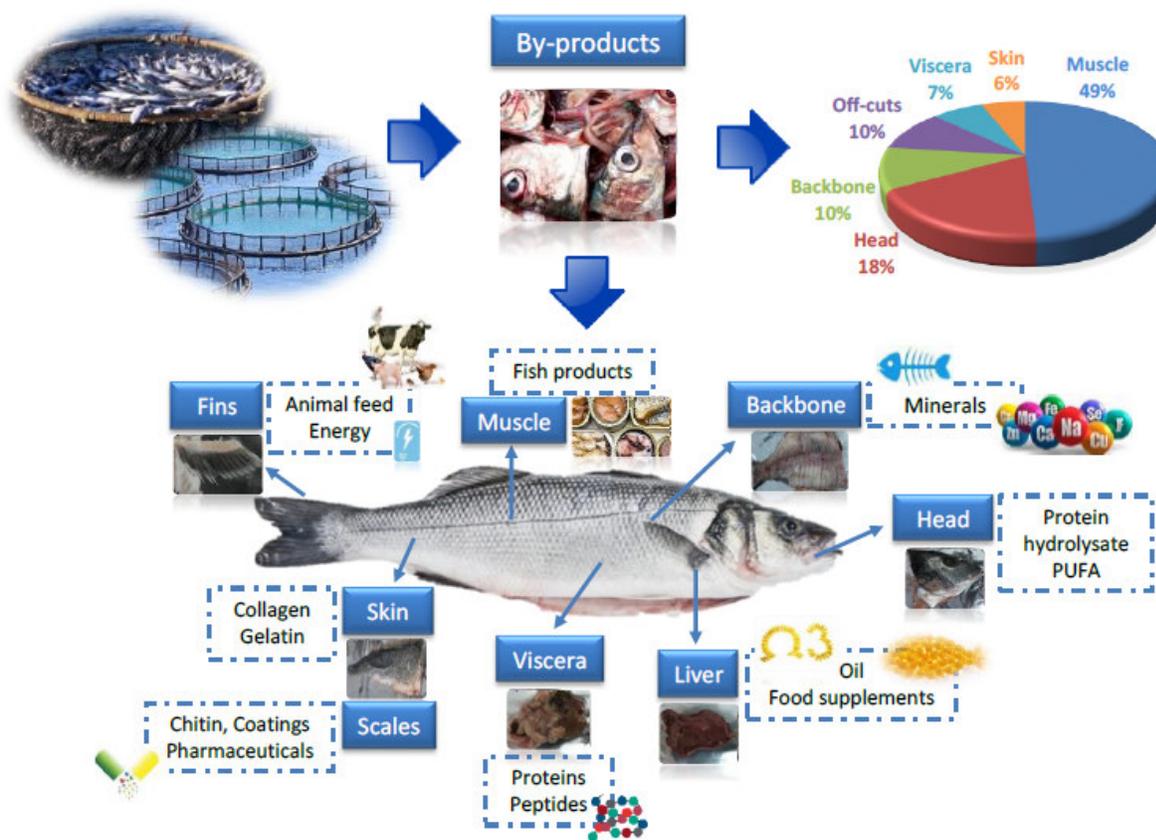


Figure 10.1. Fish processing by-product generation and end use opportunities (*Al Khawli et al. 2019*)



Fish flour and oil

The waste resulting from the processing of fresh fish and degraded fish is used to obtain fish flour and oil. As raw material are used: crushed marine fish, crayfish and frogs (*Botiș Nistoran, 2014*).

The process of valorisation (Figure 10.2.) consists of:

- **heat treatment** applied in the destroyers is necessary for the coagulation of the proteins in the oil separation phase, the sterilisation of the raw material and the deodorisation being performed;
- **pressing** makes the separation of the solid part of the mixture, liquid containing water and oil, water-soluble organic compounds and suspended solid particles.

