Pollution prevention in **Olive oil production**

Regional Activity Centre for Cleaner Production (RAC/CP) Mediterranean Action Plan





Ministry of the Environment Spain



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Study finished on January 2000 Study published on November 2000

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INTRODUCTION

The production of the olive for the obtention of olive oil is concentrated essentially in the countries of the Mediterranean basin. The process of oil extraction in an oil mill generates a great quantity of by-products and residues (spent olives and vegetable waters) which require specific management with objectives of minimisation, valorisation or attenuation of its potential negative environmental impact.

In recent years, the merging of oil mills has given rise to larger facilities and, therefore, increased requirements of management of their wastes and by-products. On the other hand, a technological evolution has taken place in the sector, particularly centred on the appearance of the continuous systems of extraction, which have forced the design of new managing strategies in this field. The demand for solutions that are technically and economically viable is patent in the sector throughout the Mediterranean area.

For these reasons, The Regional Activity Centre for Cleaner Production (RAC/CP) of the Mediterranean Action Plan has carried out this study on Pollution Prevention in olive oil production

- a) To know in depth the problems related to the generation and management of the oil mill waste and by-products in the light of the current situation of the oil mill sector in the Mediterranean countries.
- b) To identify the appropriate technological strategies that can be proposed for the different existing productive situations with the aim of minimising the production of polluting effluents, valorise by-products and waste adequately or reduce or eliminate their possible environmental impact
- c) The study is focused on the main olive oil producing countries that also have the most advanced technology, especially Spain, Italy, Greece, Tunisia and Turkey. The implementation of the available systems and technologies for managing and treating olive oil mill liquid and solid effluents must be studied in every specific case and context, and therefore we recommend the carrying out of a technical and economic feasibility analysis prior to the implementation of the mentioned options

Methodology of the Study

The study has been carried out following this methodology.

- a) Bibliographic revision of existing systems and techniques for the treatment and valorisation of oil mill waste and by-products, including the exploration of the database of the European Patents Office.
- b) Research into the "state of the art" of the subject, elaborated in collaboration with the team directed by Professor J.M. Aragón, of the Department of Chemical Engineering of the Complutense University of Madrid (Spain), who in turn has been co-ordinator of the European IMPROLIVE project. This project, with the participation of research groups from Spain, Italy, Greece, Germany and the U.K., had precisely as its object to review and propose solutions for the treatment of oil mill waste, with particular reference to two-phase spent olives. The action arranged with this university group has enabled information to be obtained from most of the agents interested in the subject on both a Spanish and international scale
- c) Direct contact with numerous oil mills and olive-kernel oil plants in the regions of Catalonia, Castille-La Mancha and Andalusia (Spain), with the aim of learning and evaluating the most modern technical solutions that are currently applied. Special mention should be made with regard to the information obtained from the firm OLEÍCOLA EL TEJAR, probably the most important one in the world for the treatment and valorisation of oil mill waste and by-products.
- d) Contacts with suppliers of products, technologies and equipment used in the treatment of this type of waste and by-products.
- e) Attendance at the conclusive seminar of the aforementioned IMPROLIVE project (Seville, April 2000, Institute of Fat of the CSIC), where the occasion arose to contrast with international experts the state of the art and the future lines of development.

Plan of exposition

As a result of the information available and obtained through applying the aforementioned methodology, this study has been drawn up with the following guidelines:

- a) Chapter I offers a general panorama on the sector of olive and olive oil production, in geographic and economical terms.
- b) Chapter II refers to the industrial processes for the obtention of olive oil as well as of the related or derived industrial activities. They are carefully analysed and the by-products and waste generated in the different useable processes or systems are quantified.
- c) In Chapter III this waste and by-products are described and characterised. It offers an evaluation of both the problems that can be generated and the attributes that can justify valorisation strategies.
- d) Finally, Chapter IV enters fully into a description and, where applicable, a technical and economic evaluation of the systems and technologies available for the management or treatment of liquid and solid oil mill effluents. Evidently, greater emphasis is placed on those processes that have shown to be more efficient or that generate greater expectations of potential application. At the end of the chapter, there is a description of three examples of large plants in Spain that have a vocation of "integral processing and utilisation", that are or have been the object of recent developments to deal with the management of two-phase spent olives. At the same time, a compilation is included by way of recommendations to decision taking at oil mill or producing area level.

Appendix I covers the references that have been considered most relevant to the purpose of the study and in another, Appendix II, a brief photographic report is included

By way of synthesis, a section of SUMMARY and CONCLUSIONS has been drawn up which is provided at the end of the exposition.

CHAPTER I: CHARACTERIZATION OF THE OLIVE OIL SECTOR

1.1. Production

Table 1.1 shows the data of worldwide and European production of olive oil for the years 1992/93 to 1998/99.

Campaign	World total	EU total	Spanish total
1992/93	1,811.7	1,391.7	623.1
1993/94	1,722.8	1,257.3	550.9
1994/95	1,871.0	1,399.0	538.8
1995/96	1,746.5	1,414.0	323.0
1996/97	2,601.8	1,801.8	947.4
1997/98 (prev.)	2,503.5	2,162.0	1,088.3
1998/99 (prev.)	2,307.5	1,680.5	738.0
Average	2,080.7	1,586.6	687.1
%	100,0	76,2	33.0

Table 1.1. Worldwide production of olive oil (x 1.000 t)

The socio-economic importance of the olive sector is appreciated considering that in the European Union there are approximately 2,000,000 olive-growing firms, that the production of olive oil in the EU represents 80% of world production and that 750,000 full-time jobs are generated.

Worldwide olive production is variable and is subjected to a multitude of factors, amongst which the meteorological ones are the most important. Indeed, the majority of world plantations are to be found in unirrigated land, so that the pattern of annual rainfalls, associated with the alternating phenomena of the species, seriously affects the harvests. An average estimate of olive and olive oil production is shown in Table 1.2.

	EU	Other countries	Spain	Total
Olives collected (t/year)	7,700,000	2,000,000	3,450,000	9,700,000
Oil produced (t/year)	1,450,000	375,000	650,000	1,825,000

Table 1.2. Average data of crops and production

Spain, with approximately 35% of world production and 44% of EU production, is the main producer of olive oil, followed by **Italy** (460,000 t), **Greece** (280,000 t), **Tunisia** and **Turkey**. The distribution of production by non-EU countries (1988-89) is shown in Table 1.3 (Data of C.O.I).

	Production	Imports	Exports
TOTAL EU - 15	1,615,000	150,000	230,000
Tunisia	150,000	-	95,000
Turkey	170,000	-	60,000
Syria	115,000	-	5,000
Morocco	65,000	-	20,000
Algeria	23,000	-	-
Jordania	18,000	2,000	-
Libya	8,000	500	-
Lebanon	7,000	3,500	500
Israel	4,000	3,000	-
Palestine	3,500		1,000
Croatia	3,000	-	-
Cyprus	1,500	500	-
Yugoslavia	1.0	-	-

Table 1.3. Production, imports and exports by countries of the Mediterranean basin
(1998-99) (Tm)

Other producing Mediterranean countries are:

- Albania, with some 45,000 Ha of olive trees and an oil production estimated at some 7,000 t (data from the University of Tirana)
- Cyprus, with 5,800 Ha and an estimated production of 2,500 t of olive oil

The extraction of olive oil takes place in the so-called "oil mills", always located within the production areas. The number of these industries in the main producing countries is shown in Table 1.4.

Table 1.4. Number of oil mills and average production of the main producing countries

	Nº of oil mills	Average production (t/year)
Spain	1,920	650,000
Italy	7,500	462,000
Greece	2,800	281,000
Tunisia	1,209	168,750
Turkey	1,141	75,000

There are two aspects that should be pointed out with regard to the **location** and the **size** of the oil mills:

1.1.1. Concentration

Of the approximately 1,900 oil mills that exist in Spain, more than half are to be found in Andalusia, this, with more than 60% of the Spanish olive-growing area, produces 80% of the national olive oil.

In Italy, 60% of the oil mills are to be found in the Southern regions, mainly in Puglia, Calabria and Sicily. In Tunisia, there exists a great concentration in the region of Sfax.

In Greece, they are situated in the regions of Peloponeso, Crete and the islands Aegea and Ionia.

The number of oil mills in some other producing countries is as follows:

- Albania: 27
- Cyprus: 32
- Israel: 105
- Lebanon: 650
- Portugal: 900

1.1.2. Average size

In nearly all the producing countries and regions, the average size of the oil mills in terms of volume of olives milled per year is really small, with figures that vary between less than 100 and 1,500 t/year. The case of Spain should not be taken into account, as in Andalusia there are numerous oil mills with volumes of 20,000-50,000

t/year. In Catalonia, only in the region of the Ebro one can find oil mills with volumes in the region of 10,000 t/year.

1.2. Consumption

World consumption of olive oil is fairly proportionate to production, reaching therefore some 2 million t/year in the last campaigns.

Nevertheless, in relative terms it only involves 3% of the world consumption of vegetable oils and occupies eighth place in the ranking of consumption of these products (Table 1.5)

Types of oil	Campaigns			
	1987/88	1989/90	1991/92	1993/94
Soya	15.20	16.11	16.42	18.19
Palm	8.57	10.99	12.24	14.41
Colza	7.48	7.96	9.62	9.38
Sunflower	7.22	7.72	8.15	7.68
Peanut	3.56	4.06	3.85	4.16
Cotton	3.64	3.78	4.45	3.63
Coconut	2.91	3.04	2.82	2.94
Olive	1.89	1.86	1.97	2.11
Palm	1.17	1.39	1.54	1.86
Corn	1.32	1.40	1.50	1.68
Others (sesame linseed, castor-oil)	1.81	1.66	1.77	1.71
Totals	54.77	59.97	64.33	67.76

Table 1.5. World consumption of vegetable oils (millions of t)

In any case, the figures in the previous Table reflect a slight tendency towards an increase in olive oil consumption, and a notable increase can be seen in countries like the U.S.A.

1.3. World Exchanges

The world exports and imports of olive oil, including intracommunitary exports, are reflected in Tables 1.6 and 1.7.

The facts shown allow us to confirm:

- a) The great weight of Italy in the world olive oil trade, in spite of the great difference in production compared to Spain, both as an exporting and importing country, which reflects also its role as re-exporter.
- b) The importance of Spain, Greece and Tunisia as exporting countries.
- c) The growing role of the U.S.A. as main importing country after Italy. Indeed, it can also be added that US imports went from being in the region of 25,000 t/year in the early nineties but nearly 200,000 t in the last campaign.

Countries	Volume (x 1,000 t)	Percentage
Spain	250.2	35.4
Italy	145.6	20.6
Greece	117.4	16.6
Portugal	11.3	1.6
Other EU countries	16.8	2.4
Total EU	541.3	76.6
Tunisia	113.8	16.1
Turkey	21.4	3.0
Other countries	29.9	4.2
World total	706.4	100.0

Table 1.6. World olive oil exports (averages of the '90s)

Countries	Volume (x 1,000 t)	Percentage
Italy	301.7	42.0
Spain	55.9	7.8
France	51.8	7.2
Portugal	26.5	3.7
U.K.	16.3	2.2
Germany	12.8	1.8
Others EU	21.6	3.0
Total EU	486.6	67.8
U.S.A.	109.9	15.3
Brazil	18.9	2.6
Canada	13.4	2.3
Australia	16.0	2.2
Japan	10.0	1.4
Rest of the world	62.7	8.3
World total	717.5	100.0

Table 1.7. Olive oil imports (averages of the '90s)

1.4. The olive oil industrial and commercial chain

1.4.1. The products

In accordance with rule COI/T.15/NC num. 2 Rev., of the International Board of the Olive Oil Industry, of 20th November 1997, olive oils are classified in the following way:

- 1. **Virgin olive oil apt for consumption or "natural"**, defined as the product obtained from the olive by physical means and in thermal conditions that do not produce alterations, with no other treatment but rinsing, decantation, centrifuging and filtering. The following types can be distinguished:
 - Extra virgin olive oil, the free acidity of which, expressed in oleic acid, should not surpass 1% in weight and with organoleptic characteristics established in the rule.

- Virgin olive oil or "fine", with acidity below 2% and organoleptic characteristics established in the rule.
- Ordinary virgin olive oil, with a maximum acidity of 3.3%, with organoleptic limitations established in the rule.
- Virgin olive oil not fit for consumption in the form it is obtained also called "lamp oil": acidity over 3.3% and with organoleptic limitations established in the rule. It is for refining or uses unrelated to food.
- 3. **Refined olive oil** that comes from the refining of the virgin olive oil for lamp oil, by means of refining techniques that do not produce modifications to the initial glyceridic structure.
- 4. **Olive oil**, made up of a mixture of refined olive oil and virgin olive oil fit for consumption (types 1 mixed with type 3).
- 5. **Olive-kernel oil**, which is obtained by extraction with solvents from the spent olives of the oil mill. It is marketed under the following typology:
 - Raw olive-kernel oil, which is for refining or uses, unrelated to food.
 - Refined olive-kernel oil obtained by refining the raw olive-kernel oil.
 - Olive-kernel oil, which is obtained as a mixture of types 5.3 and 1.

1.4.2. The agents of the sector

The following types of operators or basic "functions" intervene in the olive oil industry and market:

- a) Oil mills, normally linked to production, and so, in many cases, they are cooperatives.
- **b) Extractors** (commonly named "olive-kernel oil plants"), which extract the olive-kernel oil.
- c) **Refiners**, with installations dedicated to the refinement of various types of oil, amongst which is olive oil not fit for consumption. They obtain refined oil.
- d) Packers, whose activity consists of bottling the olive oil acquired from oil mills or other origins. They usually have oil storage installations and act as wholesalers in the commercial distribution. By means of mixing operations, they obtain the different commercial olive oils, with own brandnames or working with "blank" brands.

- e) Wholesalers, in the national or export market. They carry out activities of commercial intermediation on a national scale or in the international market.
- f) Retailers, who are the final sellers to the consumer. They include from small shops to the large food distribution chains.

Actually, this is a set of functions, some of which are carried out by the same operator. The most frequent cases of functional integration are those of the "oil mill-packer", "extractor-refiner", "oil mill-retailer", "packer-wholesaler", etc.

In recent years, and after the appearance of the two-phase system of extraction by centrifuging (see Chap. II of the study), there has appeared a "new function" consisting of the **processing of moist spent olives** (in general, drying) which can be situated between the oil mill and the extractor.

CHAPTER II: THE INDUSTRIAL PROCESSES IN OIL PRODUCTION AND THE WASTE AND BY-PRODUCTS GENERATED

2.1. General view of the olive oil industry

In figure, 2.1 a general outline illustrates the process of obtaining olive oil, the most relevant operators and the products, by-products and waste that are generated, with their most common uses. This process is described in the following epigraphs.

2.1.1. Processing in oil mill

Starting with the raw material, **the olive**, the first and basic process of extraction takes place at the **oil mill** or extractor "mill". By means of physical or mechanical procedures of milling, extraction and separation, the following products are obtained:

- a) Virgin olive oil and, sometimes **lamp oil**, the classification and description of which has been set out in the previous epigraph 1.4.1.
- b) Vegetable waters or liquid waste, made up of the vegetable waters of the olive, frequently mixed with water added in the process. They present a high, although variable, polluting power, and so must be the object of treatment or specific management to avoid negative environmental impacts. Depending on the system of separation used in the process of oil extraction, as well as the handling strategies of the liquid effluents in general, vegetable waters of differing amounts and composition are obtained.
- c) Spent olives or solid residue containing the pulp, the stone and the tegument of the olive, with a moisture level that varies between 25% and 40% and with a fat content in the region of 3-7%, depending on the process of extraction employed. The spent olives can be put to several uses:
 - Second extraction of the residual oil in extractor industry for the production of olive-kernel oil
 - Foodstuff for livestock in cattle (ovine, bovine, camelidae)
 - Solid fuel
- d) Humid olive-kernel or "moist spent olives", residue of pasty consistency with a more than 60% moisture, which is produced when the system of two-phase extraction is used (see further on, epigraph 2.2.2) This is, actually, a mixture of spent olives and vegetable water which requires previous drying for it to be utilised by the second extraction industry, or specific management systems

- e) **Fatty stoned spent olives**, obtained on occasion by separation of the stone and the pulp of the spent olives. The stone happens to be an excellent fuel.
- f) Vegetable and earthy leftovers, proceeding from the rinsing of the olive that has been harvested. Normally, they are reincorporated into the soil as organic fertiliser, with or without previous composting.

On average, the processing of 100 Kg. of olives yields some 20 Kg. of oil and, depending on the case and on the systems of extraction, the following effluents and by-products:

- 40 Kg. of spent olives with a moisture content in the region of 35% plus 40 Kg. of sewage, when the traditional system is used.
- 55 Kg. of spent olives with a moisture content of 50% plus 100 Kg. of sewage, when the continuous three-phase system is used.
- 70 Kg. of spent olives with moisture content of more than 60% plus 10 Kg. of sewage, when the continuous two-phase system is used.

The dumping or elimination of wastewaters has always meant an ecological problem of considerable importance. On the other hand, the utilisation or valorisation of the by-products and oil mill wastes presents positive aspects which one has always tried to make the most of. The quantity and quality or type of these products depends, basically, on the system of oil extraction used, as is analysed in later epigraphs.

2.1.2. Processing of spent olives

In the extracting plants or "olive-kernel oil plants", a drying takes place until process moisture (8-10%) and chemical extraction using hexane as a solvent of the fat content. The process gives rise to:

- a) **Olive-kernel oil**, the description and classification of which has been set out in previous epigraph 1.4.1.
- b) **Degreased spent olives** or "exhausted spent olives", made up of the pulp and stone of the olive which is now very dry and practically exempt of fat.
- c) **Sieved Degreased spent olives**, which is the product that results from the moreor-less total separation of the stone from the degreased spent olives by pneumatic systems or sieving.

2.1.3. The refining process

The aim of this is to recover for use as food oils initially unfit due essentially to their high acidity and the defects in taste and flavour.

From this process, refined oil is obtained and the so-called "**neutralisation pastes**", which are usually destined to industries of formulation of fats for inclusion in compound fodder for livestock or for technical uses unrelated to food.