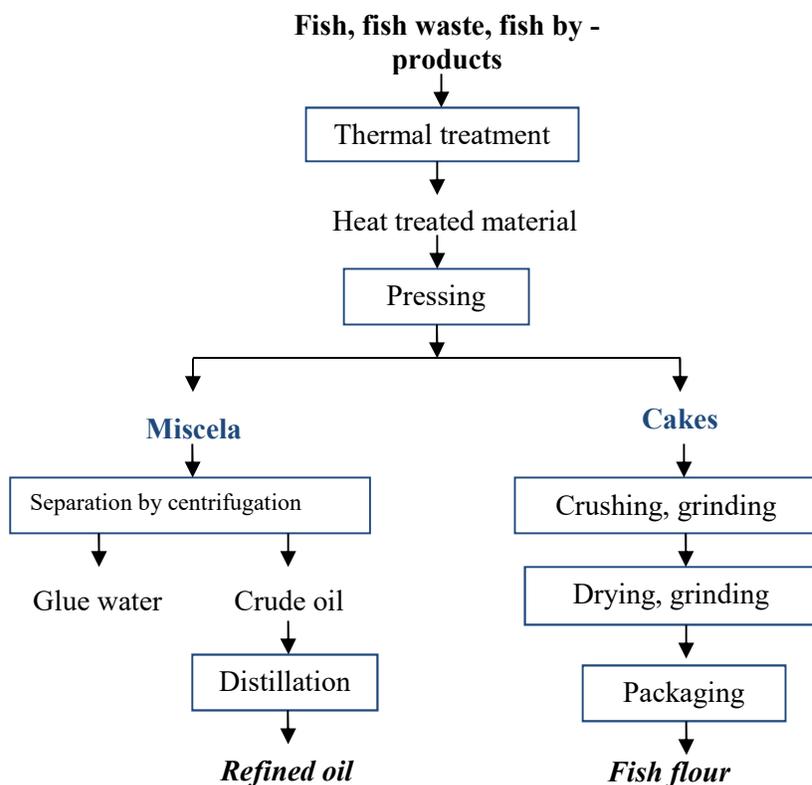


Figure 10.2. Obtaining fishmeal and fish oil (*Nistor and Muntianu , 2016*)

The cake by-product resulting from the pressing operation is processed by grinding, drying and used in the manufacture of fishmeal (*Botiș Nistoran, 2014*).

Fish meal contains: moisture (max. 10%, protein (40-50%), fat (10%), ash (28-30%) including salt used to preserve by-products and waste.

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The mixture obtained is sieved to remove impurities in suspension and then centrifuged to separate the oil from the glue water. The separated oil is still subjected to refining (polishing) operations.

From the mixture, considered the primary product, is extracted the crude oil that is refined by technologies similar to vegetable oil (*Nistor and Muntianu, 2016*) .

From a nutritional point of view, fish oil contains:

- **lipids** : saponifiable triglycerides in minimal amounts of mono- and diglycerides, unsaponifiable phospholipids, sterols, wax esters, hydrocarbons and even diacylglyceryl ethers;
- **fatty acids from the structure of triglycerides and other lipids** are saturated fatty acids (20-35% of total fatty acids), the rest being monounsaturated and polyunsaturated fatty acids;
- **omega-3** (30-40% of total fatty acids) and **omega-6** (the remaining 10% of total fatty acids); the most important polyunsaturated fatty acids found in fish oil are eicosapentanoic acid (C20: 5 ω -3) and docosahexanoic acid C22: 6 ω -3);
- **EPA (eicosapentanoic) and DHA (docosahexanoic) fatty acids** are brought into the human body at 5-6 g / day by fish consumption and can help reduce cholesterol, lower blood pressure by 3-4 mmHg and triglycerides plasma (*Banu et al. , 2009*).

Medicinal oil from fish liver

In order to obtain the medicinal oil from fish with an important quantitative content of vitamins A and D, the liver of shark, cod and tuna fish is used.

Shark liver represents 13% of body weight and contains 70% fat containing vitamins A and D (*Botiș Nistoran, 2014*).

Fish liver oil has approximately the same composition as refined fish oil, being rich in vitamins A and D. For example, shark liver oil contains 700000 IU/g - vitamin A, the cod ~ 6000 IU / g , and the one from the tuna liver ~ 250000 IU/g.

The level of vitamin E is similar to that of vegetable oils of 40-630 $\mu\text{g} / \text{g}$ (*Banu et al. , 2009*).

Hydrolysed fish proteins

Protein hydrolysates are intended for human consumption and contain as a raw material lean fish meat from which the viscera, vessels, bones and skin are excluded.

The hydrolysis process can be achieved by:

- **acid chemical hydrolysis**: it is performed at $\text{pH} = 2-4$ with the addition of pepsin and has the advantage of stabilizing the process over microbial alteration;

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- **enzymatic hydrolysis** : it is performed at alkaline pH and is produced with the addition of enzymes of animal or vegetable origin;
- **enzyme / acid hydrolysis** : it is the most recommended hydrolysis (*Botiș Nistoran, 2014*).

For efficiency, enzyme / acid hydrolysis is recommended because:

- the step of enzymatic hydrolysis with papain in two steps, at pH = 6.3-7.4 and the second step at pH = 5-5.4 at a temperature of 38-56 °C, for 6 hours;
- the step of acidic thermochemical hydrolysis with the addition of HCl at a temperature of 85-90 °C, for 20 hours (*Banu et al., 2009*).