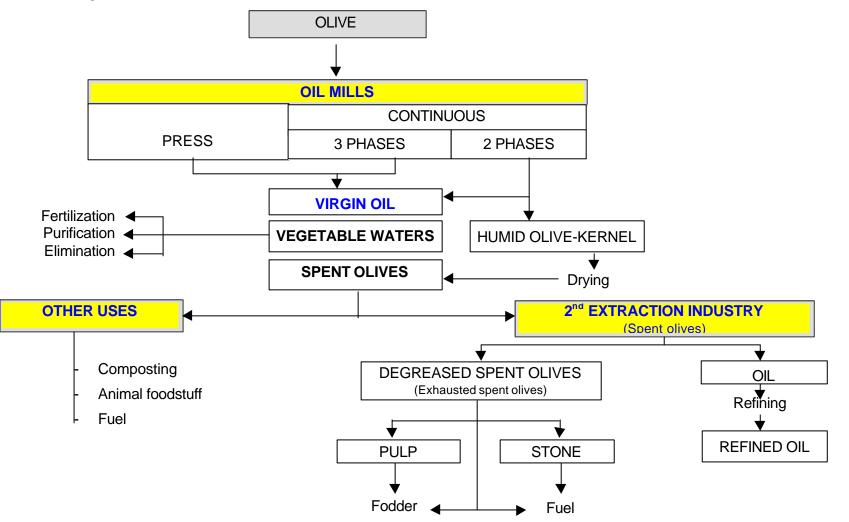


Fig. 2.1. GENERAL VISION ON PRODUCTS, BY-PRODUCTS AND RESIDUES IN THE OLIVE OIL INDUSTRY

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2.2. General description and basic operations of the process of extraction in oil mill

In figure 2.1, the general process of work is illustrated at oil mill level, that is to say, for the obtention of virgin olive oil. The basic operations and their variants are described below.

2.2.1. Reception operations

They consist of the preparation of the olive for its later milling. They are operations common to all oil mills, varying only in the degree of perfection and automatization with which they are carried out. They are, essentially:

- Cleaning and rinsing
- Control of weight and quality: aspect, acidity, fat yield.
- Storage

2.2.2. Milling and extraction operations

These operations are:

- a) The milling is carried out by means of stone mills (traditional) or with hammers or disks (modern installations). There are variants of mixed type, with previous stone milling and subsequent passing through a mill-homogenizer with blades or teeth.
- b) A subsequent **beating** at a suitable temperature prepares the **paste** or **mass** to favour the separation of the oil.
- c) The **extraction** or **separation** of the phases fat (oil) solid (spent olives) and watery (vegetation waters). The systems used can be of three types:
 - SYSTEM OF PRESSES or traditional, consisting of the pressing of the paste by means of hydraulic presses. It is a "discontinuous" system because of the necessity to proceed according to "loads" or sequential pressing cycles.

AREA/ENTRY	OPERATIONS	EQUIPMENT	OUTPUT
1. RECEPTION AREA			
Harvested olive →	UNLOADING	Hoppers, belts	
	-		
	CLEANING	Pneumatic, sieving	Leaves, Earth,
	-	T fiedifiatic, sleving	Shoots
	-		
	CONTROL	Scales, laboratory	
	-		
	STORAGE	Hoppers	
	-		
	RINSING	Water, rinser	Rinsing water
	-	,	<u>J</u>
2. OIL EXTRACTION AREA	-		
Water, system 1 →	MILLING	1. Mill stone	
	-	2. Mill hammers	
	-	3. Mixed types	
	- BEATING	Destar	
	BEATING -	Beater	
	-		
Water, systems 1 and 2 \rightarrow	SEPARATION	1. Press	Oil + Veg. water
	-	2. Decanter 3 F	+ spent olives
	-	3. Decanter 2 F	Oil + moist spent olives
	-		
Water →	CLEANING	Centrifuge and	Oil
3. CELLAR	-	decantation well	Veg. water
J. UELLAR	STORAGE	Stainless containers	
	-		
4. BOTTLING AREA	FILTERING		
Bottles, auxiliary material →	BOTTLING	Bottling line	Bottled oil
	-		
	SHIPMENT		

Fig. 2.2. General outline of the industrial oil mill process

- CONTINUOUS THREE-PHASE SYSTEM, in which the separation of the oil from the mass is done by centrifuging, using a horizontal centrifuge called "decanter" that works continuously. As in the previous case, the result of the process is the *oil*, the *vegetable water*, and the *spent olives* or solid residue.
- CONTINUOUS TWO-PHASE SYSTEM, which consists of a variant of the previous one, in which the decantering separates the oil and mixes the spent olives and the vegetation water in one phase of a pasty consistency called *humid olive kernel, two-phase spent olives*, or *moist spent olives*.

The traditional pressing system has been in use for only 20 or 30 years, when it began to be replaced with the continuous method of extraction by centrifuging. In Spain, approximately 90% of the oil mills use the two-phase system, but in Italy, half of the production is still obtained by the traditional pressing method. In Greece at the present time 85% of the production is done by the continuous centrifuging method, and especially by the 3-phase method.

d) Cleaning of the oil or separation of the leftovers of solid residue (fine) and watery residue proceeding from the previous operation. It is carried out by filtering (mesh filter, partial separation of solids of greater size from particles), decantation in appropriate pots embedded in the ground and/or centrifuging in a vertical high-speed centrifuge. The process of centrifuging requires the addition of hot water.

2.3. Traditional system

Traditionally and, until the appearance of the modern methods of extraction by centrifuge, the method of extraction by pressure has been the only existing procedure for obtaining olive oil. In this method, the olive, stored and rinsed in the yard of the oil mill, is milled in a stone mill. The solid resulting paste is laid out in fine layers upon disks of filtering material (fabric, or more recently plastic fibre), called pressing mats. These pressing mats are piled up one on top of the other in a wagon and are guided by a central needle. The ensemble formed by the wagon, the needle and the pressing mats piled up with the paste receives the name of **charge**. The latter is subjected to pressing by means of a hydraulic press. The pressure that the

charge receives is generated by a group of hydraulic pumps housed in the so-called **pump-box.**

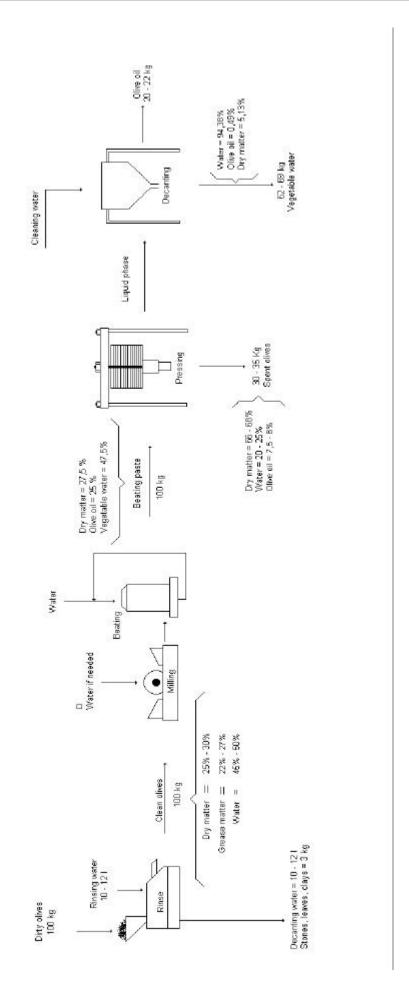
The operation described is not continuous and is composed of 3 stages:

- The stage of charge formation
- Pressing
- Removal of the pressing mats

Once the cargo has been prepared, pressure starts to be applied, obtaining a liquid that flows onto the wagon. The liquid, which is obtained at first, is a must rich in oil, the quality of which diminishes as more extracting pressure is applied. When the pressing is finished, the liquid phase is taken to deposits (pots embedded in the ground or small tanks), where the natural decantation is produced, the watery phase separating from the oily one, obtaining virgin olive oil and vegetable water (approximately 40-60 I of vegetable water per 100 Kg. of olive) In order to accelerate and improve the efficiency of the process of decantation, a vertical centrifuge can be used to separate the oil from the vegetable water.

When the pressing stage is over, the operation of the pressing mat removal is carried out. Once the solid residue has been removed, which presents a moisture content of around 26%-30% and a fat content of around 8%, the rinsing and cleaning of the pressing mats is carried out. This must be done with great care to ensure the complete elimination of particles that may have become trapped in the fabric and that, given the conditions of moisture and temperature, soon start to develop hydrolytic and oxidising processes, which can transmit to the oil a bad taste and high acidity.

The solid residue that is left in the pressing mats, spent olives, is a by-product that, after drying, is used for the extraction, with organic solvent, of the olive-kernel oil in the olive-kernel oil producing plants.





2.4. Continuous three-phase system

The continuous system was introduced in the seventies when the new technologies for the extraction of olive oil started to be applied. The modern conception of the extraction replaced the traditional pressing with **horizontal centrifuges**, called "**decanters**", which considerably improved the performance and productivity of the oil mills.

The new method presented the following advantages over the traditional method:

- Mechanical simplification
- Elimination of the pressing mats
- Continuous production
- Less labour
- Smaller surface occupied by the installation

The method of continuous extraction requires, like the traditional one, a prior milling, which is carried out in mills with hammers or disks. Once the milling has been performed, the paste is sent by means of a dosifying pump of variable speed to a horizontal centrifuge. In the centrifuge 3 phases are separated; the spent olives, the oil and the vegetable water.

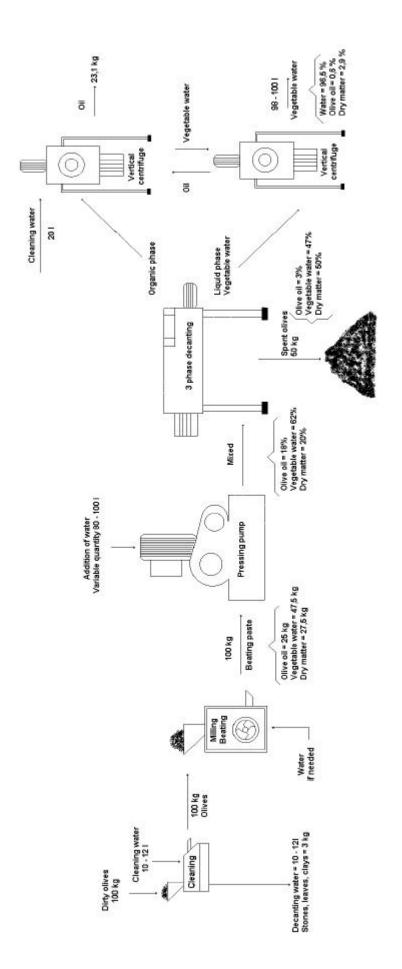
The solid phase, called spent olives or **three-phase spent olives**, contains the greater part of the solids that are to be found in olives; skin, pulp, stone, and a small portion of oil. The spent olives are sent to the olive-kernel plants to proceed with the extraction of the remaining oil, obtaining the so-called olive-kernel oil.

The watery residue called vegetable water is initially a dark liquid, of a reddish colour, which, due to a series of enzymatic processes, rapidly becomes degraded, and converts into the vegetable water. This is a foul smelling, black, highly polluting liquid. The quantity and quality of the vegetable water is variable, depending on the system, type of olive, water used, etc. The watery phase contains a small amount of oil, which separates on subjecting the vegetable water to a new centrifuging in a vertical centrifuge. On average, 1 m³ of vegetable water is generated per ton of olives, with an average pollutant load of 70 Kg. COD/t of olives.

The oily liquid phase, which contains a small quantity of vegetable water, must be purified by centrifuge, more vigorously, in a vertical centrifuge.

The consumption of water in the three-phase system is notably higher than the traditional system, amounting to an approximate total of 100 - 130 L per 100 Kg. of olives. The distribution of water consumption in the oil mills is as follows:

- In the rinsing, which is usually a closed cycle, the consumption is in the region of 10-12 L /100 Kg. olives.
- In the milling, on occasions, hot water must be added to avoid the adhesion of the paste to the surface, with an average consumption of approximately 25 L/Kg. of olives.
- In the beating hot water is used in closed circuit.
- The stage of separation or centrifuging in decanter is where the greatest amount of water is used, which must be hot to facilitate the transport. The expense is produced in two stages in a stage previous to the centrifuging with an expense of around 80-100 L/Kg. olives. For the actual centrifuging, approximately 20-I water/100 Kg. olives are added with the purpose of improving the separation.





2.5. Continuous two-phase system

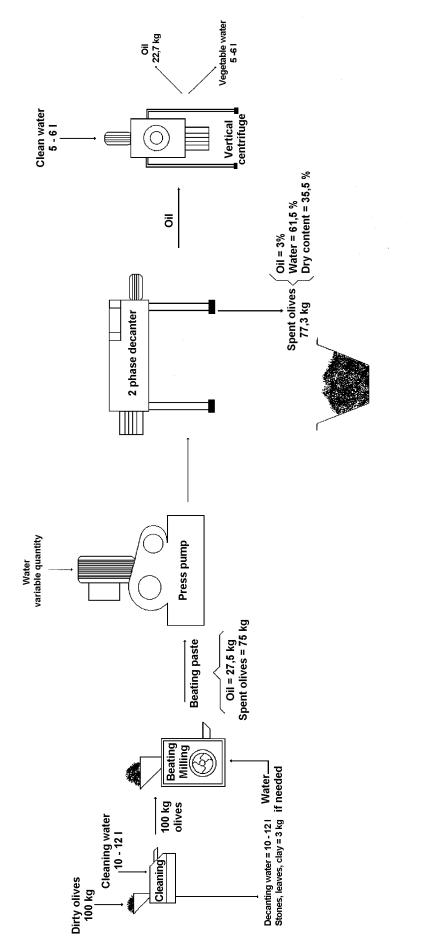
The large amount of waste generated in the process of olive oil extraction by the three-phase method, together with the increasingly demanding legislation regarding the treatment and management of oil mill waste, in some countries encouraged the development of new technologies. And the new system called "Ecologic" in **two phases**¹.

The main innovation the two-phase system brings is that of permitting the elaboration of virgin olive oil without the need to add water to the "decanter"; means, which there are practically no vegetable waters, produced. This extraction technology offers the advantage of saving of water, energy and reducing environmental impact.

The two-phase system modifies the operating conditions as it eliminates the need to add hot water in the process. Also, it is necessary to modify the "decanter". In the process two currents are generated; one which contains the oil and another that contains the majority of the solids and nearly all the constituting water, which receives the name of moist *spent olives*, although sometimes by analogy with the three-phase system it is also called *two-phase spent olives*.

The oil directly obtained in the "decanter" needs to be subjected to a more energetic process of centrifuging in a vertical centrifuge to clean the oil.

¹ For example, the system of two-phases was introduced in Spain in the 1991-1992 campaign





2.6. Comparison of the systems of two and three phases

The strong introduction that the two-phase system has had is not only due to the saving in water and the very substantial elimination of the vegetable waters, as other factors have also had their influence. The main ones are formulated below.

- The construction of the two-phase "decanter" is simpler than that of the threephase "decanter", which means it can be acquired far more cheaply.
- The oil yield of the two-phase system is somewhat greater than that obtained with the three-phase system, due to the fact that more oil is retained in the solid.
- The processing capacity of the two-phase centrifuges is higher than that of the three-phase centrifuges as they do not require the addition of water in the extraction process.
- The quality of the oil produced by the two-phase system is somewhat superior or "different", particularly with regard to the resistance to oxidation and the more bitter character.
- The cost of the operation is less.

2.7. Comparison between the three systems used

By way of compilation, Table 2.1, below, describes the "input-output" balance of material and energy in the three systems.

SYSTEM	IN	QUANTITY	OUT	QUANTITY
Press	Olive	1 t	Oil	200 Kg
	Rinsing water	100-120 I	Spent olives	
			(26% water, 7% oil)	400-600 Kg
			Vegetable waters	
			(88% water)	400-600 l
	Energy	40-60 kWh		
3 Phases	Olive	1 t	Oil	200 Kg
	Rinsing water	100-120 I	Spent olives	
			(40% water, 4% oil)	500-600 Kg
	Water added	700-1000 l	Vegetable waters	
			(94% water, 1-% oil)	1000-1200 I
	Energy	90-117 kWh		
2 Phases	Olive	1 t	Oil	200 Kg
	Rinsing water	100-120 I	Moist spent olives	
			(60% water, 3% oil)	800 Kg
			Cleaning water Oil	100-150 I
	Energy	< 90-117 kWh		

Table 2.1.	"Input-output" analysis of material and energy in the three systems
	of elaboration of olive oil.

To have a complete picture of the three systems, it should be added that:

- a) Labour costs are greater in the pressing system.
- b) Quality of the oil, as far as its stability is concerned, is somewhat superior in the two-phase system.
- c) Investment per tonne processed is smaller in the continuous systems and, within these, in the two-phase system.

CHAPTER III: CHARACTERIZATION AND PROBLEMS CAUSED BY OIL MILL WASTE

3.1. Introduction

The standardisation of the terminology used to denominate the waste generated in the olive oil production has not been obtained and depends on a host of factors, the main one being geographic. Table 3.1 contains a summary of the main terms coined in Mediterranean countries to refer to these residues.

Table 3.1. Terminology used to designate the residues generated in oil mills

	Traditional and continuous 3-phase system ²	Two-phase system			
	Orujo (Sp)				
Solid waste	Pirina (Gr/Tk)				
	Husk (Eng.)	Alpeorujo (Sp)			
	Pomace (It)	Orujo de 2 fases			
	Cake (Eng.)	(Sp)			
	Sansa (It)	Sansa humida (It)			
	Grignon (Fr)				
	Alpechín (Sp)				
	Margine (Fr)				
	Katsigaros (Gr)				
Liquid	Jamila (Sp)				
waste	Aque di vegetazione (It)				
	Olive-mill wastewater (Eng.)				
	Olive vegetation water (Eng.)				

The main by-products and waste generated in the olive oil extraction process are as follows:

² Eng.: English; Gr: Greek; It: Italian; Sp: Spanish; Tk: Turkish; Fr: French

a) Liquid waste:

- Generated in the process of preparation of the olive for its milling:
 - Rinsing water of the fruit
 - Drainage water of the storage hoppers
- Generated in the extraction process:
 - Vegetation waters of the actual olive
 - Waters from the cleansing of the oil
 - Water added in the process

The ensemble of which makes up the genuinely denominated "vegetable waters".

b) Solid waste:

- Conventional spent olives, coming from the pressing or continuous three-phase systems.
- Moist spent olives, humid olive-kernel or two-phase spent olives.
- Vegetable and earthy leftovers and stones generated in the process of cleansing of the harvested olive.

Each one of the waste or by-products mentioned presents characteristics and utilities that require appropriate management. In the following points, these aspects are dealt with in depth.

3.2. Main liquid residues: vegetable waters

3.2.1. Composition

The composition of vegetable waters is very variable and depends on a host of factors, amongst which we should mention the type of olive and the oil production process. Table 3.2 shows the average composition of the vegetable waters according to data gathered from the bibliography and Table 3.3 shows a comparison between the composition of the vegetable waters obtained by the traditional system and the continuous three-phase system.

	Unit	Pompei	Fiestas	Steegmans	Hamadi	Andreozzi
		(1974)	(1981)	(1992)	(1993)	(1998)
РН	g/L	-	4,7	5,3	3-5,9	5,1
COD	g/L	195	-	108,6	40-220	121,8
BOD ₅	g/L	38,44	-	41,3	23-100	-
Total solids	g/L	-	1-3	19,2	1-20	102,5
Total organic solids	g/L	-	-	16,7	-	81,6
Fats	g/L	-	-	2,33	1-23	9,8
Polyphenols	g/L	17,5	3-8	0,002	5-80	6,2
Organic Ac.	g/L	-	5-10	0,78	0,8-10	0,96
Total nitrogen	g/L	0,81	0,3-0,6	0,6	0,3-1,2	0,95

 Table 3.2. Summary of the average composition of vegetable waters according to different authors

Table 3.3- Comparative data of the composition of vegetable waters depending on the system of olive oil production

	Units	Traditional system	Continuous system
рН	G/L	4,5-5	4,7-5,2
BOD ₅	G/L	120-130	45-60
COD	G/L	90-100	35-41
Solids suspension	G/L	1	9
Total solids	G/L	120	60
Mineral salts	G/L	15	5
Volatile substances	G/L	105	55
Fat	G/L	0,5-1	3-10

Tables 3.4 and 3.5 contain a summary of the mineral and organic composition of vegetable waters generated by the traditional system, or by pressings, and those produced by using the three-phase system. The composition corresponds to average values and can not be taken as standard as they can vary depending on the campaign and the type of olive.

	Pressings	3-phase system
Total sugars (ppm)	20,000 – 80,000	5,000-26,000
Nitrogenated substances (ppm)	5,000 – 20,000	1,700 – 4,000
Organic Ac. (ppm)	5,000 – 10,000	2,000 - 4,000
Polyalcohols (ppm)	1,000 – 1,500	3,000 – 5,000
Pectins, mucilages (ppm)	1,000 – 1,500	2,000 – 5,000
Polyphenols (ppm)	1,000 – 2,400	3,000 – 2,300
Fats (ppm)	300 – 1,000	5,000 – 23,000

Table 3.4 Average composition of the organic matter of vegetable water

One can observe that the composition values of vegetable waters generated in the continuous 3-phase process are nearly always inferior to those of the pressing system. This is due to its greater dilution (more water added in the continuous system).

Table 3.5 Average mineral composition of vegetable water

	Pressings	3-phase system
Phosphorous	500	96
Potassium	3 000	1 200
Calcium	350	120
Magnesium	200	48
Sodium	450	245
Iron	35	16

3.2.2. Production

Logically, in all countries that produce olive oil this type of waste is generated. Furthermore, the oil mill are invariably concentrated within the producing areas. Because of this, the management of residues and by-products affects all productive situations to a greater or lesser extent.

The estimated worldwide production of vegetable waters is shown in Table 3.6.

		Vegetable waters	Spent olives	Moist spent olives
		(t/yr)	(t/yr)	(t/yr)
		Pressing/3 pH/2 pH	Pressing/3pH	2 phases
		85,938	42,969	1,441,570
	Andalusia	357,618	182,967	
		97,583		
		2,821	1,365	
	Catalonia	11,739	6,006	46,592
N		3,494		
SPAIN		7,254	3,510	
	Castille	30,186	15,444	119,808
		8,985		
		4,733	2,290	
	Extremadura	19,706	10,082	80,652
		5,865		
		130,897	63,337	-
	GREECE	1,028,882	526,405	
		-		
		3,075	1,488	-
	Northern	4,265	2,182	
		-		
		70,283	34,008	-
TALY	Central	97,489	49,878	
E		-		
		572,880	277,200	-
	Southern	794,640	406,560	
		-		
		78,120	37,800	-
	TUNISIA	617,265	315,810	
		-		
		34,875	16,875	-
	TURKEY	274,125	34,875	
		-		

Table 3.6. Estimated production of vegetable waters and spent olives in the main olive-producing countries

In additional information, the production of vegetable waters is estimated at 210,000 t in Morocco, 32,000 t in Albania, etc.

Over 30% of world olive oil production takes place in Spain, of which the greatest amount is produced in Andalusia, more specifically in Cordoba and Jaen, which generate more than 80% of the vegetable waters of Andalusia. Table 3.6 shows the number of oil mills and the extraction technology for the 1997 campaign.

	Jaen		Cordoba	
Oil mills with presses	71	24%	31	19%
2-phase oil mills	115	38%	98	59%
3-phase oil mills	15	38%	30	18%
Mixed oil mills	-	-	7	4%
Total	301	100%	166	100%

Table 3.7. Number of oil mills (1997) Jaen and Cordoba

The aforementioned campaign generated the liquid waste (vegetable waters) shown in Table 3.8.

Table 3.8. Volume of vegetable water in m³ generated in the 1997 campaign.

	Jaen		Cordoba	
Traditional oil mills	189 000	17%	30 345	10%
Two-phase oil mills	225 750	20%	147 560	46%
3-phase oil mills	702 000	63%	140 100	44%
Total	1 116 750	100%	318 005	100%

3.2.3. Polluting power

The polluting power of vegetable waters has several causes (H. Fernández 1991), the most important of which are:

- The pH, which is the main and direct cause of the death of fish when the vegetable waters, is dumped in riverbeds.
- The fat content, which provokes the formation of a layer on the surface of the water which impedes its correct oxygenation and the passing of sunlight, preventing the normal development of the fauna and flora in rivers.
- The organic content, which contributes to the consumption of the dissolved oxygen.

The relative polluting power of vegetable water can be evaluated, in terms of BOD_5 , on observing Table 3.9, which shows the typical values of other industries. From the data shown in the table, one can deduce that, considering an average value per inhabitant per day of 60 g of BOD_5 , the pollution of vegetable water would be equivalent to approximately the contamination generated by a population of 6 million people during one year.

Industry	BOD₅ (mg/L)	
Oil mills	60,000	
Alcohol plants	20,000	
Dairy	3,000	
Slaughterhouses	2,000	
Sugar factories	2,000	
Tanning	2,000	

Table 3.9. Typical values referring to BOD_5 of diverse industries

3.2.4. Fertilising value

The organic and mineral element contents of vegetable waters are, as indicated, very variable. For their use as fertilisers they must, in any case, be duly characterised at each oil mill level.

In spite of this, and based on average contents provided by the technical literature in this respect, we point out the following elements of interest and the main restriction for the use of this sewage as fertiliser.

- a) The most frequent average composition is as follows:
 - Nitrogen: 3-4%
 - Potassium: 6-8%
 - Phosphorous: 0.2-0.3%

Complementary information on this composition is provided by Professor Fiestas with the following data:

	Pressing system	Continuous 3-phase system
Organic mat.	105.00	26.00
N	2.00	0.60
Ρ	0.50	0.10
к	3.60	1.20
Mg	0.20	0.04

Contents in Kg/m³ of vegetable water

- b) Therefore, a dose of 20 m3/ha would provide:
 - 80 UF of organic nitrogen
 - 140 UF of potash (K2O)
 - 4-6 UF of phosphorous (P2O5) and magnesium (MgO)
- c) In this way, in liquid form, the product responds to the composition 1-0,1-1,5 in N-P-K.
- d) The rate of organic matter varies from 5% to 10%. At a dose of 50 m3/Ha and a content in OM of 5%, the provision of organic matter per Ha would be 2,500 Kg., equivalent to some 10 T/Ha of manure. The relation C/N of the product is generally found to be between 9 and 10, which is normal in organic amendments for agriculture. Because of this, the provisions of vegetable water should not modify the nutritional microbiological balance of the soil.
- e) The pH is acid, with values normally below 5.5. Because of this, problems should not appear in alkaline and calcareous soils, so frequent in the Mediterranean basin, but this factor should be borne in mind when trying to fertilise acid soils. In these cases, the correction of the pH with milk of lime would be convenient.

- f) The electric conductivity is high, in the region of 8 to 16 mmho/cm. Therefore, special attention should be paid to the risks of salinization of the soil.
- g) There is also an appreciable amount of organic phytotoxic compounds, particularly in relation to the phenols, phenolic glucosides, flavonoides and tannins. For this reason, the quantities and the strategies of application must be carefully studied depending on the crops.

3.3. Other liquid waste

3.3.1. Olive rinsing waters

This is the water used in the olive rinsers, with a very variable consumption and depending on the type of product coming from the land (the greater or lesser number of olives gathered from the ground) and can be situated at around 80-120 litres of water per tonne of olives.

This water basically carries away particles of dust or earth, as well as small quantities of fat coming from damaged fruits. Its organic content is of low value and it can usually be easily recycled by means of simple decantation and/or filtering. An composition of this type of effluent is shown as a guide in Table 3.10 (Alba, 1997):

	Values
Solids (%)	0.50-0.67
Cont. Oil w/o humid mat.(%)	0.10-0.16
COD (g/Kg)	7.87-10.35

Table 3.10. Composition of olive rinsing waters

3.3.2. Oil rinsing waters

These are the waters coming from the last centrifuging of the oil, during which a proportion of hot water is added to the oil that varies between 15 and 50% of the volume of the latter.

The resulting waters are, therefore, a mixture of the actual watery residue contained in the oil coming from the extraction and the hot water added. Actually, this residue is incorporated traditionally into the liquid residue generated in the extraction in press or decanter, together they constitute the "vegetable water".

Nevertheless, in the oil mills that function under the continuous two-phase system, this water would constitute practically the only existing liquid residue, since no production of vegetable water exists in the extraction process.

Tests carried out by the Institute of Fat (Borja R. et al., 1993) give the following composition for these effluents (Table 3.11):

	2-phase system
рН	5.0
COD (g/l)	3.5
Total solids (g/l)	1.69
Mineral solids (g/l)	0.24
Volatile solids (g/l)	1.45
Total solids in suspension (g/l)	0.52
Volatile acidity (g/l) (acetic)	0.25
Total phenols (g/l) (Caffeic ac.)	0.08
Alkalinity (CO ₃ Ca) (g/l)	0.12

Table 3.11. Composition of the oil rinsing waters(addition of 13.3% hot water before centrifuging)

With regard to the COD of these waters, studies carried out in industrial installations (Alba, 1997) provide values between 11.70 g/Kg (2-phase system) and 12.91 g/Kg (pressing system).

3.3.3. Vegetable waters of the 2-phase system

As previously indicated (table 2.1), olive oil production by the two-phase system also generates a liquid residue similar to vegetable water but in a quantity significantly less, as can be seen in the results of matter in figures 1.2 and 1.3. In the two-phase process, the vegetable water is generated fundamentally in the rinsing of the oil and in the draining waters of the storage hoppers.

The two-phase vegetable waters contain approximately 95.95% of water, 3.25% of dry residue and 0.8% of oil, whilst vegetable waters coming from the three-phase elaboration process (92.86%, 6.22%, 0.93%). This similitude is also reflected in more exhaustive analyses, as seen from the one shown in Table 3.12.

	Values
Total sugars (ppm)	15,500
Nitrogenated substances (ppm)	2,500
Organic Ac. (ppm)	3,000
Polyalcohols (ppm)	4,000
Polyphenols (ppm)	5,500
Fats (ppm)	5,200

Table 3.12. Orientative composition of two-phase vegetable water

3.4. Solid Waste: Spent olives

3.4.1. Characterisation

The main solid residue generated in the olive oil production is the spent olive. As indicated previously, this residue contains a certain quantity of residual oil which is not possible to extract by physical means and which is extracted in the extracting plants of olive-kernel oil.

It is evident that the composition of the spent olives depends on the system employed in the elaboration of olive oil. In Table 3.13, an analysis of the spent olives obtained in the elaboration of olive oil by the three methods is shown. It should be explained at this point that the spent olives coming from the two-phase system is known as "moist spent olives" or also "two-phase spent olives" or simply spent olives.

Table 3.13. Composition and characteristics of spent olives according to the system of origin (Cal, 1998)

Press	sed spent	ent olives ³ 3-phase spent olives Moist spent olives			3-phase spent olives		olives	
M (%)	FY dry	FY moi.	M (%)	FY dry	FY moi.	M (%)	FY dry	FY moi.
28.2	7.2	5.2	48.3	5.1	2.6	59.5	6.3	2.9

³ M = moisture content; FY dry: Fat yield of dry sample; FY moi.: fat yield of moist sample

One can see a clear difference between the fat yield of the pressed spent olives and the spent olives of continuous systems. The difference is due fundamentally to the efficiency of extraction of the continuous systems compared to traditional systems. The reduction in the fat yield of the spent olives has caused difficulties in the sector of olive-kernel oil extraction, as the sector was structured to process spent olives with humidities between 25% and 30%. On introducing the continuous three-phase process the spent olives arrived at the olive-kernel oil plants with humidities of 35-45%, which meant a considerable rise in the costs of drying and additional technical difficulties (caramelization phenomena).

However, the most serious problem appeared with the continuous two-phase system. The by-product that arrives at the olive-kernel oil plant presents humidities of between 60% and 70%.

Some olive-kernel oil plants that receive the three types of spent olives have opted for the homogenisation of the moisture content of the spent olives to be extracted, mixing the three types of spent olives in the adequate proportion until reaching mixture humidities in the region of 48% - 50%, very similar to those of the three-phase spent olives, the drying problem of which had been solved prior to the appearance of moist spent olives.

3.4.2. Calorific power

A traditional use of the spent olives has been as fuel, on a domestic scale or in the actual oil mills for production of the heat necessary in the process of extraction (hot water, heating of premises). The calorific power of the different by-products related to spent olives is shown in Table 3.14.

	Value (kcal/Kg)
Pressed spent olives	2,800-3,000
3-phase spent olives	2,500-2,800
Degreased spent olives	3,500
Stone	4,000

Table 3.14. Caloric power of spent olives and by-products

3.4.3. Nourishing value for livestock

Spent olives and by-products have had a certain application in the nourishment of cattle, in particular ovine, caprine, and camelidae. The facts that follow in relation to the nutritional value correspond to several studies carried out by NEFZAOUI, A (1991).

Composition

	Crude spent	Degreased spent	Sieved degreased
	olives	olives	spent olives
Dry matter	69.8-90.3	86.0-95.0	88.2-90.5
Total ashes	3.1-14.7	5.8-9.3	11.0-22.3
Nitrog. M. totals	5.0-10.3	12.4-16.2	9.6-11.3
Fat	5.3-12.5	1.1-7.4	2.0-6.5
Crude cellulose	32.0-47.5	32.6-53.3	14.5-26.3

Table 3.15. Composition in % of dry matter

The following comments should be made:

- The contents in *nitrogenated matter* are in the region of 10%, although the major part is linked to the parietal fraction and therefore, less available for the animal. The composition in aminoacids is similar to that of barley, except for a large deficit in glutamic acid, proline and lisine.
- High content in *fat*, basically in oleic acid (65%), linoleic (12%) and palmitic (10.5%).
- Very low content in *phenolic substances*, which during a long time were thought to be responsible for the limited nutritional value of the spent olives.
- High content in *fibre*, but with an important presence of parietal fractions, such as, which is undigestible. Sieving reduces the content of these fractions.

Nutritional value

Digestibility and degradability

On average, the coefficients of apparent digestibility are those indicated in Table 3.16.

	ОМ	Nitrog. Mat.	Crude Cellulose
Crude spent olives	26-31	6-10	0-30
Sieved degreased spent olives	32-40	29-38	21-47

Table 3.16. Coefficients of apparent digestibility (%)

The degradability in the stomach is very slow, in the region of maximum 32% after 72 hours, due to the lignocellulosic character. The degradability of the nitrogenated matter is also very low.

Consumption

The information available refers to sieved degreased spent olives, which are consumed in a large quantity, above all if they can be previously treacled. Rapid transit, so that there is not usually enough time to exploit all the potential degradability.

Alimentary comportment

The case of the sieved degreased spent olives is similar to that of chopped hay, assuring normal rumination. It can easily replace other voluminous foodstuffs (hay, straw,...)

Fodder value

Energetic value reduced from 0.32 to 0.49 UF "milk" and 0.21 to 0.35 UF "meat". Content in nitrogenated digestible matter also small (15-25 g/Kg. of dry product matter).

It is confirmed that the sieving (removing the stone) is an indispensable operation to improve the alimentary value of the spent olives or their by-products.

With regard to the crude or fresh spent olives, their rapid deterioration when piled up should be pointed out. Experiments carried out in Cyprus (HADJIPANAYIOTOU, 1999), show that the voluntary consumption of spent olives kept in uncovered piles 1.5 m high decreases with the storage time until becoming practically null after 10 days. This is associated with the presence of moulds and the fact that the fat content quickly goes rancid. The aforementioned author proposes and describes a technique of ensilage as an efficient and low-cost system to preserve the spent olives as fodder for animals.

3.5. Patsy residues: Moist spent olives or two-phase spent olives

The progressive introduction of the continuous two-phase systems to avoid the generation of vegetable waters has, in turn; given rise to more moist spent olives, as a by-product of pasty consistency because of its high moisture⁴.

As an example, one could indicate that in the middle of the eighties the production of spent olives in relation to that of olives was in Spain in the region of 40-42%, whilst at the present time this proportion has come to be more than 65%.

The transformation to two phases is not as rapid in other producing countries with small-sized oil mills. But in countries such as Tunisia, Greece and to a lesser extent in Italy, this type of change is also taking place. Consequently, the problem of the management/reuse of moist spent olives is being raised as one of the greatest bottlenecks of the oil mill sector at a scale of any producing region.

Mention has already been made of its composition and of the problems that moist spent olives generate at extractor industry level, essentially due to the drying requirements much larger than for conventional spent olives. Also, the manipulation and the transport are more difficult because of the pasty consistency of the product, which forces the use of lorries of the "bath" type with special "breakwater" protections to avoid accidental spillage.

As a complement to what has been said in epigraph 3.4.1, Table 3.17 shows the average characteristics of "typical" moist spent olives.

⁴ This is particularly true in Spain due to the large-scale change from classic and 3-phase oil mills to this new system.

	Values (%)
Fat	3-4
Protein	5-6
Sugars	13-14
Crude fibre	14-15
Ashes	2-3
Organic acids	0.5-1.0
Polyalcohols	0.5-1.0
Glucosides and polyphenols	0.5
Water (moisture)	65
Apparent density (Kg/m³)	1,035
Highest calorific powers (kcal/Kg) dry base	5,052

Table 3.17. "Typical" composition of moist spent olives

3.6. Organic leftovers from cleaning

One of the basic operations for the obtention of quality olive oil is the cleaning of the fruit. Traditionally, the agriculture cleaned the fruit in the field by using sieves, which separate the larger impurities (branches) and soil. But this operation is costly and does not clean the fruit well. Therefore, it is normal for the olive to arrive at the oil mill covered in impurities, which makes it necessary to carry out a double operation of dry "cleaning" and "rinsing" with water.

The cleaning operation is done in cleaning machines that function by sieving (the olives fall into a vibrating sieve or strainer) and simultaneous application of a blast of air. This operation gives rise to two types of residues which usually collect in the oil mill yards:

- a) Vegetable remains: leaves and branches of the olive-tree
- b) Soil and dust, particularly present when the olive is gathered from the ground by mechanical means.