Fish glue

Fish glue is obtained by using the raw material consisting of fish by-products and waste: swim bladders, scales, heads, bones, fins, cartilage.

a) Glue from bladders and fins

From sturgeon blisters, a good quality glue obtained under the name of ichthyocol is obtained (*Nistor and Muntianu, 2016*).

b) Fish glue glue

Fish glue can be obtained from fish scales from canneries by fractional boiling, vacuum concentration and drying.

Fish glue can be prepared in the form of plates, granules or liquid glue (*Botiș Nistoran, 2014*).

Fish glue is used to glue theater sets, glider plywood and other special purposes.

Liquid glue is obtained from pearl glue by diluting it with 20% water and heating. For preservation, 2% concentrated acetic acid is added.

Hygienically processed liquid glue can be used to clarify wines. It is also used for medicinal purposes for the preparation of patches (*Botiș Nistoran, 2014*).

Guanina from fish scales

Guanine is a chemical of the formula $C_5H_5N_5O$ which is found in very low concentrations in the most varied materials of plant and animal origin, such as: legume embryos, brewer's yeast, tea, sugar beet, in the scales and skin of some fish, etc.

Guanine is prepared from both natural and synthetic products.

By synthesis, a non-crystallised substance is obtained in the form of a white powder. From natural products it can be extracted in crystallized form, which is the basic raw material necessary for the manufacture of the varnish for artificial pearls, for nail polish, for varnishing ornamental objects, etc.

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In this case, the raw material for the manufacture of crystallised guanine consists of fish scales, crushed silver marine fish and generally all fish waste. Guanine is also used in other fields: iridescence of plastics used for packaging, in the cosmetics industry, in the textile industry, in the formation of artificial flowers, in the pharmaceutical industry, as a raw material for the preparation of caffeine (*Botiș Nistoran, 2014*).

Red caviar oil (red caviar)

These caviar are obtained from *Salmon* (quality red caviar is obtained from *Oncorhynchus salmon*). After removing the ovaries from the fish, they are washed with water to remove blood vessels and mucilages, then rubbed on a sieve for separation.

Once separated, the eggs are salted in a saturated salt solution, previously boiled and cooled, stirring for 20 minutes. After salting, the red eggs are drained on a sieve for 24 hours and then packed (*Banu et al., 2009*).

Salmon caviar oil (red caviar caviar) can be the extracted oil that represents 12% of the mass of the caviar. Red caviar oil contains 45% polyunsaturated fatty acids with 20 and 22 carbon atoms. Of the total lipids 1/3 are phospholipids (lecithin).

Caviar protein is of superior quality and contains all 8 essential amino acids (isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine) in substantial amounts. Proteins in red eggs have a high content of lysine, methionine, isoleucine (*Nistor and Muntianu, 2016*).



11. RECOVERY OF BY-PRODUCTS AND CEREAL WASTE

Agriculture is a key sector at European level, given that it is the main supplier of inputs to the agri-food chain and makes a decisive contribution to the occupation and development of rural areas.

Cereal cultivation was the first step in agricultural activities and it is considered that cereals, by their nature resistant to storage conditions, have created the conditions for population growth as a result of ensuring a sufficient and constant diet.

Cereals are plants of the grass family grown mainly for their starch-rich seeds and other valuable components for human nutrition; moreover, the general meaning of the term cereals is that of cereal seeds.

The most well-known and frequently used cereals (Figure 11.1.) for human food are the following: wheat, rye, triticale, corn, barley, rice, oats, millet, sorghum; to these are added the so-called pseudo-cereals (buckwheat, quinoa, amaranth, sesame) although they do not belong to grasses, but to other botanical families.

The list of the top five most widely grown cereals in the world contains: corn, wheat, rice, barley and sorghum.



Figure 11.1.Cereal plants [88]

Cereals and their derived products are of great economic and social importance, and it is estimated that for human nutrition, they provide about 65% of daily calories and 45% of protein. To these important nutrients are added a significant intake of carbohydrates, vitamins (especially from group B) and minerals (P, K, Mg, etc.).

Cereals are especially important for their energy intake in the form of carbohydrates. They are also a major source of vitamins and dietary fiber.

Three major directions are the beneficiaries of the growing quantities of cereals produced in the world: human nutrition, animal feed and industrialization.

Cereal grains have a high technological and nutritional potential, and can be processed in a diverse range of products: cereals, flour, pasta, bakery products, food concentrates, etc.

Almost two-fifths of world grain production is used for animal feed. In the form of whole or ground grains, as green, dried or ensiled plants, as waste (straw, chaff or stalks of maize) and by-products (bran, germs) they are used in the food of all human-raised animal species.