It is, then, a basically vegetable residue that is usually reincorporated into the land as organic fertiliser, with or without prior composting.

The amounts generated are very difficult to evaluate, given their dependence on the collection systems used. In terms of weight, this may oscillate between 2% and 15% of the load of olives, with a density in the order of $150-300 \text{ Kg/m}^3$.

CHAPTER IV: TREATMENT AND VALORISATION OF OIL MILL WASTE AND BY-PRODUCTS

4.1. Introduction

The production of olive oil generates a great quantity of **solid and liquid waste.** Particularly, the latter have opened a multitude of lines of investigation, which in most cases have lead to great advances, amongst which one must highlight the continuous production system because of the two-phase system, which was developed to foment the "ecological" olive oil production.

The waste generated in olive oil production, as previously indicated, is fundamentally of two types; solid and liquid. The solid waste, fundamentally **spent olives** (proceeding from pressings and three-phase systems) have been used traditionally, once extracted, as a source of energy for both the extractor and ceramic industries and the like. On the other hand, the liquid residues, mostly **vegetable waters**, require specific treatment. However, just when all the vegetable water treatment systems were practically established, the new two-phase continuous extraction system appears with a new residue, called **moist spent olives**. The new residue, which at first was thought to be similar to traditional spent olives or to the hypothetical mixture of spent olives and vegetable water, did not respond in the same way to the systems known and implemented for the treatment of vegetable waters or of spent olives.

In this section, the main technologies available for the treatment and/or purification of the waste generated in the production of olive oil will be expounded, and which are as follows:

LIQUID WASTE:

- Fertilising irrigation
- Natural and forced evaporation
- Thermal concentration
- Purification:
 - Anaerobic digestion
 - Ultrafiltration
 - Inverse osmosis

- Adsorption/biofiltration
- Damp oxidation
- Combined processes

SOLID WASTE:

- Drying and extraction of residual oil
- Fuel
- Animal nutrition

- Composting
- Incineration
- Gasification
- Combined processes

It should be pointed out that the processes expounded are those that are obtaining the best results in industrial phases or that are creating the most expectation in the laboratory investigation or pilot plant phase (such is the case of certain processes relating to biomass gasification).

Many of these processes can be applied individually or combining several of them to obtain the desired result.

Liquid waste (vegetable waters) and solid waste (two- or three-phase spent olives and degreased spent olives) are considered. Nevertheless, in the explanation, the treatment of spent olives (pressing and 3 phases) is distinguished from moist spent olives (2 phases) since, despite having much in common, there are relevant and specific differences in the treatment of each of these types of by-product.

Every system or technology identified is presented under a descriptive guideline and in evaluation with the following contents guide:

- 1. Foundations or technical bases
- 2. Person(s) responsible for the development
- 3. Phase of development (investigation, pilot plant, and industrial application)
- 4. Technical description (diagram of the process, elements, material and energy balances, yields, costs, limits and determinants of the application)
- 5. Examples of use

It should be said that, in certain cases, not all the information mentioned can be provided due precisely to the scant level of development.

4.2. Liquid effluents: Vegetable waters

4.2.1. Introduction

In Chapter III of this study the characteristics of vegetable waters have been analysed in detail, and in particular, its high pollutant power which, alone, requires appropriate management to prevent potential negative impact on the environment.

For this reason, from the seventies on, this effluent has been the object of great attention on the part of scientific institutions, firms and public organisations with the object of studying and proposing the best strategies and technologies of minimisation, valorisation or elimination.

This intense activity has generated considerable technical and scientific literature. Amongst the most relevant publications, it is worth citing some with contents of revision, to which the interested reader is remitted. The two most important ones would be the following:

- TREATMENT OF VEGETABLE WATERS. Minutes of the International Meeting on the subject, Cordoba (Spain) 31 May-1 June 1991. Publication no. 18/91 of the Department of Agriculture and Fisheries of the Junta de Andalucía.
- LES EXPÉRIENCES MÉDITERRANÉENNES DANS LE TRAITEMENT ET L'ÉLIMINATION DES EAUX RÉSIDUAIRES DES HUILERIES D'OLIVES. Ministry of the Environment and Land-Use Planning. National Water Treatment Agency (ONAS). Tunis, 1996.

It should be said that this second publication to a certain extent recommends the system of continuous two-phase elaboration as the best "minimising" solution of vegetable water production. In fact, the change of oil mills to the two-phase system has been made widespread in some countries, such as Spain, with which the problem of vegetable water dumping has been enormously reduced.

Nevertheless, there still exist in the majority of producing countries numerous oil mills functioning under the pressing or three-phase continuous system. On the other hand, the two-phase system itself generates liquid waste that resembles vegetable waters. Because of this, in the epigraphs that follow, one seeks to provide sufficient

information about the "state of the art" regarding the systems of treatment and valorisation of the vegetable waters, with special reference to those, which have shown or show minimum technical-economical viability. In this sense, the specific properties of this effluent that condition the potential application of the different possible strategies must be pointed out from the start.

These are:

- a) The intrinsic composition of the vegetable water and its high pollutant power, which we need not dwell on here.
- b) The seasonal feature of its production throughout the milling campaign, which lasts no longer than 3-4 months and that, due to the requirements of the quality of the oil, really becomes shorter from year to year.
- c) The variability of the problem or impact depending on the characteristics of the oil mills with regard to:
 - Their location
 - Their size or milling capacity
 - Their concentration in the territory

4.2.2. Usable systems

More than 20 procedures or technologies applicable to the treatment of vegetable waters with aims of minimisation, elimination or valorisation are mentioned in technical and scientific publications on the treatment of vegetable waters. They deal, in most cases, with elemental or combined operations tested in a laboratory or pilot plant, without posterior industrial projection.

Thus, and only as a summary, the following technologies have been described as potentially applicable:

- Natural evaporation in ponds or lakes
- Use in fertilising irrigation
- Dehydration forced evaporation thermal concentration
- Incineration
- Destillation
- Membrane processes: Ultrafiltering, inverse osmosis
- Microbiological degradation, obtention of proteins
- Physical-chemical purification
- Anaerobic and aerobic biological purification

Some of the systems tested contain numerous variants.

A detailed description of all these systems can be found in the second publication mentioned in the previous epigraph.

The work carried out for the drawing up of this study has enabled those treatment and valorisation systems that present some degree of industrial applicability to be selected, either for their state of development or because they are endorsed by sufficiently prolonged experience.

These systems can be grouped into five main sections:

- Fertilising irrigation
- Natural and forced evaporation
- Thermal evaporation/concentration
- Purification with diverse variants
- Combined systems

4.2.3. Use of vegetable waters as fertilising irrigation

4.2.3.1. Technical bases

Section 3.2.4 of Chapter III contains comprehensive information on the fertilising value of vegetable waters.

Since olden times, the use of this effluent as a fertiliser has been advised. Indeed there are records of it from the 11th (Abu Zacaria) and 16th (Alonso de Herrera) centuries. From 1960 onwards, numerous studies have been carried out on the subject by authors such as ALBI (1960), ZUCCONI (1969), POMPEI (1974), TELMINI (1976), ESCOLANO (1976), etc.

A summary of the most recent studies follows:

 a) FIESTAS (1977): Informs about the very widespread practice of using vegetable water as fertiliser with a dosage of 100-120 l/olive tree, with the possible addition of lime. He provides information about increases in productivity when used in corn and wheat fields.

- b) FERREIRA LLAMAS (1978) refers to the benefits of this practice in the olive groves in Jaen.
- c) DELLA MONICA (1978 and 1980) and POTENZ (1980) explain the experiments performed in calcareous soils with provisions of 480 m³/Ha and in which they prove the fertilising value of vegetable water and warn about the precautions to be taken in relation to the accumulation of salts and potassium in the soil.
- d) MORISOT (1979-81) reports on a detailed study of the evolution of the soils watered with vegetable water and its effects on the olive tree. He concludes that:
 - Doses of 100 m³/Ha/year do not bring about unfavourable changes.
 - Absence of toxic effects on microflora of the nitrogen cycle.
 - Significant enrichment in potassium
 - Without modifications to the foliar contents of the olive tree
 - Doses equivalent to 400 m³/Ha cause, in gramineae in pots, decreases in yield of around 50%.
 - When applied to cereals, sowing must be carried out at least 45 days after the application of the vegetable water.
 - 30 m³/Ha and 100 m³/Ha of classic or continuous system vegetable waters, respectively, are recommendable.
- e) CATALANO et al (1985, 1989) come to similar conclusions. Long-term applications of 150 m³/Ha in 10-year-old olive trees show the beneficial effects of the application with no negative effect either on the trees or on the soil.
- f) CATALANO and DE FELICE (1991), on the basis of their own experiences and those of other scientific bodies, provide the following guidance:
 - The high organic load of vegetable waters is degraded in the soil within a relatively short period. Therefore, in general, there is no accumulation after the distribution in doses of less than 100 m³/Ha per year.
 - Provided that the distribution is carried out uniformly, at the doses stated the strata underneath the ploughable layer (>60-65 cm) do not appear to be affected by the penetration of organic matter.
 - The soil treated with vegetable waters becomes clearly enriched with nutritive elements: nitrogen, phosporous and, above all, potassium.
 - The greater fertility of the treated soil favourably affects the olive tree and the vine. On the other hand, in annual species like the potato, the phytotoxic

effect prevails over the fertilising one if the sowing or planting is carried out less than 80-90 days after the application.

- The phytotoxic effect is also evident on weeds and has a duration of 80-90 days.
- g) PROIETTI et al. (1988): Confirm the beneficial effects of an application of 800 m³/Ha in olive plants in pots and in graves. They do not observe modifications in photosynthetic activity, transpiration, and stomatical conductivity or in the specific weight of the leaves. 14 months after the application, no changes were observed in the microbic load of the soil.
- h) GARCIA RODRIGUEZ (1991) informs about several tests carried out on winter cereals in the Oliveculture Station in Jaen using continuous 3-phase system vegetable water at a dosage of 100-200-300 l/m², with a period of 3 months between application and sowing. Productivity was higher on the plots of land, which received the largest doses. The modifications in the salinity, pH and mineral contents of the soil are minimum after 3 years' application.
- DE SIMONE Y MARCO (1996): Leaving 50-60 days between application and sowing, doses of 80 m³/Ha did not negatively influence the germination and sprouting in crops of corn, sunflower, barley and wheat.
- j) LEVI-MINZI et al (1.992): Using doses of 80, 160 and 320 m³/Ha in spring crops (corn), they observe that:
 - Expressions of phytotoxicity due to phenols and volatile acids, with negative effects on germination and sprouting, disappear within two months of the application.
 - The salinity indicators do not present significant differences compared to the untreated controls.
 - Increases in content of assimilable phosphorous and scarcely any difference in the other nutritive elements
- k) PAGLIAI (1996) studied the effects on the physical characteristics of the soil. He observed an increase in the porousness of the land, with the consequent advantage over the capacity of water retention and permeability.
- TAMBURINI et al (1999): They carry out a revision of the state of the art and, after advocating this system of re-use of vegetable waters, they provide guidelines on storage and distribution systems. They conclude that:

- Information on the use of vegetable waters as fertilisers is comprehensive and precise.
- The maximums permitted by Italian legislation (Law 574 of 1996) (50 m³/Ha/year of vegetable water from pressings and 80 m³/Ha/year of continuous 3-phase vegetable water) are too low (3-5 t/ha/year of dry material). These doses could easily be doubled with no problems.

4.2.3.2. Guidelines and conditions of use

On the basis of the information and studies available, the following guidelines can be provided:

- a) Application period
 - Any, if the absence of rain so permits
 - If this is not the case, the waters should be stored in pools or ponds
- b) Crops
 - Perennial crops, in particular olive trees, vine, forestry, fruit trees,
 - Annual crops: cereals, oleaginous, industrial with applications 2-3 months before sowing.
- c) Analytical characterisation and doses
 - Soil studies and analysis of vegetable water must be available in each case.
 - Orientative doses of 30-50 m³/Ha/year of vegetable water from pressings and up to 100 m³/Ha/year of continuous 3-phase-system vegetable water.
 - The characterisation of the soil and of the vegetable water itself must provide the applicable doses with greater precision.
- d) Storage
 - Waterproof reservoirs far from urban centres or transit areas to avoid the effects of bad smells.
- e) Distribution
 - For small oil mills, transport and distribution with barrels for liquid manure of a capacity of 6-12 m³
 - For specific situations, irrigation networks can be used.

- f) Capacity of oil mill and necessary areas.
 - In the region of 1, Ha for each 100 t of milled olives.
- g) Controls
 - Every two years, analysis of the soil and subsoil to check: pH, CE, OM, nutritious elements.
 - Analysis of growing leaves.
- h) Costs
 - Depend on the storage strategy and the transport distance.
 - For example, in the case of distribution with a 6,000-litre cistern of and 1.2 hours per load (loading, transport and unloading), the cost fluctuates in the region of 0.006E/m³, well compensated by the value of the fertiliser provided.
- i) Conditions of applicability:
 - Availability of appropriate soils and crops.
 - Without storage, not more than 40-60 m³/day, which entail some 100 t/day of olives in the pressing system and some 40-50 t/day of olives in the 3-phase continuous system. That is to say, for oil mills of medium and small size.

4.2.4. Natural evaporation: lagoonage

<u>Foundation</u>: Also called **lagoonage** or natural evaporation in pools. Consists of a natural evaporation, favoured by the action of the sun and wind.

<u>Person(s)</u> responsible for the development. The method of lagoonage was the first process to solve the problem of vegetable waters in Spain, and was proposed by the Directorate General for the Environment in 1980.⁵

Phase of development: Complete and widely tested development.⁶

⁵ With the aim of reducing the pollution of public water supply and the underground waters of the Guadalquivir basin, in Spain in 1981 Royal Decree 3499/81 was passed which contemplated a series of measures to avoid the indiscriminate dumping of vegetable waters.

⁶ It has been the method used on a large scale for years in the south of Spain.

Technical description:

The characteristics of these reservoirs are usually as follows:

- a) Depth of 60-70 cm and, in any case, not more than 1.50 m. although in many cases this depth has been widely surpassed as a consequence of the demands in cost and area.
- b) Waterproofing with sheets of plastic material and with concreted bottom to facilitate its cleaning by mechanical means (tractors equipped with shovel).
- c) Location far from urban or transit zones.
- d) Perimeter fencing for security reasons.

The capacity of these reservoirs is very variable and depends, naturally, on the capacity of the small oil mills up to more than 70,000 m³. ⁷

<u>Costs</u>: Those of the land and preparation and maintenance of the pools. This depends on the place, availability of free land and nearness to important urban centres. The cost of the operation is less than 0.03 E/m^3 of vegetable water.

<u>Examples of use in Spain</u>: There are numerous co-operatives in Jaen and Cordoba that adopted it (for example, in Úbeda, Baeza, Lucena, and Baena). In the province of Jaen there are 998 pools, with a total occupied surface of 250 ha and a capacity of 2.5 million m³; in Cordoba there are 369 pools, occupying an area of 62 ha and a capacity of 0.9 million m³.

Large pools have also been built in Tunisia, amongst which are those of Kalaa Kébira (30,000 m³) and more than 40 in the city of Sfax.

<u>Limits and determinants of the application</u>: At the present time, the main limitations are the lack of space and of suitable sites to install new pools. The dumping of vegetable waters in public water supplies must be avoided.

After several years'experience, the problems detected are as follows:

⁷ Achievable quantities in some parts of Andalusia.

- a) The need for large areas, which is not always easy next to the oil mills. If they must be far away, there is a problem of transport and its associated costs.
- b) Insufficient evaporation: formation of an oily layer, which prevents the action of solar radiation.
- c) Emission of bad smells and attraction of insects.
- d) Dangers of infiltration
- e) Formation of sludge at the bottom and difficulties for its emptying and use.

On the other hand, vegetable water stored in tanks is subject to a series of biological processes that tend to degrade the organic material. It is a process of self-purification, capable of reducing the BOD to less than half in two months.

To relieve as far as possible the bad evaporative functioning of the ponds, some complementary solutions have been developed. The most noteworthy are listed below.

4.2.4.1. Addition of degradation micro-organisms

A bacterian compound based on purple bacteria of the type THIOBACILUS is added to the pools. This comes in the form of a commercial product. This microbiological preparation degrades the fat contained in the vegetable water in such a way that it avoids or eliminates the formation of a surface film thus noticeably improving its evaporative efficiency.

Tests carried out by the Institute of Fat in Seville studied the addition of the product to highly concentrated vegetable waters ($COD_t = 112.300 \text{ mg } O_2/I$), 1.06% fat, Total solids = 71.745 mg/l, pH = 5.2) at an initial dose of 10 ppm and 4 ppm per week during 12 weeks, in conditions of aerobia, optional (simulating an evaporation pool), and of anaerobia (without stirring). A synthesis of the results is as follows:

- a) In conditions of aerobia, the COD was reduced by 75% after 80 days. The fat was reduced by 100% after 100 days. The pH was stabilized in values nearing 8. No bad smells were produced during the process.
- b) In optional conditions, the COD was reduced by 40% after 20 days. The fats were eliminated until they were stabilised at 6.6%. Absence of odours. The pH reached the value of 7.1 after 80 days.

c) In general, the reduction of COD is significant, and there is also a considerable reduction in fats and dry residue.

In life-sized pools, the following is recommended:

- a) Shock treatment with 5 litres of preparation per 500 m³ of vegetable water stored.
- b) Two more monthly additions, in the region of 1 I for every 500 m³

This brings about highly efficient evaporation and, therefore, elimination of vegetable waters.⁸

The price of the product is about 49.19 E/I. With a recommended dosage of 7 l/year for each 500 m³ of vegetable water, the cost of the operation is 0.68 E/m³ that is to say 0.0007 E/I of vegetable water.

4.2.4.2. Installation of nebulizers and cells (forced evaporation)

This is a procedure to favour the formation of fine watery particles by means of highpressure injection in aspersion or nebulization nozzles. This favours the action of solar radiation and wind and the evaporation is noticeably improved.

Pumping equipment is installed on the edge of the pools, which sucks in the vegetable water and injects it into a network of nebulization nozzles. The non-evaporated excess falls back into the pond.

Other elements that favour evaporation are cells of great reticular surface exposed to the sun and air, watered intermittently with vegetable water by sprinklers. This increases the evaporation capacity up to 40 times.

These systems⁹ require considerable investment and energy and do not solve the problem of sediments at the bottom.

⁸ Experiments in an oil mill in Catalonia gave doubtful results. It is not known if it was due to the functioning of the product or because of the handling conditions (dose, moment of application, etc.) In the 1999/2000 campaign, some thirty Andalusian oil mills have used this procedure in their evaporation pools.

⁹ Installed in some reservoirs in Andalusia (see photographs)

4.2.5. Thermal concentration-evaporation

<u>Foundation</u>: Consists in the use of thermal effect to concentrate the vegetable water, eliminating part of the water, by means of a simple or multiple effect evaporation. The solid waste can be put to good use, enabling the waste to be completely eliminated, that is to say, no dumping.

Person(s) responsible for development: A series of plants at pilot and industrial level have been developed for some years. (FABRICA SAN CARLOS, NUCLEOS DE INTERFASE SA, NIRO ATOMIZER SA etc.) More recently, TRAINALBA SA, based on European Patent EP 0 718 397 has carried out some installations and continues working on this technology. In Italy, the technology called "FRILLI-ENEA" has been used, acquired by the society SOLVIC of Bari. (AMIRANTE, P and MONTERVINO, A, 1996).

<u>Phase of development</u>: Phases of investigation pilot plant and industrial application have been completed.

<u>Technical description</u>: The method allows the obtention, on the one hand, of a concentrate that can be used as fuel or as fertiliser or can even be added to fodder thanks to its nutritional value and, on the other, the condensation water, which, after purification, can be dumped in natural water channels. The process is carried out by means of a combination of suitable physical-chemical and thermal treatments. In the first place, the vegetable water is prepared using various physical-chemical processes, then going on to a continuous simple- or multiple-effect evaporation, following the outline in Fig. 4.1.

The heat required is produced by means of a steam boiler, which can use the actual spent olives or the concentrate of the installation as fuel. The following products can be obtained:

- Steam from the water, which is released, into the atmosphere
- Condensation water, which can be purified and recovered.
- Concentrated vegetable water, containing the undissolved matter, of nutritional value in livestock farming.

Examples of use:

- a) The TRAINALBA system (Spain): The research of TRAINALBA, in the treatment of vegetable waters with thermal evaporation, have materialised in two plants, the first called TRAINALBA-M1 and the second TRAINALBA-F1. The first was installed on a mobile platform and has been shown at several trade fairs: Expoliva`93, Maga`93, Amposta`93, Montoro`94 and `98. The second, TRAINALBA-F1, is installed in Sotoserrano (Salamanca) with a vegetable water purification capacity of three phases, from an oil mill that presses 50,000 Kg of olives daily. With the application of the TRAINALBA S.A. method various byproducts are obtained that can be used in different ways. The main novelties and characteristics of the process are mentioned below:
 - The water consumption involved in the process is considerably reduced due to the fact that both the water from the olive and that, which is later added, is recovered and recycled, and it is even possible that a surplus of drinking water appears.
 - Conversion of solids, together with spent olives and other vegetable residues from the area, for the manufacture of fertilisers by means of a process of composting and/or adjustment for the manufacture of compound fodder.

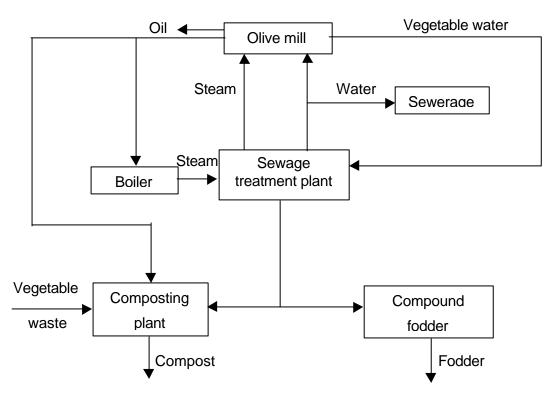


Figure 4.1. Outline of the treatment of vegetable waters proposed by TRAINALBA

- b) Experiments in Italy: the thermal concentration systems have been recommended and adopted in half a dozen plants in Puglia and Basilicata, with a total purification capacity of about 25 m3 of vegetable water per hour (unitary capacities of 5 to 8 m³/h). With this system, the following by-products per M⁸ of vegetable water treated are obtained:
 - 350 Kg/h of a hydroalcoholic mixture obtained in the first phase, with an alcohol percentage that varies between 2.5 and 15%
 - 400 Kg/h of condensed (distilled water), separated in the second phase, with an average COD of 1,500-2,000 ppm.
 - 150 Kg/h of concentrate with humidity at 47% (53% of dry matter) and high carbon, nitrogen and potassium content.

The thermal consumption, very variable depending on the number of phases used, were:

- One phase: 1.20-Kg steam/Kg water evaporated
- Two phases: 0.65-Kg steam/Kg water evaporated
- Three phases: 0.36-Kg steam/Kg water evaporated

The average characteristics of the original vegetable waters and of the three fractions obtained were as follows:

	Unit	Veg. Water	Concentrate	Phlegms	Condensate
Density	Kg/l	1.06	1.19	0.985	1.00
Dry residue	%	8	53		
Sup. Calorific power	Kcal/Kg		19,285		
Alcoholic degree	%		2.5-4.0		
COD	Ppm	100,000		60,000	2,000

The process is completed with the composting of the concentrate mixed with other agricultural or zootechnical waste.

Information on costs:

- a) In a pilot experiment carried out by Niro Atomizer S.A. for the Hydrographic Confederation of the Guadalquivir (Spain) (1991-92), it was estimated that the cost of installing of a forced evaporation plant for 5,000 m³ of vegetable water per year is 180,000 E, with a total operation cost (energy, staff, materials) of 6.8 E/m³.
- b) Complementary information can be obtained in report nº 2/91 of the Research Department of the Environmental Agency of the Junta de Andalucía (Spain)
- c) For a production of some 10-12,000 t/year of olives in the Co-operative of Jimena (Jaen. Spain), the total investment in the vegetable water treatment plant can reach some 300,000 E.
- d) Italian sources inform of the following cost levels:

•	Investment (for 5 m ³ /h):	300,000 E
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• Cost of operation: 13,19 E/m³

Application limits and determinants:

Thermal evaporation/concentration systems present the following problems:

- a) High investment only justified in conditions of very high production.
- b) Emissions into the atmosphere, which must be attenuated by means of the installation of costly equipment for the filtering and washing of gases.
- c) High-energy consumption and maintenance costs.

4.2.6. Purification

4.2.6.1. Introduction

References of application of the following techniques are available:

- Aerobic treatment
- Anaerobic or biomethanization treatments
- Membrane processes
- Adsorption and biofiltration processes
- Damp oxidation

4.2.6.2. Aerobic treatment

<u>Foundation</u>: Aerobic treatment (*bioremediation*) consists of the biological degradation of the organic pollutants present in vegetable water, by means of micro-organisms that consume the oxygen dissolved in the water modifying the natural balance. To eliminate or counteract the negative effect that the dumping of organic substances can have on the surface waters, these must be previously eliminated. The amount of oxygen required by a current polluted by organic biodegradable substances is determined by means of a standard analysis known as biological oxygen demand (BOD_5) .

Person(s) responsible for development:

- University of Harokopio, Ms. Antonakou, Tel. +30-1-95-77-051, Fax. +30-1-95-77-050, Dpt. of Nutrition, Dietetics and Food Science, 70, El. Benizelou, 176 71 Athens (Greece). They have developed several pilot and demonstration biorremediation plants in Kalamata.
- CSIC- Centre of Edaphology and Applied Biology of Segura, Murcia (Spain).
- CSIC-Institute of Fat (Seville. Spain).

<u>Phase of development</u>: fundamentally at investigation and pilot plant level. See photos of Greek biorremediation pilot plant.

<u>Technical description</u>: the treatment, apart from pursuing the reduction of BOD_5 , aims to reduce or eliminate other types of compound (inorganic salts, nitrogenized or ammoniacal compounds) the quantification of which is performed by means of another standard analysis called chemical oxygen demand (COD).

The aerobic treatment plants are plants where the biological degradation that would normally take place in the natural environment is facilitated accelerated and controlled. The microorganisms present in water degrade the organic matter present in the environment and transform it into CO_2 , water and cellular mass. The oxygen necessary for the microorganisms to perform the degradation is supplied to the aerobic reactor by means of propagators or simply by means of paddles or stirring rods.

The microorganisms that carry out the degradation can be in suspension or fixed and the process can be carried out continuously or discontinuously. After a suitable treatment period, which depends on the operating conditions and on the pollutant load of the vegetable water, one proceeds to the clarification of the waste water, obtaining a clean effluent, an active sludge that is recirculated to the treatment tank, and an old sludge that must be eliminated and that in general can be used as substratum or organic corrector in farming land.

Traditionally, vegetable water has been treated by depositing it in sedimentation pools where it has not been possible for the aerobic degradation to occur adequately as the pools are not sufficiently aired, which favours uncontrolled digestion and the emission of bad smells. The problem can be reduced if ventilation (oxygenation) equipment is available in the pools, which supply the oxygen necessary for the aerobic digestion of the biodegradable organic matter to take place.

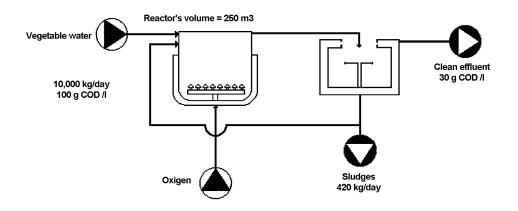


Fig. 4.2 shows a generic outline of a vegetable water aerobic treatment system.

Figure 4.2. General outline and approximate result of aerobic treatment of vegetable water

In all the experiments carried out, the results are discouraging due to the great amount of time necessary and the inefficiency of the processes used.

The main cause of this "failure" is the high concentration of compounds of phenolic nature that are characterised by their high antimicrobian effect, which is amply documented in technical-scientific literature (RAGAZZI Y VERONESSE, 1967;

FEDERICI I BONGI, 1983; MORENO ET AL, 1983; RAMOS CORMEZANA, 1986; MAESTRO Y BORJA, 1990, etc).

<u>Limits and determinants</u>: The main advantages of this type of treatments are: low toxicity and danger of the gaseous effluents that are generated in the process, the controllability of the process and that the liquid effluent obtained can be dumped directly into the natural water channel. The main disadvantages are scant decrease in chemical oxygen demand.

<u>Operation costs</u>: they have been estimated in FiW (**FIW = Forschungsinstitut für Wasser und Abfallwirtschaft)** at 23,000 E for a campaign of 90 days, where approximately 1,000 m³ of vegetable water are generated.

<u>Examples of use:</u> In recent years, great investments have been made in all olive oilproducing countries, and especially by those in the Mediterranean area, to find microorganisms that resist the high toxicity of the vegetable waters. See photographs of plants in Greece.

4.2.6.3. Anaerobic treatment or biomethanization

<u>Foundation</u>: Treatment or anaerobic digestion, methanization. It is a biochemical fermentation process in which the organic substances such as proteins, fats or carbohydrates are degraded by means of fermentation into intermediate products, fundamentally acids and alcohols. To achieve high performance in the process, these intermediate compounds must be completely degraded to methane (30 m³ per 100 Kg of influential COD) and carbon dioxide.

<u>Person(s) responsible for the development</u>: BIOTECNOLOGÍA, S.A. and Alpechín S.A. (Spain) Pilot experiments were carried out in the S.A.T. oil mill, San José de Puebla de Cazalla (Seville) and in the Jimena S.A. oil mill, Atarfe (Granada), both subsidised by the Hydrographic Confederation of the Guadalquivir (campaign 1991-92). CSIC- Institute of Fat (Seville).

<u>Phase of the development</u>: In the particular case of the treatment of vegetable waters, at present there are no industrial plants. Nevertheless, there are a host of experiments and research in pilot plants.

<u>Technical description</u>: See Fig. 4.3. Anaerobic treatment admits residual currents with a heavy pollutant load (COD > 1,500 g/L), and also, produces a small amount of excess sludge and has a considerable energy yield by generating methane in the process and requiring little space.

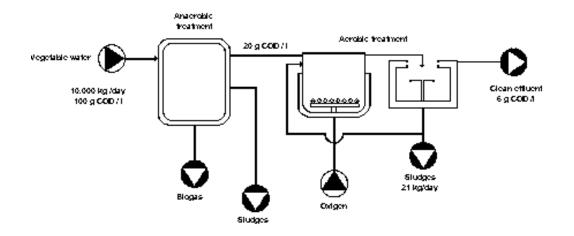


Figure 4.3. General outline and approximate result of anaerobic treatment of vegetable water

<u>Fundamental advantages of anaerobic treatment</u>: the high efficiency obtained in the degradation (decrease of COD), the small reactor volume and of space necessary in comparison with the aerobic system, the small amount of excess sludge generated compared to the aerobic treatment, the low cost of the operation as no energy consumption is necessary for the airing and ventilation of the watery residue and the obtention of a fuel gas which can be used in electricity generating plants.

<u>Cost of treatment</u>: Estimated as being the same as the aerobic treatment (campaign of 90 days, treatment of 1,000 m³ of vegetable water) the cost is 18,000 E, significantly lower than that of the aerobic. Nevertheless, anaerobic treatment in itself does not generate an effluent that can be dumped directly into the surface waters, which makes it necessary to have a system of subsequent aerobic treatment similar to that described above with a cost near to 23,000 E. In summary, **the total cost of the anaerobic-aerobic treatment would be excessive,** some 41,000 E, that is to say 41 E per m³ of vegetable water.

Examples of use:

There is a pilot experiment of the Alpechín, S.A. system, which was subsidised by the Hydrographic Confederation of the Guadalquivir in 1991-92 (Spain).

The method was developed jointly by la Stazione Sperimentale per le Industrie degli Oli e dei Grassi, of Milan, and by the firm Alpechín S.A., which has assumed its commercial management. The method consists of purification in **anaerobic** phase, by using a reaction unit. The installation is composed of a deposit of vegetable water, a deposit of homogenisation where the pH is adjusted and where, if necessary, nutrients, various anaerobic digestor deposits and equipment for inverse osmosis, are added.

Once the vegetable water has been previously treated in the homogenisation tank, it is warmed to be introduced in the anaerobic reactor. In the process, methane gas is given off, which is used for the heating of the anaerobic digestor and for diverse uses in the very oil mill. In the stage of anaerobic digestion, a reduction of 86% of the COD is acquired and there is practically no sludge produced. The effluent coming from the digestor is subjected to a process of inverse osmosis where it is filtered, obtaining almost clean water and that can be poured into the rivers or used as irrigation water.

The cost was **also excessive**: some 180,000 E investment for 4,000 m³ of vegetable water, that is to say 3.6 E/m³ of treated vegetable water, with exploitation costs of about 6 E/m³.

The microorganisms responsible for methanization are very sensitive to temperature, and reach optimum activity at temperatures of between 30 °C and 40 °C and with a narrow pH differential between 6.8 and 7.5.

4.2.6.4. Membrane processes

<u>Foundation</u>: Membrane processes, such as, for example, ultrafiltering and inverse osmosis, are often used in the treatment of certain residual liquid currents, as it allows the elimination of the pollutants of the water generating a clean current and a concentrated current.

Person(s) responsible for development: see the examples of use.

Phase of development: investigation and pilot plant.

<u>Technical description</u>: In the particular case of vegetable water, two currents are obtained; one of water that can be poured directly into the rivers and a second one with a great concentration in pollutant components of the original vegetable water.

The process enables the original COD of the current to be eliminated 100%. Nevertheless, the membranes undergo a rapid degradation, which has direct repercussions on the cost of the operation. This means the residual current, vegetable water, must be subjected to a previous treatment, for example an aerobic treatment. Fig. 4.4 gives an outline of the proposed treatment.

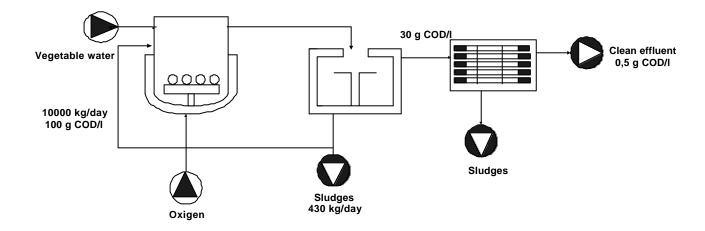


Figure 4.4. System of combined treatment, Aerobic/Inverse Osmosis

<u>The main advantages</u> of the treatment are the great reduction in COD, the little space that the plant requires and the possibility of re-using the clean effluent. On the other hand, the process requires a pre-treatment and has a high-energy demand, both of which considerably increase the cost of the whole process.

<u>The total cost</u> of the combined treatment is high (estimated by FiW for 1000 m^3 of vegetable water per season) is of 50,000 E, of which 23,000 E correspond to the aerobic treatment and 27,000 E to the inverse osmosis operation.

<u>Examples of use:</u> In 1991-92 there were pilot experiments subsidised by the Hydrographic Confederation of the Guadalquivir (Spain):

- Ultrafiltering: carried out by Fernández Saro S.A., for the oil mill Molino de las Torres de Alcaudete (Jaen).
- Ultrafiltering: carried out by Scandiavision S.A., for the oil mill Martínez Montañéz de Alcalála Real (Jaen)
- Inverse osmosis: carried out by Itin-Indelpa S.A. for the oil mill Coop. N^a S^a de la Merced en Montoro (Córdoba).

In all the cases, **the costs are also very high**, between 150,000 and 180,000 E for the installation $(3 - 4.2 \text{ E/m}^3 \text{ of treated vegetable water})$ and for the exploitation, about 6 E/m³.

4.2.6.5. Processes of adsorption and biofiltration

<u>Denomination and foundation</u>: The processes of filtration are used frequently to eliminate solids from the wastewaters. The solids contained in the water are retained, forming a cake, which increases the resistance to the passing of the residue, increasing at the same time the efficiency of the filtration and the cost of operation. In conventional filters the compounds dissolved pass through with the watery residue and remain untreated. Nevertheless, biofiltration processes are an exception; in this case, the filter also serves as a nutrient for the bacteria, so that a process of biological degradation of the dissolved organic substances takes place. The biofiltration plants eliminate 100% of the solids and between 70% and 80% of the dissolved organic compounds.

<u>Person(s) responsible for development</u>: Recently, a project on biofiltration and filtration-adsorption has been proposed to the European Commission by the Polytechnic University of Toulouse (France) and the Complutense University of Madrid (Spain) (Prof. Aragón, Dept. of Chemical Engineering).

Phase of development: Investigation

<u>Technical description</u>: The process of biofiltration requires that in some way the amount of oxygen necessary to carry out the aerobic process be supplied, Fig. 4.5. The washing of the filter provides a concentrate, which can be used on farmland.

Examples of use: None known.

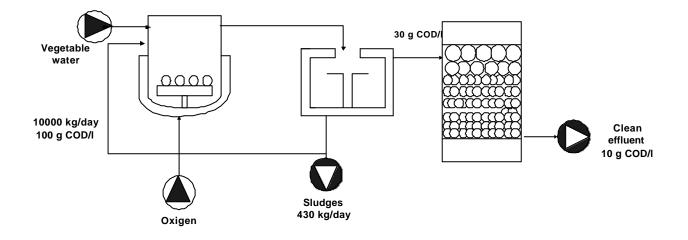


Figure 4.5. Outline and result of approximate material balance of the biofiltration process

<u>The operation costs</u> estimated by FiW for the process described with treatments capacities of $1,000 \text{ m}^3$ of vegetable water is 23,000 E or 46,000 E if the aerobic pretreatment is included.