The use of cereals for industrial purposes covers three areas:

- a) production of alcoholic beverages (fermentation of cereal puddings and their distillation, processes by which: ethyl alcohol, absinthe, brandy, whiskey, gin, vodka, sake, etc. beer are obtained from germinated and roasted cereal extracts, fermented)
- b) the manufacture of starch derivatives, syrups, dextrose, polyols, etc., with countless uses in the food industry (food for the contemporary consumer, especially American consumers, is mostly corn and corn derivatives, under infinite hypostases), but also in pharmacy, stationery, wood industry and other industrial sectors;
- c) straw and other plant residues are used for making litter (hygienic protection layers in contact with the floor necessary for animal farms, and after use and soaking with animal manure becoming valuable organic fertilisers); spikes, cobs and other parts of plants are used, after cleaning the grains, as a raw material for fermentation processes and obtaining bioethanol - alcohol used in engines instead of gasoline and diesel. More and more countries have adopted strategies for the conversion of cereal production and the development of technical plant production for biofuel production (Schileru, 2016).

WHEAT

Wheat is the main grain in the world diet. Wheat is a cereal belonging to the genus *Triticum*.

There are two species of wheat:

- durum wheat (*Triticum durum*) - flour obtained from this type of wheat is used in the manufacture of pasta
- *Triticum estivum* L. (common wheat) - occupying 90% of the cultivated areas in the world.

Wheat grains are used in animal feed as such or ground. Also, in animal feed, bran resulting as a by-product from the grinding process is used, which is rich in proteins, lipids and mineral salts (Ion, 2010).

Wheat grains serve as a raw material in various industries, for obtaining starch, gluten, alcohol, spirits (vodka, whiskey), beer, biofuel (bioethanol) (Ion, 2010).

Wheat milling by-products are:

- straw (dry stems and leaves left after the harvest of wheat),
- bran (outer seed coat of a wheat kernel),
- shorts (more inward layers of the seed coat that contain some starchy or floury components),
- middling (an intermediate fraction that consists of a combination of bran and shorts) are mostly used as livestock bedding or low-grade animal feed providing minimal return. At present only about 3.2% of the economic return on wheat is from straw (Dunford & Edwards, 2010).

Utilization of wheat by-products can also support the medicine, cosmetics, soil fertility, bio charcoal, fuel, livestock bedding and fodder, basket-making and fermentation industry. They can also be a source of an additional income for the farmers (Patsios et al., 2016).

Straws

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Straw (Figure 11.2) consists of dry stalks of cereals such as rice, wheat, oats, barley, rye, etc. after being harvested and baled in various forms.



Figure 11.2. Straws [89]

They do not contain the seed end (as in the case of hay) and thus have a low nutritional value and are not attractive to pests.

Chemically, straws contain mostly cellulose, hemi-cellulose and lignin - just like wood - but unlike wood, straws have a very high content of silicates.

Thousands of years ago, our ancestors had local resources at their disposal to build their shelters.

Among the most common and accessible materials were earth, straw, grass and reeds, which were easy to process to form light structures and a roof over their heads.

The second most common traditional method of using straw in construction is the combination with earth (most often clay) and other binders, in various formulas, resulting in construction elements such as adobe, adobe-clad jute walls and other similar techniques very often used in our country as well.

In general, straws are often either left in the field to decompose, or ground and mixed with the soil for the next harvest or burned, often being the only solution for farmers to get rid of them.

Straw, wheat, rye, barley, oats, rice, can be used in several ways, even having one as follows:

- fuels for thermal power plants with high powers, generally over 100 Kw, for obtaining thermal energy, fuels for cogeneration units for simultaneous production of electricity and heat, raw material for obtaining gaseous biofuel, syngas, used in the operation of thermal engines. Using straw for heating means saving forests and clean air and reusing waste, so to speak, which optimally closes the production cycle.
- animal feed
- bedding for animal stables
- organic fertilizer by incorporation into the soil after harvest or by composting
- raw material in the pulp and paper industry (*Ion, 2010*).

Wheat straw holds various bioactive compounds such as policosanols, phytosterols (PS), phenolics, and triterpenoids, having enormous nutraceutical properties like antiallergenic, anti-

arterogenic, anti-inflammatory, anti-microbial, antioxidant, anti-thrombotic, cardioprotective and vasodilatory effects, antiviral, and anticancer (*Patsios et al., 2016*).

From wheat, different types of flour and by-products are obtained by grinding - wheat bran, wheat germ.

Wheat bran

Wheat bran (Figure 11.3) is the by-product of the dry milling of common wheat (*Triticum aestivum* L.) into flour (*Patsios et al., 2016*).



Figure 11.3. Wheat bran [90]

Chemical composition of wheat bran (fodder) is presented in Table 11.1.

Table 11.1 Chemical composition of wheat bran (*fodder*) (*Patsios et al., 2016*).

Parameter	Value (average)
Dry substance (% wt) ^{am}	87.0
Crude protein (% wt) ^{db}	17.3
Crude fiber (% wt) ^{db}	10.4
Neutral Detergent Fiber (NDF) (% wt) ^{db}	45.2-51.0 (48.8)
Acid Detergent Fiber (ADF) (% wt) ^{db}	13.4-39.0 (29.6)
Lignin (% wt) ^{db}	3.0-11.1 (6.0)
Ether extract (% wt) ^{db}	3.9
Ethanol / Toluene extract (% wt) ^{db}	10.8
Ash (% wt) ^{db}	5.6-7.0 (6.3)
Starch (% wt) ^{db}	23.1
Total sugars (% wt) ^{db}	7.2
Gross energy (MJ / kg dry substance)	18.9

am: as measured; db: dry base

Wheat bran, considered a by-product, can be used both in bakery for various varieties of dietary products (making bread with bran, biscuits with bran, pretzels with bran, pasta with bran) and in animal feed as fodder.

Recently, bran has become increasingly used in human food due to the high content of natural fibers that play a beneficial role in intestinal transit and also in diets due to low nutritional value and the feeling of satiety it leaves. after consumption.

From the fermentation of the bran, the husks are obtained from which a sour juice called borscht is made, with which the soups are thickened.

Wheat germ

Modern grinding technologies allow the separation of about 1% wheat germ (Figure 11.4), germs that in recent years have begun to be used in bakery products.



Figure 11.4 Wheat germ [91]

Wheat germs are high in protein, vitamins, minerals and essential fatty acids. Among the vitamins, in high proportion, in wheat germ, is vitamin E, which is currently considered the most effective antioxidant.

Mainly wheat germ is used in bakery products, to increase the nutritional value and to add flavor to the finished product.

Wheat germ is currently processed in two ways:

- for obtaining germ oil, rich in tocopherols (vitamin E) which is subsequently processed to obtain food-medicine;
- for obtaining stabilized wheat germs, which have a longer shelf life, compared to raw wheat germs obtained in the mill.

At present, the bakery industry uses stabilized wheat germ, which can be stored for a longer period of time and which gives the finished products a specific aroma, similar to roasted walnuts, while preserving or even improving their nutritional characteristics.

Wheat germs added to the manufacture of bakery products fulfill the following functional roles:

- increasing the water binding capacity;
- improving gas retention capacity;
- improving the texture.

Wheat germ is added to the manufacture of a wide range of products such as: breakfast cereals, snacks, bread, biscuits, cookies, muffins, some varieties of cakes.

Wheat germ is used in animal feed to stimulate reproduction.

MAIZE

Corn belongs to the family Gramineae, subfamily Panicoideae, tribe Maydeae, genus *Zea*.

Maize is used in human nutrition, in animal feed and as a raw material for various industries.

In *human nutrition*, corn is used in the form of corn (flour) from which polenta or various pastries are prepared, corn flakes, preserved corn in the form of grains or cobs for salads and garnishes, boiled or baked corn, popcorn (popcorn).

In *animal feed*, maize is the basic concentrated feed for all animal species. The nutritional value of corn is 1.17 - 1.30 nutritional units per 1 kg of grains.

Corn grains are used as a raw material to obtain starch, glucose, dextrin, isoglucose (liquid sweetener), whiskey, etc.

Corn grains are widely used to obtain biofuel (ethanol) (*Ion, 2010*).

From **the corn germs** resulting from the grinding of the grains, by pressing a very good quality edible oil is obtained, appreciated in the dietary diet.

Corn is also used as animal feed.

The whole plant harvested and chopped at the ripening stage in milk-wax is used to obtain silage, which is widely used in the feeding of dairy cows. In addition, the whole plant can be used as a green mass (*Ion, 2010*).

Maize stalks

Maize stalks refer to dry stalks left in the field after maize harvesting (Figure 11.5).



Figure 11. 5 Maize stalks [92]

Corn cobs are cheap, have a high resistance and insulate well. They can be used to build walls, for furniture or doors. Corn stalks (cochineals) resulting from grain harvesting can be used as fodder. Corn stalks can be used in the pulp industry and in the manufacture of particle board (*Ion, 2010*)

Maize cobs



Maize cobs refer to the central fibrous rachis of the female inflorescence (ie the maize ear), after grain removal (Figure 11.6).



Figure 11.6 Maize cobs [93]

Ground chocolates can be used in ruminant feed. Furfural can be obtained from hammers or used as fuel. Also, in traditional households, corn stalks are used as fuel.

Gloves are used for various traditional braids.

Corn silk (stigmas of female flowers) can be used for medicinal purposes, and corn pollen is easily collected by honey bees (polleniferous plant) (*Ion, 2010*).

12 . VALORISATION OF BEEKEEPING BY-PRODUCTS

Beekeeping is a branch of animal husbandry which studies the biology and technology of beekeeping and exploitation, in order to obtain quality bee products and increase seed production in entomophilous agricultural plants (where pollination is done by insects).