<u>The main advantages</u> of the process lie in the retention of solids and in the elimination of most of the dissolved organic compounds. The most important disadvantages are the risks of the filter blocking and the high pollutant power of the resulting concentrate (cake).

<u>A variation or alternative to biofiltration is adsorption</u>. Adsorption consists of the concentration of the organic pollutant in solid support with a large specific surface, generally active carbon ($500 -1,500 \text{ m}^2/\text{g}$). In the treatment of vegetable waters, adsorption is aimed at biodegrading those organic compounds that have bactericidal effects, inhibitors or colouring (tannins, phenols, etc).

The main advantages of absorption lie in the little pollution it generates in the soil, air or water and the fact that this requires few qualified staff. The main disadvantages are that it is impossible to re-use the active carbon (however, thanks to its high calorific power, it can be used in combustion processes) and that it is necessary to carry out a pre-treatment. The cost of the adsorption treatment is estimated at 47,000 E, which is itemised in the following way; 23,000 E correspond to the aerobic pre-treatment plant, and 24,000 E to the adsorption plant.

4.2.6.6. Damp oxidation

<u>Foundation</u>: Damp oxidation is the name given to the process by which the oxidation of the organic substances in liquid phase is carried out using oxygen or another chemical oxidising agent, such as ozone or hydrogen peroxide. The process is carried out at high pressure (10 - 220 bar) and at relatively high temperatures (120 - 330 °C). The process of oxidation basically yields CO₂ and water, although normally other oxides are generated.

<u>Person(s) responsible for development</u>: FiW (Germany) Experiments in the treatment of vegetable water with ozone have been carried out by BELTRAN DE HEREDIA, J et al. (2000), in the University of Extremadura (Spain).

<u>Phase of development: Only</u> theoretical estimations comparable to other wastewater. It has not been applied directly to the purification of vegetable waters, with the exception of the treatments with ozone reported in the previous paragraph.

<u>Technical description</u>: When oxidation is not complete, the compounds which are either difficult to biodegrade or are non-biodegradable, are transformed into biodegradable fragments, so that a biological treatment plant is normally positioned downstream from the oxidation plant.

<u>The cost</u> of the operation is, approximately, 18,000 E and if it is necessary to use an aerobic treatment plant, the costs increase to 41,000 E per m3 of treated vegetable water.

<u>Advantages:</u> The main strong points of this treatment are the small amount of space that it requires and that, also, the water treated by this method can be discharged normally to the rivers. Nevertheless, and despite the high degree of purification that is reached, the disadvantages fundamentally are due to the emissions into the atmosphere and the high energy demand that the treatment plant requires.

4.2.7. Combined systems and others

Six original methods are described below that consist of more or less complicated combinations of other methods:

4.2.7.1. Thermal purification and concentration (TRAINALBA S.L. Spain)

This involves a combination of the systems of:

- a) Physical-chemical treatment by flocculation of the vegetable waters, which is translated into a separation of solids in suspension and the carrying away of phenolic substances, which give rise to a paste that, with the addition of molasses, can be used as a food product for livestock or can be added in composting processes.
- b) Treatment by thermal concentration as already described in epigraph 4.2.5.

This type of plant has been installed in the Agricultural Co-operative of Jimena, amongst other locations.

The limiting and conditioning factor of the applicability of the system is the large investment required.

At the present time, TRAINALBA SL is projecting the installation of a treatment plant in Baena, together with large stock pools for vegetable water, to use a system of electric cogeneration characterised by:

- The use of natural gas as fuel which drives motor-alternators of great power
- Re-use of the heat of the exhaust as a source of heat for the drying or evaporation of the vegetable waters.

The special rules for cogenerators to which the installations of biomass treatment can have recourse means a return can be made on the investment.

4.2.7.2. Integral purification by physical-chemical and biological processes

<u>Foundation</u>: Numerous studies show that the polyphenols of vegetable water, the main antimicrobian agents and responsible for the poor functioning of the biological

purification systems, can be degraded by fungus and bacteria prior to enzymatic hydrolysis. In view of the good results obtained in the elimination of these phenolic components (BORJA et. Al, 1990), the Institute of Fat in Seville (Spain) tackled the successive application of the anaerobic, aerobic and physical-chemical purification processes with the object of achieving an effluent with adequate characteristics for dumping in rivers channels.

Technical description: Successive application in four stages:

a) Bioconversion:

The objective is the recovery of the oil emulsioned with the vegetable water and to eliminate the phenolic components. The following is achieved:

- Formation of a lipoprotein mass that retains practically all of the oil, with the following composition:
 - Humidity: 60%
 - Olive oil: 7%
 - Protein: 10%
 - Carbohydrates: 11%
 - Minerals: 12%
 - Yield: 56 Kg/m³
- Elimination of 70% of the polyphenols content
- Elimination of the solids in suspension, colloidal substances and part of the mineral salts

The characteristics of the effluent of the bioconversion process, after 15 days, are as follows:

- pH: 4.5-5.5
- COD: 20,000-30,000 ppm
- Solids in suspension: Exempt

b) Biomethanization

Process of anaerobic purification that implies the break-down of the organic molecules until they are transformed into methane and carbon dioxide by means of the symbiotic action of 3 groups of micro-organisms: hydrolytic bacteria, acetogenic bacteria and methanogenic bacteria.

Due to the presence of inhibitory polyphenols in the fresh vegetable water, the hydraulic residence times in the bioreactors are very high, in the region of 30-40 days, which has repercussions in the form of high installation costs. But on applying anaerobic digestion to the resulting effluent of the bioconversion, the inhibitory effect disappears and the hydraulic residence times do not exceed 4 days. The optimum process temperature is 35-37 °C.

The characteristics of the biogas obtained are as follows:

- Volume: 10 m³/ m³ vegetable water
- Calorific power: 6,000 kcal/m³
- Energetic equivalent: 6 Kg fueloil / m³ vegetable water 17 Kg degreased spent olives

The characteristics of the anaerobic effluent are as follows:

- pH: 7.2-7.5
- COD: 4,000 5,000 ppm
- Purification efficiency. 80%

c) Aerobic treatment

A process of airing (aerobic) is applied to the previous effluent. A bacterian biomass is obtained and the aerobic effluent, with the following composition:

- Bacterian biomass:
 - Humidity: 70%
 - Protein: 10%
 - Carbohydrate: 12%
 - Minerals: 8%
 - Yield: 3 Kg/m³

- Aerobic effluent:
 - pH: 7.0-7.2
 - COD: 1,000 ppm
 - Purif. efficiency 80%

d) Physical-chemical treatment

To eliminate the colouring of the resulting liquid and continue to diminish its COD, a physical-chemical treatment is applied consisting of the addition of small quantities of sulphate of alumina as polyelectrolite. That leads to a final effluent with the following characteristics:

- pH: 6.5-7.0
- COD: < 500 ppm
- Dissolved salts: 5-7 Kg/m³
- Colouring: Exempt

Altogether, a total hydraulic residence time of less than 15 days achieves total purification (99.6%) of the vegetable water and the obtention of:

- 56 Kg/m³ of lipoprotean mass, with the possibility of extraction of the residual oil
- 10 m³/m³ of biogas, which is equivalent to an energy of 60,000 kcal/m³ of treated vegetable water.
- 3 Kg/m³ of bacterian biomass that can be used to feed livestock

<u>Costs</u>: the repercussion estimated per cubic metre of treated vegetable water in a plant of medium- to large-sized plant (in the region of 1,000 m3/year) has the following values:

- Operation: 7.8 E/m³
- Amortisation: 3.6 E/m³

No income whatsoever has been deducted for the value of the biogas nor of the oily residues or useful proteans.

Examples of existing installations in Spain: Two plants of this type were installed in the Co-operative of Puebla de Cazalla (Cordoba), with a 500-m³ digestor and in

Monterrubio de la Serena (Badajoz), with a digestor with a capacity of 1,000 m³. They were able to reduce the COD to about 500 ppm. The case of the purifier of Soller, based on similar principles, is described in the following epigraph.

4.2.7.3. The case of the purifier of Soller (Majorca)

In the area surrounding Soller there are three oil mills (Cooperativa San Bartolomé, Can Deià y Can Repic), with a production, which varies from 600 to 1,200 m3 of vegetable water per campaign.

In order to solve the problem of the environmental impact of this waste, in 1998, the INSTITUT BALEAR DE SANEJAMENT (IBASAN) built and put into operation a purifying plant capable of treating some 8 m³/day of vegetable waters. The idea was really to carry out a pre-purification before sending the waters to the existing wastewater Treatment Plant.

The process is as follows:

- a) Reception of the vegetable waters: Transport to the plant from the oil mills is carried out with barrels of the type used for liquid manure.
- b) Roughing-down: by means a paper filter of 15 mm.
- c) Physical-chemical processes of neutralisation and flocculation to eliminate the dissolved solids and carry away the phenolic components. The sludge and liquid swimming on the top are separated.
- Regulation of flow to anaerobic treatment, by means of lung-tanks with airers. The vegetable water receives here its first airing.
- e) Biological treatment with two reactors with a high rate of oxidation, with formation of bacterian biomass in special supports. The lyophilised bacteria, specially selected to resist and degrade the phenolic components, are added in each campaign. The hydraulic retention time is 22 days.
- f) Secondary decantation in a unit designed for a surface load of $1.02 \text{ m}^2/\text{m}^2/\text{h}$
- g) Deposit for supply to the treatment plant for the treatment of urban sewage.

The COD of the fresh vegetable water on entry varies between 45,000 and 74,000 ppm and the installation nearly always has a yield of more than 90%.

The cost of the investment was in the region of 240,000 E and the annual operation costs are in the region of 18,000 E/year. Counting an amortisation at 15 years, the total cost would be of some 33,000 E/year, which is translated into some 0.02-0.03 E/litre of treated vegetable water if 1,000 m³/year were treated.

During the 1998-99 campaign a total of 512 m³ of vegetable water was treated (poor harvest and one of the oil mills was not in operation). The consumptions of reagents from the purifier, for this quantity of incoming fluid, were as follows:

•	Lime (CaO):	5.5 Kg/m ³
•	Polyelectrolite:	0.068 "
•	Sulphuric acid:	0.0976"
•	Pure oxygen (O ₂):	100.2 "
•	Lyophilised bacteria consortium:	0.016 "

4.2.7.4. Other systems

4.2.7.4.1. Pieralisi, S.A. System

This actually consists of a drying or evaporation process of a mass made up of the spent olives to which the vegetable waters are added (Fig. 4.6). Together they go through a drying installation or evaporation plant formed by the following elements:

- Oven or combustion chamber, formed of two concentric cylindric bodies
- Burner of solid fuel, which can be dry spent olives, degreased spent olives, or stone.
- Firebreaking pre-chamber
- Drying sieve, rotary, double-circuit
- Cyclones and filters for the elimination of solid particles from the steam
- Chimney

In fact, it is the same equipment used for the drying of moist spent olives. Designed with capacities from 500,000 to 12,000,000 Kcal/h.

The advantage of the system radicates in the enrichment of the spent olives with the fat contained in the vegetable water, together with the complete elimination of this residue. In a way, one is drying a mixture similar to moist spent olives or two-phase spent olives.

The inconvenience of the procedure is the large investment required, with a minimum of some 180,000-210,000 E for an oil mill of 10,000 t of olives per year. Also, particular attention must be paid to the emission into the atmosphere of solid particles.

We will come back to this system when, in the following Chapter, the drying strategies of the moist spent olives are analysed.

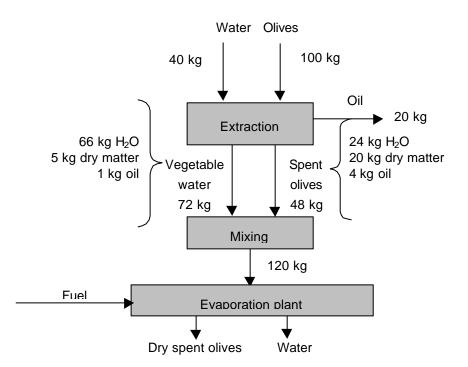


Figure 4.6 Approximate material balance in the Pieralisi system of drying of spent olives + vegetable water

4.2.7.4.2. Nebulization/Incineration

This consists of nebulizing the vegetable waters and putting them in an oven, to form a mixture with the combustion gases. The evaporation of the water is produced at the same time as the incineration of the organic matter of the vegetable water.

4.2.7.4.3. SAEM Method

Developed in Italy, it again consists of a purification system based on physicalchemical processes. The treatment has five stages (fig. 4.7) and is produced in 5 tanks one after the other. In the first 4 tanks the vegetable water is treated with lime and in the fifth with sulphuric acid.

The treatment with lime induces the formation of sludge in tanks 1 and 2, which are pumped to a decantation pool. The water swimming on the top loaded with lime, as well as the water of tanks three and four, is incorporated into a homogenisation pool in the proportion 1:4. An alkaline pre-treatment is obtained and a great dilution of the original pollutant load. In tank 5, the treatment with sulphuric acid is produced so as to adjust the pH. The dumping is done after a residence time of some 21 hours.

The process was introduced for the treatment of some 30 m³/day of fresh vegetable water, which gives rise to some 3,600 Kg of sludge, which must be removed or subjected to specific management. The purification yield is 99%. Due to its high pH the sludge is well stabilised and can be used as an agricultural organic additive.

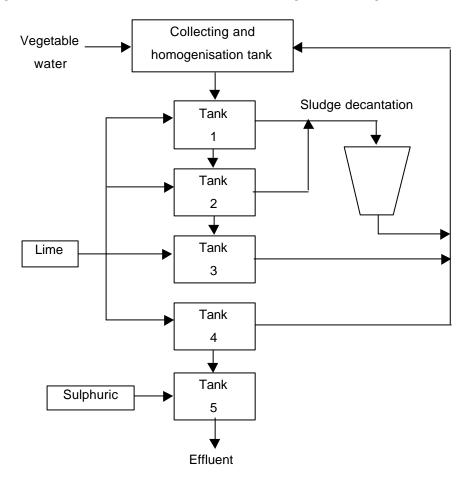


Figure. 4.7. –SAEM method scheme

4.2.7.4.4. Fernández Saro Method

Combines systems of flocculation-decantation with methods of vacuum filtering or ultracentrifuging. Afterwards, an aerobic process is produced and final treatment of the sludge obtained.

4.2.7.4.5: LV de Salamanca Ingenieros System

Tested at the end of the eighties in an oil mill situated in Sierra de Cazorla (Andalusia. Spain), this involves the following stages:

- a) Extraction of the residual oil from the vegetable water by means of a polar solvent
- b) Flocculation
- c) Carbonisation by means of treatment with lime and carbon dioxide
- d) Aerobic-anaerobic treatment
- e) Adsorption with active carbon

4.3. Treatment of solids: Spent olives

4.3.1. Introduction

The **main solid wastes** generated in the production of olive oil are **spent olives** and **moist spent olives**. Once the olive-kernel oil has been extracted from the spent olives and moist spent olives, **degreased spent olives** are obtained.

In Spain, at the present moment, the great majority of spent olives generated are two-phase; that is to say **moist spent olives**. In some oil mills, a **second extraction or reprocessing-over** is being carried out centrifuging in decanter of two or three phases.

In Italy and Greece, the situation is very different, due to the great dispersion of oil mills and their normally small size. The fact of their being dispersed and of limited capacity is repeated in the majority of producing countries. Only in the case of Tunisia can one speak of a strong concentration in the city of Sfax, although the industrial units are also small.

The treatments available on an industrial and economically viable scale when the mills are of suitable size are as follows:

- 1. Drying of spent olives and extraction of olive-kernel oil (traditional extractors or olive-kernel oil plants, present in the large producing countries, but not in some small ones).
- 2. Drying of mixtures of spent olives and moist spent olives followed by extraction (examples of ACEITES PINA, COMERCIAL D'OLIS I DERIVATS, etc.)
- Second extraction by centrifuge of the moist spent olives and incineration of the treated moist spent olives to produce electricity (example of VETEJAR, OLEÍCOLA EL TEJAR, S.A.)
- 4. With certain limitations (market, demand, distances), part of the waste is utilised with other aims: composting of spent olives or moist spent olives, pyrolisis of stones to obtain active carbon (EI Tejar, S.A.) and additives for animal fodder (mixtures of pulp with other residues).

Italy, Greece, Turkey and Tunisia present great differences compared to Spain, due to the aforementioned, as there is no large-scale production of spent olives, vegetable waters and moist spent olives concentrated in a single area, at least not on the scale on which they are produced in Andalusia. In fact, the introduction of twophase systems in these countries has not become as widespread as it has in Spain, so that the solutions for the moist spent olives are, at the moment, practically useful only for Spain.

4.3.2. Use for extraction of residual oil

4.3.2.1. Description

It has been said already that the spent olives that come from oil mills working by pressing or by the three-phase continuous system have a residual oil content in the region of 4-8%, which justifies its extraction by solvent (hexane), with a process similar to that used for the extraction of seed oil (soya, sunflower, colza).

In the majority of olive oil-producing countries, there also exist industries of second extraction (extractors or olive-kernel oil plants) dedicated to such activity. Such is the case of Spain, Italy, Greece, Turkey, Tunisia, Syria, etc. Because of this, this use is

the most recommended for these situations, with which the oil mill receives, in Spain, a price in the region of 30.01-0.02 E/Kg of conventional spent olives (for the moist spent olives the price paid is not usually more than 0.005 E/Kg).

The process involves the following basic operations:

- a) Transport from oil mill to olive-kernel oil plant
- b) Storing in plant
- c) Drying, from 25-35% humidity, to 8-10%, which is the extraction humidity
- d) Extraction in current of hexane, with which the following is obtained:
 - Olive-kernel oil
 - Degreased spent olives or extracted spent olives

In the extracting plant the separation of the stone from the pulp can take place, with which the "stone" and the "sieved degreased spent olives" are obtained, with the following more frequent uses:

- Stone and degreased spent olives: fuel
- Sieved degreased spent olives: foodstuff for animals

In Chapter III of this study, the appropriate information is given in relation to the performance of these residues for the indicated uses.

4.3.2.2. Limits of applicability

The investment in drying and extractor plants is high, so that the capacities of processing must forcibly be high. As a guide, it can be said that in the European context a plant with a treatment capacity of spent olives lower than 200,000 t/year would not be justified. Also, these plants usually function throughout the year in the extraction of seed oil.

Because of this, in nearly all cases, they are usually installations that give service to various oil mills and situated at distances of not more than 200 Km. from them.