Beekeeping is a branch of activity that contributes to ensuring the prosperity of the population, especially in rural areas, through an additional source of income and the superior use of natural and human resources.

In addition, beekeeping is becoming increasingly important by supporting and stimulating the natural environment through its undeniable effects on floristic biodiversity.

Obtaining honey is the main purpose of beekeeping, from ancient times to the present day.

Honey is the main product of beekeeping, appreciated both for its nutritional properties and for its therapeutic effects.

Honey is a bee product derived from the transformation and processing of nectar by bees and its storage in honeycomb cells, to feed the population of the hive.

Beekeepers can also obtain other by-products (Figure 12 .1) such as: pollen, pasture, propolis, wax, venom and royal jelly (*Berteau M., 2015*).



Honey



Royal jelly



Beeswax



Pollen



Propolis

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Figure 12 .1 Bee by-products

Bee products are substances that they secrete or produce bee by collecting, converting, processing and storage of natural substances collected by the man of the hive or directly to the poison (venom) (*MARD, 2015*).

In general, honey contains a variable percentage of water, around 17% and 83% dry substance, of which sugars represent 80% and 20% represent minerals, vitamins, enzymes, pollens.

Therapeutic properties of honey

Honey is an important nutrient with bactericidal properties and effective therapeutic actions in treating various disorders and diseases.

It is used as an aerosol, by electrophoresis and local applications. The therapeutic effects of honey depend, to a large extent, on the plant species from which the nectar was collected.

Lime honey is indicated for coughs, insomnia, bronchitis, laryngitis, tracheitis, asthma, pulmonary tuberculosis, diseases of the gallbladder, kidneys, purulent wounds, burns, etc.

Acacia honey is recommended as a cough reliever, it is antiseptic, diuretic and antidiuretic.

Flower honey - the sun is used in the treatment of atherosclerosis.

Rapeseed honey is good for regenerating and maintaining the elasticity of vascular walls and lowering cholesterol levels.

Bee honey:

- is indicated in the treatment of diseases of the digestive and cardiovascular system.
- has antimicrobial, anti-inflammatory, anti-allergic, expectorant and nutritious actions.
- it is recommended for neurasthenia, manifested by severe restlessness, headache, dizziness, profuse sweating.
- it is recommended for the treatment of infectious influenza diseases, typhoid fever, cough, convulsions, etc., for skin and gynecological diseases.
- has a favourable effect in improving the general condition of the body and is indicated in pediatrics.

At the same time, the consumption of honey is not recommended for patients with diabetes, people with hypersensitivity to honey.

Bee honey is especially recommended in the diet of children, the elderly, performance athletes.

Bee honey is also used in the cosmetics industry to make many products.

Honey has been used since ancient times in the preparation of many pastries, in the production of candy and caramels, in the preparation of mead and other honey drinks, in the production of apple cider vinegar (*Eremia, 2013*).

Beeswax

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Wax is the secretion product of worker bees, used to build honeycombs in the nest or to cover honeycombs with honey or brood (Romanian Beekeepers Association, 2011).

The composition of the wax includes elements such as: carbon - 80%, hydrogen - 13% and oxygen - 7%, resinous substances and esters - 70%, volatile fatty acids - 13-15% and water - 2.5%.

From time immemorial, beeswax has been used to prepare candles.

Wax is used in painting and engraving, in leather, wood processing, for polishing and maintenance of furniture, in adiotechnics, in the textile industries, polygraphy, etc.

Waxes are made of busts, statues, figures, molds. There are famous museums of wax figures in Paris, London, Amsterdam. The wax obtained considerable (70-80%) is used for preparing artificial combs, returning to the hive to change combs old c onstrucția new ones.

At the same time, the wax is used in varnishes and paints in the industry, pharmaceutical, cosmetic, food, chemical, optical, glass, plating, printing, paper and agricultural industry in the preparation of ointments necessary to grafting trees etc.

The wax is composed of balms, ointments, ointments, creams, ointments, emulsions, depilators, suppositories, cosmetic masks, lipsticks, mascara, plasters, perfumes, dental molds and is used to polish medicinal tablets.

Beeswax as a medicine is used to treat asthma (Eremia, 2013).

Pollen

Pollen is the microscopic grains that are on the anthers of flowers in pollen sacs and that open at maturity to release and fertilize the female part of the flowers of that species (Romanian Beekeepers Association, 2011). The bees collect it and mix it with their salivary secretions and nectar to store it in the hive as protein food, in the form of pasture, without which the life of the bee family would be practically impossible.

Pollen is the source of protein and mineral food for the bee family.

Pollen is rich especially in amino acids, proteins, lipids and fatty acids, enzymes, minerals and trace elements. It also contains all B vitamins, significant amounts of beta-carotene, vitamins C, D and E.

Pollen is widely used in various branches, especially in medicine and dietetics (Eremia, 2013).

Pollen, one of the richest sources of selenium, is effective in treating diseases related to the colon and intestinal transit and improves brain activity.

Raw fodder or pollen helps strengthen the immune system, lowers cholesterol and is used to treat cancer.

Propolis

Propolis is a mixture of natural resinous substances, vegetable wax and beeswax, collected by bees from the buds, bark and branches of some trees and shrubs, in order to protect the bee family against diseases and natural enemies.

Among the main substances identified in the composition of propolis are: resins, flavones, carbohydrates, various organic acids, minerals (phosphorus, potassium, calcium, silicon, manganese).

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Propolis contains 55% resins and balms, 30% waxes, 10% essential oils and 5% pollen, vitamin A, C, B, micro- and macroelements, has bactericidal properties, therapeutic and antiseptic actions.

Propolis is the most powerful natural antibiotic known.

Propolis is used in pharmacology and cosmetics. Due to the wide variety of beneficial substances contained, it is used in the treatment of many diseases related to the following medical fields: ophthalmology, dermatology, radiology, radiotherapy, otorhinolaryngology, oncology, infectious and lung diseases.

Propolis is used in pharmacological preparations in various forms: crushed, in granules, powder, soft and dry extracts, as well as in the composition of many preparations.

Several apitherapy preparations containing propolis are experimented, among which are listed: propolized honey, suppositories, syrups, pills, ENT preparations, ointments, etc.

Propolis is used to make toothpaste, mouthwash and creams (*Eremia, 2013*).

Royal jelly

Royal jelly is a complex secretion that nurse worker bees use in feeding of fish larvae and queen (*Association of Beekeepers in Romania, 2011*).

Royal jelly is considered the "elixir of youth", due to its multiple therapeutic properties.

Royal jelly contains objectionable vitamin C, B complex vitamins, amino acids, trace elements (potassium, phosphorus, iron, calcium, silicon, enzymes and coenzymes), protides (proteins), lipids, sugars and minerals.

It is recommended in the treatment of hypertension and spasms of the coronary arteries, helps to rejuvenate and tone the tissues affected by chemotherapy, offers therapeutic solutions for certain dermatological diseases, stops hair loss and prevents Alzheimer's disease.

Royal jelly is used in medicine and especially in the treatment of post-surgical diseases.

Royal jelly is also widely used in cosmetics in the manufacture of the following preparations: face cream, products with cleansing action, skin care and nourishment, hair lotion.

Freeze-dried royal jelly is a super-concentrated natural food. The preparation is used in food, having vitalizing, toning and regenerating effects on the human body (*Eremia, 2013*).

Bee venom

Bee venom is a product secreted by the venom glands and eliminated by working bees under the action of external stimuli (Romanian *Beekeepers Association, 2011*).

Bee venom is a transparent, colorless liquid with a specific, irritating, characteristic, tasteful taste - pungent, bitter.

Bee venom is a complex mixture of proteins, minerals, enzymes, hormones, essential oils and other volatile substances.

Bee venom, being used correctly, is a curative-prophylactic remedy, which acts not only on an organ or a disease, but on the whole organism, contributing to the mobilization of all defense functions.

Bee venom, through its characteristics, stimulates blood circulation, is antibacterial and anti-inflammatory and fights arthritis.

Bee venom is used in the form of direct stings by bees, injections, pills, capsules, creams, ointments, solutions, aerosol, etc. (*Eremia, 2013*).

13. VALORISATION OF THE WOOD PROCESSING BY-PRODUCTS AND WASTE

The forest means life, fresh air, but also a valuable renewable natural resource, which can fully contribute to economic development, mainly due to wood products or wood derivatives that have an important added value (*Pop, 2019*).

The forest is a source of raw materials (wood products - working wood and firewood - energy source - but also non-wood products - food source).

Wood is the main product of the forest because it has many uses and uses, including working wood (resonant, for veneer, construction, etc.), firewood and even debris (legs, stumps, leaves) that can be used for various purposes (chopping, unique pieces of furniture, tools, accessories, etc.) (*Chiriac, 2011*).

The chemical composition of the wood represents a special importance in the behaviour at its industrialisation, explaining the physical-mechanical resistances and the existence of the chemical composition of some industrial by-products.

For example, wood, the raw material for cellulose has four basic components: cellulose, hemicelluloses, lignin and extractive substances.

Table 13.1. shows the main chemical components in softwood and hardwood.