4.3.3. Other uses

Only in the case that it were not possible to send spent olives to an extractor, other valorisation systems of the spent olives must be applied. The most usual ones are:

4.3.3.1. Use as fuel:

Direct use in domestic heaters or ovens, with a calorific capacity in the region of 3500 kcal/h.

4.3.3.2. Foodstuff for livestock:

Taking advantage of the nutritional values described in Chapter III of the study, the product can be dosed for feeding cattle (ovine, caprine and camelidae).

We should insist on the fact that the appetising quality is moderate and that is for two basic reasons:

- Presence of lignocellulosic components
- Rapid degradation due to fermentations if kept for a short period of time

For these reasons, **ensilage techniques** have been tested with good results. A recent study (M. HADJIPANAYIOTOU, 1999) developed in the Institute of Agricultural Investigation of Cyprus (OLIVAE, no. 76, April 1999) provides a quite simple and efficient technique. Their conclusions are:

- Ensilage technique in piles with fresh spent olives, not more than 7 days old, covered by plastic sheet (29.25 m² of plastic to cover 20 t of spent olives).
- Possible mixture with other residues, such as hen droppings.
- Mould did not appear. Pleasant colour and smell.
- No sign of salmonellas, listeria or clostridia.
- Very appetising for cattle

4.3.3.3. Composting

Composting is a controlled bio-oxidative process, which is carried out on organic heterogeneous substratum in a solid state by the action of micro-organisms. It implies passing through a thermophylic stage and a temporary production of phytotoxins, generating as biodegradation products carbon dioxide, water, minerals and a stabilised organic matter, free from phytotoxic and pathogenic compounds, rich in humus.

Composting is carried out if the substratum is given the adequate conditions of airing, temperature, nutrients, pH and humidity. The critical factor is the airing. The composting can be done in three main forms:

- In rows: piled up in rows and periodically turned to air the mixture, liberate the excess heat and favour the elimination of volatile compounds.
- In static piles: Similar to the previous piling but without turning. The airing is obtained by a base network of perforated tubes.
- In closed reactor: To accelerate the process from something more than 30 days to only three or four days.

To obtain correct compost it is best to mix the spent olives with other residues, such as cereal straw, spent grapes from wine producing, etc. The process of composting is being used in valorisation plants of moist spent olives, as explained further on.

The addition to the spent olives of the vegetable and earthy residue coming from the cleansing of the olive is a recommendable strategy.

4.4. Treatment of solids: Moist spent olives

4.4.1. Introduction

The appearance of the moist spent olive or two-phase spent olive as a solution to the production and management of vegetable waters, has brought with it the need to put the finishing touches to strategies and techniques of treatment and valorisation of this "new" by-product.

A general vision of the circuits and operations which moist spent olives are being subjected to are expressed in figure 4.8. So, the possibilities are:

- a) Drying and extraction of the residual oil in hexane extractor, as in the case of the 3-phase spent olives. With previous extraction of the stone (stoning) or without.
- b) Manufacture of compost as a fertiliser or organic manure.
- c) Combustion in electric co-generation process.
- d) Combined operations: plants of integral exploitation of moist spent olives.

As indicated previously, the majority of these processes has been, and still are, at their maximum level of development in Spain as a consequence of the enormous diffusion of the continuous two-phase elaboration system.

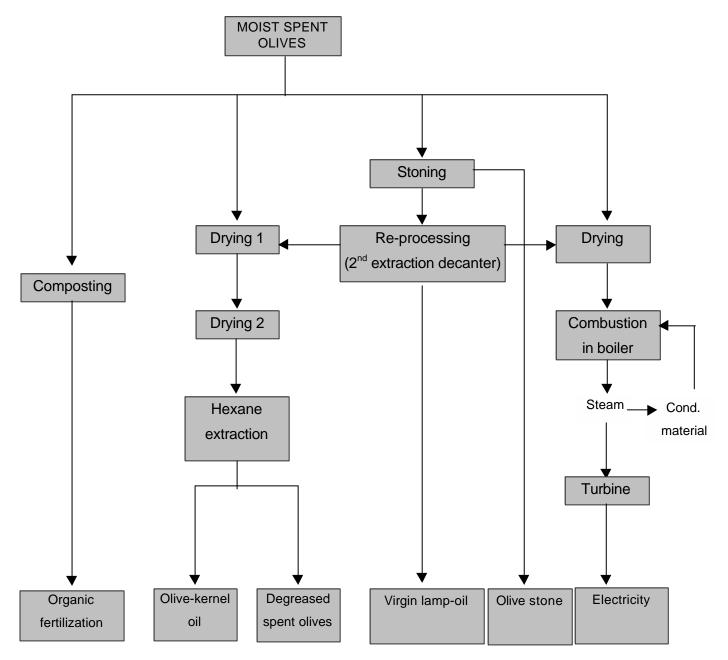


Fig. 4.8. General vision of the moist spent olive valorisation systems

4.4.2. Composting of moist spent olives

<u>Foundation</u>: The main objective of composting is to reduce the mass, eliminate the smells and drain the residue as far as possible to produce an organic compost of great quality and low-polluting power.

<u>Technical description</u>: The composting of residues of vegetable water (dry) and of spent olives is well defined and developed. Fresh moist spent olives contain a large amount of water, which would impede the diffusion of oxygen in the first days of composting, and so composting of moist spent olives requires the addition of some dry structural material such as wood shavings, leaves, straw and even dry compost. When it is necessary to treat a large amount of moist spent olives; a large amount of structural matter must be added. The amount of **space** required for this is considerably increased.

The compost generated can be used in agriculture (especially if it is a high quality compost and designed "to measure" for high value-added crops, such as flowers, greenhouse horticulture...)

<u>Costs</u>: When the composting plant functions adequately no liquid residues are generated. The cost of the operation for the treatment of 3,500 tonnes of moist spent olives (dry) is 50,000 E and it is possible to degrade 40% of the organic matter.

Research carried out by Professor Balis (University of Harokopio. Greece) reveal that the cost of the composting can be considerably reduced if structural material is added only at the beginning of the process and, afterwards, already composted moist spent olives are used as structural material. Applying this procedure, **the process can be economically profitable.**

Examples of use:

- Pilot composting plants of Prof. Balis in Kalamata (Greece). Co-operative of Kalamata (Messiniaki, S.A.)
- Plant in La Gineta (Albacete, Spain). See description in epigraph 4.5.2. of this Chapter.

4.4.3. Drying and extraction of olive-kernel oil

<u>Foundation</u>: Usually, it is dried to provide the product with the characteristics necessary for the extraction of olive-kernel oil, or to be able to incinerate it adequately and produce electricity.

The drying procedure, either by means of natural evaporation, by convection or by radiation, is the method most used for the treatment of **spent olives** and **moist spent olives**. The main disadvantages that the drying in pools presents are the odours that are given off in the process and the volatile organic compounds that are transferred to the atmosphere.

The drying in order to follow up with other treatments of the solid (especially olivekernel oil extraction) is carried out by convection in which all the heat of the hot gases of combustion of degreased spent olives is taken advantage of for the drying of the spent olives, moist spent olives or mixtures of moist spent olives-spent olives. Rotary ovens are nearly always used, of the type described in epigraph 4.2.7.4.1 of this same Chapter (example of PIERALISI, S.A. dryer).

<u>Phase of the development:</u> Industrial scale, operative rotary dryers. Other types (fluidised bed, rings, and cyclones) only on a pilot scale.

<u>Technical description:</u> The following variants can be found:

a) Drying in oil mill

It is a question of reducing the humidity of the two-phase spent olives (60-70%) until that corresponding to pressed or three-phase spent olives is obtained (25-35%). With this, the following is achieved:

- Solve the problems of transport to extracting plant, typical of a pasty product like moist spent olives.
- Increase the price received, until it is on a par with the one obtained from normal spent olives.

For this operation rotary, high-capacity ovens are used, with a minimum calorific power in the region of Mkcal/h, with an installation cost in the region of 180,000 E.

As fuel, "degreased spent olives" coming from the extracting plant itself are used, in "return" transport.

It is evident that the most important limitation is the large investment in the drying installation, which is only justified with production of more than 10,000 t/year of olives.

b) Drying in "extractor" or appropriate plant.

Obviously, the optimisation of the drying is only produced when the quantities handled are considerable. Consequently, the drying processes must normally centre on:

- The actual extracting plants, that process the product coming from numerous oil mills.
- In plants of integral exploitation, that responds to the same philosophy of scale.
- In both cases, it is necessary to have consistent storage structures in large waterproof reservoirs, of the same type as those used for vegetable waters, but deeper.
- Also in both cases, the drying is optimised by means of previous mixture of moist spent olives and conventional spent olives, so that the combined humidity decreases noticeably.
- c) Previous stoning and "going-over"

A frequent operation prior to the drying is the so-called "going-over" of the moist spent olives. It consists of a new centrifuging with decanter to extract part of the residual oil contained in the by-product. When this is done, there is usually a prior "stoning" with appropriate machines that permit:

- Obtention of the "stone", which is an excellent fuel.
- Noticeably improve the performance in the extraction of oil.

<u>The cost</u> of the drying of moist spent olives is high due to the large water content, and amounts to 200 E per tonne of dry moist spent olives (the thermic necessities are in the region of 1.30 Kw/h/Kg of evaporated water).

Examples of use:

- a) <u>Pilot plant</u>: The team of investigators of Professor Aragón of the Dept. of Chemical Engineering of the Complutense University of Madrid (Spain) has developed a new contactor for the drying of moist spent olives (FLUMOV). The system developed permits the use of air, or gases, at low temperature (120 °C) for the drying of the moist spent olives. With this system the degradation of the residual oil that moist spent olives contain is avoided, and permits its extraction, as verified by the firm OLEICOLA EL TEJAR (Spain).
- b) <u>Industrial</u>: ACEITES PINA SA, probably the major private user of moist spent olives in Spain, GENERAL D'OLIS I DERIVATS SA (Lleida). OLEICOLA EL TEJAR SA. and UNION DE COOPERATIVAS ALBACETENSES (La Gineta, Albacete), as co-operative firms. With regard to drying at oil mill level, COOPERATIVA AGRICOLA DE SANTA BARBARA (Tarragona).

4.4.4. Incineration of moist spent olives and electric co-generation

<u>Foundation</u>: Use of moist spent olives as fuel in a grill or bed fluidised boiler. Turbine action with the thermal energy generated and transformation into electricity.

The direct incineration of moist spent olives requires the use of an additional fuel if the water content of the latter is more than 55%. On the other hand, due to the residual oil content of the fresh moist spent olives, the extractors of olive-kernel oil prefer to apply before incineration the classic methods of extraction that generate olive-kernel oil and "two-phase degreased spent olives" which can be incinerated or gasified.

<u>Persons(s)</u> responsible for development: VETEJAR SA. Society formed by OLEICOLA EL TEJAR Y ABENGOA (Spain)

Phase of the development: R&D and industrial

<u>Technical description:</u> The degreased spent olives or the moist spent olives with adequate humidity (less than 40%) are burned in a fluidised bed with elements of heat transference to produce steam. A Siemens turbine that functions at 3500 rpm is used.

From the environmental impact assessment report it can be seen that the gaseous emissions are not noxious and easily within the established legal limits in that respect. The liquid residues generated in the cleaning processes, purged from the refrigerating system and effluent of the demineralisation system after the corresponding treatment, can be dumped directly, as they pose no risk for any living being. The solid residues, fundamentally made up of ashes and slags, are completely inert and can be used in the fabrication of cement or other similar uses.

Examples of use in Spain: Plant installed by VETEJAR SA in the lands of OLEICOLA EL TEJAR, El Tejar (Cordoba), with an installed capacity of approximately 12 MW. El Tejar has another 19.4-MW installation functioning at the moment in the town of Palenciana (Cordoba).

The co-operative Oleícola El Tejar is to build two electricity-generating plants, which use residues of olive-trees as fuel. These plants will be built in the town of Pedro Abad (Cordoba) and in the town of Algodonales (Cadiz). The new Cordovan plant will have a power of 25 MW and will burn moist spent olives, although there is also the possibility of using branches pruned from the olive-tree. The construction of this plant will mean an investment of 24,000,000E, and the owner is Agroenergética de Pedro Abad, a firm belonging to Oleícola El Tejar.

With regard to the Algodonales plant, with a power of 6 MW, the foreseen investment amounts to 7,200,000 E.

In addition to these projects, construction works will commerce on another plant of these characteristics in Baena (Cordoba) with a cost of 24,000,000 E and a power of 25 MW.

4.4.5. Gasification of degreased spent olives: method of the Complutense University of Madrid (UCM. Spain)

<u>Denomination and Foundation</u>: Gasification in 'flumov''. The CUM has developed a new contactor based on the technology of a fluidised bed combined with a mobile bed (*flumov*), which facilitates enormously the process of gasification of **degreased spent olives**. The results obtained in this respect have been satisfactory as can be seen from the evaluation report issued by OLEICOLA EL TEJAR. In this particular case, the combustion and/or gasification process may prove economically profitable.

<u>Residue or by-product treated</u>: degreased spent olives, possibly applicable to "reprocessed" moist spent olives.

<u>Person(s) responsible for development</u>: Prof. Aragón, Dept. of Chemical Engineering, Complutense University of Madrid (Spain)

Phase of development: investigation, small pilot plant (5 Kg/h).

<u>Technical description</u>: The calorific power of degreased spent olives, around 4,000 Kcal/Kg, enables it to be used in combustion and gasification boilers. Also, and given the low sulphur content of the residue (<1%) according to analysis of the Centre of Energetic and Environmental Research (CIEMAT), it enables a gas that contains basically water and carbon dioxide to be discharged.

The method consists in feeding the degreased spent olives, which can contain up to 20-30% humidity (on dry base) into a FLUMOV reactor. This type of system is formed by a mobile bed located at the top of the reactor, to which the moist spent olives (or degreased spent olives) are fed. In the bottom part of the system, there is a fluidised bed, in which a combustion process takes place. Both the fluidised bed and the mobile bed are in the same container and there is no physical device that separates the fluidised bed from the mobile bed.

The gases generated in the fluidised part, which are at a high temperature and have a low oxygen content, reach the top part of the reactor where the mobile bed is, which produces the gasification of the moist spent olives localised in the mobile bed, in much the same way as occurs in a conventional mobile bed. The main advantage of the system is in the temperature at which the gasification process takes place. Fig. 4.9 shows an outline of the plant.

The method developed enables gasification whilst taking advantage of the good gassolid contact of the mobile beds but without the inconveniences of working at high temperatures (1,000°C). With regard to the gasifiers of fluidised bed, the performance increases on improving the gas-solid contact. The gases generated during the gasification with air possess an approximate calorific power of 6 MJ/Nm³ of gas generated (including the N₂) and the average composition of the gases at a temperature of 750°C – 800°C is 10% of H₂, 18% CO and 6% CH₄.

<u>The cost</u> of the direct incineration of fresh moist spent olives, without counting the possible benefits of co-generation, is of approximately 300 E per tonne of degreased spent olives. Approximately 30 Kg of ash per tonne of degreased spent olives is generated.

Examples of use: only the pilot unit of the CUM.

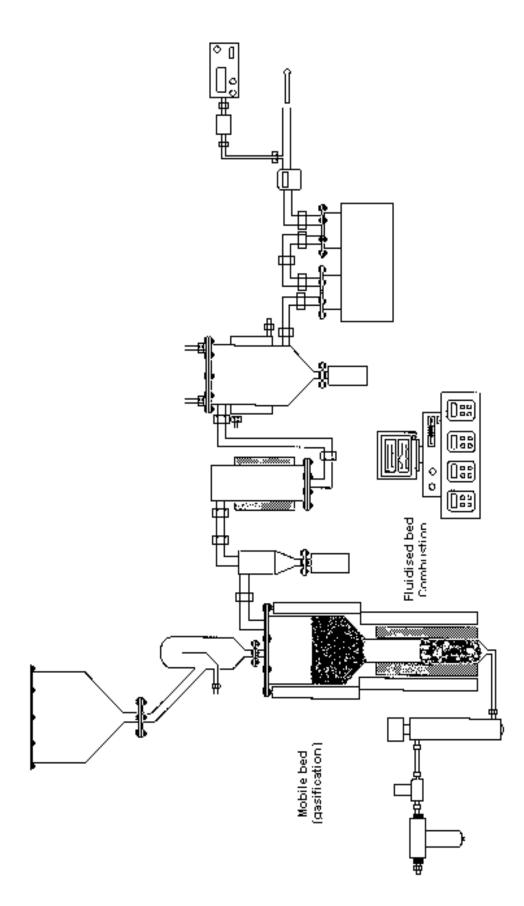


Figure 4.9. – Pilot plant scheme of a spent olives gasification installation developed by the Chemical Engineering Department of UCM

4.4.6. Gasification: GASBI-Senerkhet Process

<u>Foundation:</u> Gasification in mobile bed. The firm GASBI (Gasificación de Biomasa, S.L.) has developed gasification plants for the residues generated in the extraction of olive oil, based on the principles of subsidiariness and self-sufficiency, to obtain social and economic benefits.

Person(s) responsible for development: D. Sebastián Querejeta, GASBI S.L.

<u>Phase of development</u>: Not tested on moist spent olives. In accordance with information from the firm, it can function if they are previously dried to less than 40% humidity.

<u>Technical description:</u> GASBI S.L markets modular mobile bed gasifiers which can generate up to 10 Mwe/h. The gasification plant requires 300 m² of surface, and uses as fuel the degreased spent olives that come from the extraction of olive-kernel oil, with a maximum of 40% humidity. The fuel gas generated in the process is burned in a motor, producing by means of an alternator, electricity for the plant's own use.

<u>The main advantage</u> of the gasification is the increase in performance of the conversion of thermal energy to electric from 25% (typical of combustion with steam and turbine generation) to 30-45% (burning the gasification gases in motors or gas turbines).

Examples of use: The GASBI plants supply themselves with electric power between 600 and 1,000 kW. The thermal power that the plant produces is 1.4 times the electric. There is no specific use of biomass from the olive-oil industry.

4.4.7. Plants of integral exploitation of moist spent olives

4.4.7.1. Introduction

In areas of large-scale production of moist spent olives, such as the Spanish regions of Andalusia and Castille-La Mancha and also, with the growth of co-operative oil

mills, in recent years, community installations have been introduced with a double objective :

- To solve the problem of the management of moist spent olives for the associated oil mills that, due to their size, could not afford the investments required.
- To valorise this by-product in the most complete way possible
- To solve the possible problems of environmental impact

It is because of this that in the following epigraphs two of the most relevant experiments developed in Spain are detailed.