Table 13.1. Proportions of participation of chemical components in softwood and hardwood (*Chiriac, 2011*)

Chemical components	Resinous species (Fir, spruce, pine, yew, larch) , %	Deciduous species (Beech, oak, walnut, ash, birch), %
Cellulose	50 ÷ 57	42 ÷ 52
Hemicelluloses of which:		
- pentose,	20 ÷ 26	23 ÷ 28
- haxozani,	10 ÷ 12	16 ÷ 23
- polyuronic acids	13 ÷ 14	3 ÷ 5
Lignin	28 ÷ 34	18 ÷ 27
Extractable substances	5 ÷ 10	5 ÷ 10
Ash	0.2 ÷ 1.7	0.2 ÷ 1.7

Wood can be used worldwide and nationally for the development of an important industry, it can be considered as a fuel reserve and a natural structure of the earth necessary for the protection of the environment.

The exploitation and industrialisation of the wood mass results in partially capitalized by-products.

Wood by-products are a set of products and materials whose origin is found in all stages of the wood industry, from logging to the manufacture of finished products. Also, scrap wood (boxes, crates, pallets) represent not negligible quantities (*Timofte, 2004*).

The wood wastes generated by various wood industries are presented in Table 13 .2.

Table 13.2. Analysis of residues generated in wood processing (*Bowyer and Smith, 1998*)

Source	Type of residue
Forest operations	Branches, needles, leaves, stumps, roots, low grade and decayed wood, slashings and sawdust
Sawmilling	Bark, sawdust, trimmings, split wood, planer shavings, sander dust
Plywood production	Bark, core, sawdust, veneer clippings and waste, panel trim, sander dust
Particle board production	Bark, screening fines, panel trim, sawdust, dust sander

Wood waste (Figure 13.1.) is usually composed of:

- Saw dust: produced during wood processing,
- Wood offcuts
- Wood barks: bark is the outer most layer of wood plants, wood bark overlays the wood.
- Plain shavings: are wood wastes that result from smoothing or planing of wood.

- Wood rejects: are wood / timber that have been rejected either due to degradation or pest infestation (eg beetles and fungi).
- Wood chips: are medium sized solid materials made by cutting, or chipping, large pieces of wood (*Owoyemi et al., 2016*)



wood chips



wood shavings



wood bark



sawdust



wood offcuts



wood flitches

Figure 13.1. Wood wastes (*Owoyemi et al., 2016*)

Forest residues are a byproduct from forest harvesting, which is a major source of biomass for energy (*Saal et al., 2017*).

Recovery of wood waste

Wood bark

The bark of the trees has an important weight in their volume, the proportion of participation depending on the wood species, the basic diameter, the age, the relative position on the trunk height, the type of section.

From a chemical point of view, the bark differs substantially from wood, being characterized by a higher content of extractable substances, lignin and ash.

The variation limits for the main chemical components of the shell are between 17 ÷ 30% cellulose, 27 ÷ 37% lignin and 10 ÷ 20% pentosans.

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The bark is used to fertilize the soil, having a dominant content of organic substances and significant amounts of minerals.

The bark of trees in an absolutely dry state has a higher calorific value than wood due to its high lignin content, it is recommended as a combustible material.

The bark can be used chemically to obtain products such as tannins, waxes and furfural.

Spruce and oak bark contain valuable tannins used in the leather industry and willow and birch bark is used in tanneries. Tannin is also obtained by extraction, from chestnut wood 6 ÷ 8% and oak 3 ÷ 4%.

Dry bark can also be used to obtain waxes obtained by treatment with organic solvents, the products made are used as binders, as a product in forming and casting materials.

Sawdust

Sawdust resulting from the processing of timber into furniture elements are used as raw material for chipboard, and secondary resources for PFL.

Sawdust, wood chips, bark and residues mixed with mineral binders give replacement products of energy-intensive thermal insulation boards.

Sawdust is used in the manufacture of porous bricks and with good results in obtaining wood flour - for obtaining plastics (thermoactive, phenolic, urea-formaldehyde, linoleum, wallpaper), glues, explosives (dynamite), finishing materials, etc. *Timofte , 2004*).

Other ways of valorisation

- Obtaining compost
- Valorisation of packaging and pallets:
 - by reuse after repair
 - by recycling
- Degreasing of metal parts
- Litter for animals
- Obtaining inferior quality charcoal
- Smoking meat and fish
- Nutrient substrate for growing cultivated mushrooms (eg *Pleurotus ostreatus*).
- Obtaining sawdust briquettes

Sawdust briquettes are made by pressing the residual sawdust used in the technological process of wood processing with the addition of inorganic binder. They have a higher calorific value and a price about 12% lower than firewood (*Timofte, 2004*).

By-products of the forest industry, like bark and peat, contain bioactive molecules with potential applications in medicines, cosmetics, industrial chemicals and plant protection products. This means that rather than burning these renewable, naturally occurring raw materials, high-value products that will boost rural economies and sustainable forestry could be created (*European Union, 2015*).



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