4.4.7.2. Plant of the UNION DE COOPERATIVAS AGRICOLAS ALBACETENSES

Characteristics of the raw material. Description of the work process

As a by-product of olive oil extraction in the two-phase oil mills, one obtains fatty spent olives. These mills have the two-phase system, without production of vegetable waters, but where the MOIST SPENT OLIVES have a greater humidity than the spent olives obtained by conventional systems (pressing and three-phase), apart from a semi-fluid texture which makes it difficult to transport from the production point and subsequent storage. The fundamental identifying characteristics of the raw material we are dealing with, that condition the size of the reception park and the machinery are:

HUMID MOIST SPENT OLIVES:

- Humidity \cong 60%
- Content of fat (humid) \cong 3%
- Semi-fluid texture

DRY MOIST SPENT OLIVES:

- Average contents of the dry substance
 - 50% pulp
 - 50% stones

Transport has to be carried out in semi-cisterns and not in normal boxes, with breakwaters so it does not overflow, and with storage <u>in waterproof pools</u>, which, in years of large harvests, causes the process costs to cause the by-product to be considered as <u>WASTE</u> and its management, therefore, to be the same. This may even mean having to pay for them to be discharged from the oil mills. The utilisation that is normally recommended is:

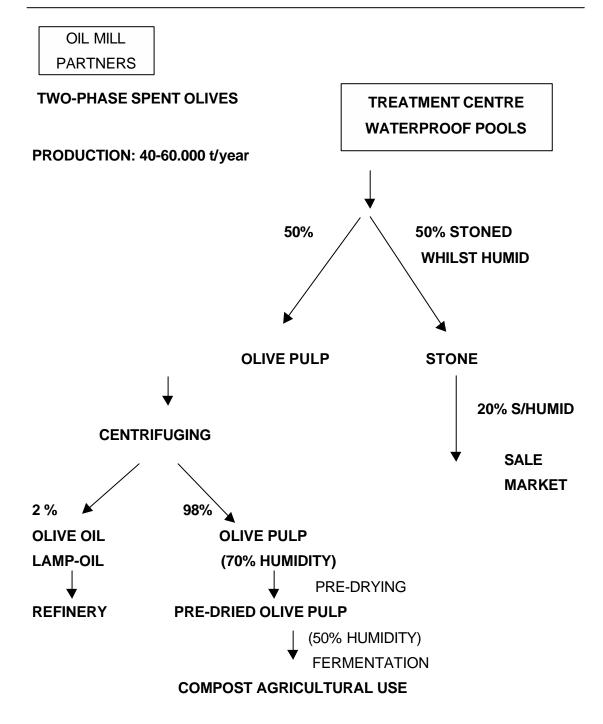
- A) <u>Drying until 10% humidity and then extraction of the residual oil with solvents, to</u> <u>obtain crude olive-kernel oil</u> and use of the residual degreased spent olives (the leftovers after being extracted and used as fuel for drying) in co-generation plants, or suitably corrected, as fodder.
- B) <u>Submitting the moist spent olives, after stoning (partially or totally) while humid, to a second centrifuging,</u> a process which, if carried out daily, can recover 50% of the residual oil in the spent olives in the form of olive lamp-oil.

The resulting product, partially degreased olive pulp, contains between 65/70% humidity approximately, and a larger or smaller percentage of stone. The options are:

- 1. Burn whilst humid in co-generation plant.
- 2. Pre-drying and later conversion to organic material by fermenting processes.

Option A is the one that 30% of the extractors have adopted and B, option 1 is the one OLEICOLA EL TEJAR have developed, whilst option 2 has been developed by Cooperativas Agrícolas Albacetenses.

The work outline is:



Having taken all the correcting measures, including that of recovering the leaching that compost produces, by rainwater, the process is <u>completely clean</u>, and closes the circuit in a satisfactory, profitable and ecological way.

Characteristics of the products obtained

The products obtained will be:

VIRGIN OLIVE OIL

Working on a day-to-day basis, the product obtained, which we will call from second centrifuging, normally will have the characteristics of an <u>olive lamp-oil</u>, with defective taste and colour and analytically with rates **within** standards, the most problematic being the content in waxes, near to the limit rate (350 p.p.m) on average and in certain campaigns the erythrodiol (one of the sterol batches) near to the maximum limit (2% according to humidity received).

OLIVE STONE

The olive stone, separated from the spent olives while humid, contains some humidity (\cong 18%) being perfectly valid to use as fuel, without any manipulation whatsoever. It has a caloric power of around 5,300 Kcal/Kg (dry product) and it is obtained in a percentage of 20% of the weight of moist spent olives.

COMPOST FOR AGRICULTURAL USE

The values of the most significant rates of the compost obtained are :

- pH 7.5/8
- Humidity: 40%
- Organic matter 75/80%
- Humic + fulvic acid: approx. 21/25%
- Heavy metals: exempt
- Total nitrogen: $\cong 2\%$
- Phosphorous: $\cong 2\%$
- Total potassium $\cong 2.2\%$
- Conductivity: exempt of problems

4.4.7.3. The case of OLEICOLA EL TEJAR

OLEICOLA EL TEJAR is a 2nd grade co-operative dedicated for years to the processing of conventional spent olives for the extraction of residual oil. It is to be found in the towns of El Tejar and Palenciana, in the province of Cordoba (Andalusia. Spain).

As a result of the appearance and great diffusion of the system of extraction in decanter in two phases, the firm had to consider new systems of management and treatment of moist spent olives. Since then, it has undergone considerable development in this field and, in general, in the broader one of valorisation of residues and by-products of the olive-tree, from a pruned branch to the typical process of oil production. It is, then an example of action characterised by:

- a) The co-operative base structure
- b) Large size (processing more than 600,000 t/year)
- c) The continuous activity of technological innovation in this field

The firm is currently carrying out the following main activities:

- 1. Reception and store of conventional spent olives and moist spent olives ("fuel park").
- 2. "Reprocessing" or second extraction of residual oil in decanter, with or without prior stoning.
- 3. Drying of spent olives and moist spent olives.
- 4. Plant for olive-kernel oil extraction with solvents
- 5. Plant of electric co-generation using moist spent olives of less than 40% humidity as fuel for the production of steam which activates a turbine and alternator, as described in epigraph 4.4.4 of this Chapter. This activity is carried out through the VETEJAR society, in which the co-operative itself, the electricity firm SEVILLANA DE ELECTRICIDAD and the installing firm ABENGOA participate. Later, the firm has conducted and is running new co-generation plants using of moist spent olives in other towns.
- 6. Production of active carbon from the stone
- 7. Production of compost for agriculture
- 8. Production of pulp for animal foodstuff.

Actually, processes 1,2,3 and 6 are based on systems similar to those described in epigraph 4.4.7.2 for the Unión de Cooperativas Albacetenses, of which OLEICOLA EL TEJAR has been, really, the precursor.

4.4.7.4. The example of ACEITES PINA

At the present time, the PINA family have 5 plants. Villarta: 3000 t/day, La Carolina: 2,000 t/day; Tarragona, 1,000 t/day; Puebla del Hijar 500 t/day and another producing 500 t/day. A Total 7000 tonnes of moist spent olives and other spent olives a day.

In the Villarta plant, 6,000 t/day enter **but only 3,000 can be processed.** Typical composition of intake is: spent olives from Jaen, of which approx. 98% is moist spent olives. Spent olives from Castille-la Mancha, 70% moist spent olives, 25% three-phase spent olives and 5% pressed spent olives. The different spent olives are mixed in such proportions as to give a mixture of 48-50% humidity, which is what goes into the rotary ovens and is dried to 8%, from where it goes to extraction with hexane to obtain olive-kernel oil. The plant works continuously for 3-4 months.

Rotary *dryer* ovens (trommels). 30 m x 3 m. Two units followed by a mill in each of them. In the first trommel the air enters at 500°C and the spent olives at 60% humidity; the solid, pre-dried to 30% humidity, comes out, passes on to a mill and enters in the next trommel. The air leaves the second trommel at 80°C and the solid at 8-10% humidity. The air finally passes through two cyclones (filters are not necessary, as the size of the particle carried away is relatively large and is gathered efficiently in the cyclones), some 115-120 mg/Nm³ of solids leave via the chimney (the legal maximum is 150 mg/Nm³; really the limit is 50 ppm, but as one starts with moist spent olives which has more fine solids that before were carried away with the vegetable waters, this greater limit is authorised for Spanish spent-olive plants that use moist spent olives).

The dried spent olives goes to extraction with hexane. The final degreased spent olives from the hexane extraction process (some 700 t/day) have 40% pulp and 60% stone (separated by means of a pneumatic system, vacuum and gravity). Part of the pulp can be used as an additive for animal fodder and the stone goes to combustion. The amount of pulp obtained is 280 t/day.

In the region there are many chicken and pig farms that sell the droppings as fodder material (at 0.005 E/Kg), which means great competition to be able to compete with the pulp as an additive.

On the other hand, before the degreased spent olives (stone) were in demand as fuel for cement and ceramic works. Now, with the price of natural gas, the outlook is not the same.

To get over this negative situation of the final by-product market, they are studying the installation of an electricity-generating plant which will use 100,000 t/year of degreased spent olives to produce 16 Mwe. The plant will have a Foster-Wheeler boiler with a semi-fluidised grill (the stone is used) and pulp injectors (the pulp has many volatile compounds and burns well as a flame). They will work at about 600-700 °C to avoid the formation of nitrous oxides.

4.5. Conclusions and recommendations

The analysis given in the previous epigraphs of this Chapter enables us to make the following comments:

 The systems of management and treatment of waste and by-products, in order of technical viability and economic interest within certain conditions that must be analysed in each case, are as follows:

a) Vegetable waters:

- 1. Fertilised irrigation
- 2. Natural evaporation with addition of degradation micro-organisms
- 3. Thermal concentration
- 4. Integral purification

b) Solid spent olives (press and 3-phase)

- 1. Sale to olive-kernel oil extracting plant for 2nd extraction with solvent
- 2. Fuel
- 3. Animal fodder (better with extraction of stone), ensilage.
- 4. Composting

c) Pasty spent olives

- 1. Transport to olive-kernel oil extracting plant for drying and extraction
- 2. Composting
- 3. Combustion-electricity generation

- The other technologies available have either not got past the R&D or pilot plant phases, or cannot be recommended due to problems of technical reliability and/or excessive cost.
- The choice of one system or another depends on a series of factors related to :
 - a) The location of the oil-mill and the surrounding conditions
 - availability of lands with appropriate crops
 - urban or rural character
 - existence of "demand" or capacity for use of residues and by- products
 - isolated or concentrated location (several oil-mills close together)
 - b) The dimension of the oil-mill in terms of volume of olive milled, that is to say, quantity of residues and by-products generated.
 - c) The existence of olive-kernel oil or 2nd extraction industries at a reasonable distance.
 - d) The organisation or degree of integration, current or potential, between oilmills in the same area.
- The system of milling by presses is not advised basically and amongst other factors, due to its high costs of operation. This means that, progressively, this type of installation will be substituted by others of continuous type functioning in 3 or 2 phases. In this sense, it can be concluded:
 - a) That in small oil-mills (not more than 3000 t/year) the 3-phase system can be used if there is an appropriate destination for the spent olives and if there is land available for the application of vegetable waters as fertiliser, with or without previous stocking.
 - b) That in large oil-mills or areas where they are concentrated, where the generation of vegetable waters must be avoided, the 2-phase system should be installed or substituted. In this case, the application should be possible of one of the systems of vegetable water treatment recommended, so that the choice will depend essentially on the volume of by-product generated.

SUMMARY AND CONCLUSIONS

The worldwide production of olive oil amounts to some 2 million t/year and is concentrated in more than 90% of the countries in the Mediterranean Basin. Spain is the main producing country (35% of the total), followed by Italy, Greece, Turkey and Tunisia. Practically all countries of the basin undertake olive growing, to a greater or lesser extent.

The extraction of olive oil is carried out in oil mills. In the majority of producing areas, the installations of small to medium size (150-3000 t/year) predominate. Only in Andalusia, the largest producing region in the world, can one find oil mills that exceed 50,000 t/year. Middle-sized mills are frequent in some other Spanish regions, in the South of Italy, in Greece and Tunisia. In the last few years, the capacity of the oil mills has tended to increase, often due to concentration policies.

Olive oil occupies only eighth place in the "ranking" of demand of vegetable oils and involves only 3% of the total. Nevertheless, consumption is on the increase. Italy, Spain, Greece and Tunisia are the main exporting countries. Italy is the major operator on an international scale and the U.S.A. is the main importer, after Italy.

In the industrial olive oil chain, the following functions/agents take part:

- Olive growers
- Oil mills (virgin olive oil)
- Olive-kernel oil extractors
- Refiners
- Packers
- Wholesalers
- Retailers

Frequently, the same operator carries out several of the functions mentioned.

The extraction of oil in an oil mill is a physical process with common elements in the reception phase (unloading, cleaning, control, rinsing and storing of olives) and with notable differences in the phase of separation of oil, which can be performed by

means of three procedures: by pressing, 3-phase continuous extraction and 2-phase continuous extraction.

Each of these systems gives rise to different types of residues and by-products:

- c) Pressing: Concentrated vegetable waters + Solid spent olives (25-30% humidity)
- d) 3 phases: Diluted vegetable waters (in large amounts) + Solid spent olives (35-45% humidity)
- e) 2 phases: Very diluted vegetable water, (in small amounts) + Moist spent olives or "pasty spent olives" (55-65% humidity, pasty consistency)

On the study, we present an "input-output" table of comparison between the aforementioned systems.

The vegetable waters or vegetation waters possess a high contaminating power (COD that varies between some 50 g/l in 3 phases and 125 g/l in a pressing system), that can produce serious environmental problems when dumped in water channels or deteriorate the public sewage systems by corrosion. On the other hand, they are useful as fertiliser. For both reasons, they must be objects of proper management. This is more necessary when we consider the aspects of temporary concentration (3-4 months per year) and territorial concentration in their production.

The so-called two-phase system was developed, precisely, to avoid the generation and consequent dumping of vegetable waters at oil mill level. The system, however, generates a new residue or by-product, moist spent olives that contain the solid part of the olive together with the vegetation water. Therefore, new management strategies have had to be developed for this material.

Spent olives and their solid components (pulp, stone) are also elements of economic interest: residual fat content, nutritional value for livestock, calorific power as fuel. They are or should be, therefore, the object of valorisation.

The detailed information on each of the systems and technologies available for both the process of extraction in oil mill and for the treatment of residues and by-products, are expounded in Chapters II and III of this study. As complementary information, Appendix I contain a list of useful references where one can obtain the additional information necessary to frame any decision making on the subject.

To resolve the problem of the elimination or to induce the re-use of vegetable waters, several systems have been studied, in particular from the sixties onwards. Amongst these we can mention, in order of interest and efficiency:

- Fertilised irrigation, under certain conditions of application.
- Natural or forced evaporation
- Thermal concentration
- Purification by different physical, chemical and biological procedures
- Combinations of the previous systems

The pressed and 3-phase spent olives can also be valorised by means of the following main procedures:

- 2nd extraction of olive-kernel oil by solvent
- Fuel
- Animal foodstuff, with recommended extraction of the stone
- Organic composted fertiliser

The following systems exist for the treatment and valorisation of the two-phase spent olives or "moist spent olives":

- Drying and extraction of olive-kernel oil.
- Composting
- Combustion-electricity generation

The choice of one or other system must be the object of specified analysis for each oil mill and each productive situation. Indeed, the following main factors affect the selection:

- The location of the oil mill and the conditions of its surroundings
- The size or processing capacity
- The existence of 2nd extraction industries within a reasonable distance
- The organisation or rate of integration, present or potential, between oil mills in the same areas

The system of milling by press is not advised, essentially due to high operational costs. This means that, progressively, this type of installation will be or are being

replaced by others of continuous type functioning in two or 3 phases. In this context, we can conclude:

- That in small oil mills (not more than 3000 t/year) the 3-phase system can be used if there is an appropriate destination for the spent olives and if there is land available for the application of the vegetable waters a fertiliser, with or without previous stocking.
- That in large oil mills, or in areas where they area concentrated, where it can be imperative to avoid the generation and dumping of vegetable waters, the 2-phase system should be installed or substituted. In this case, the application of one of the treatment system recommended should be possible, the choice depending on the by-product generated and on the prices of the possible "outputs" produced (compost, energy, olive-kernel oil...)

Frequently, the application of particular systems of management or treatment of oilmill residues and by-products requires large investments and operation costs that are not within the reach of the oil-mill sector, especially of small capacity mills. In these cases, experience demonstrates that policies of integration or concentration between oil mills are necessary, together with co-ordinated actions of public support to the sector. Such has been the case of the regional policies introduced in the South of Italy, in several Spanish regions, and in other countries, which have financed programmes of industrial transformation (going-over to the 2-phase system) or of centralised treatment plants (waste water treatment plants, reservoirs, plants for the integral treatment of moist spent olives, etc.)

APENDIX I : REFERENCES

I.- Centres and institutions that makes studies and/or treatment of milling wastes.

II.- R&D projects within the EU programme framework dealing with wastes generated in the olive oil extracting process.

III.- Bibliography

IV.- Patents

I. Centres and institutions that makes studies and/or treatment of milling

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II.- R&D projects within the EU programme framework dealing with wastes generated in the olive oil extracting process

- New Olive Mill to Produce Only First Quality Oil and Total Recovery of Subproducts for Industrial Scale (1987 1991) ENDEMO C. Ref. EE./00337/87
- Energy Production Plant for Biomasses. (1993 1997) THERMIE 1. Ref. BM./00496/93
- Development of a Combustion Technology for Agrofood Industry Waste. (1995 1997). NNE-Thermie C. Ref. BM./00185/95
- Natural Antioxidants from Olive Oil Processing Aguas residuales. (1997 2001). FAIR 9730333
- Composting of Husk Produced by Two Phase Centrifugation Olive Oil Milling Plants. (1998 2001). FAIR. Ref. FAIR973620
- Water Recovery from Olive Mill Wastewaters after Photocatalytic Detoxification and Desinfection. (1998 2001). FAIR T. Ref. FAIR983807
- New Process for the Generation of Squalane by Supercritical Fluid Extraction from Waste of Olive Oil Production and Hydrogenation to Squalene. (1996 – 1999). FAIR. Ref. FAIR961075

III: Bibliography

- Alkahamis T.M., Kablan M.M. "Olive cake as an energy source and catalist for oil shale production of energy and its impact on the environment". Energy Conversion and Management, 40, 1863,1999.
- Andreozi, R. "Integrated treatment of olive oil mill effluents (OME): Study of ozonization cupled with anaerobic digestion". Wat. Res. Vol 32,8, 2357, 1998.
- Aragón, J.M. 'Proyecto IMPROLIVE: Tratamiento del alperujo para mejorar su aprovechamiento". Alimentación, Equipos y Tecnología, 3, 117, Abril 1999.
- Balis, C. 'Bio-transformation of olive oil mill residues and wastes into organic fertilisers". Report of the Microbiology Laboratory of the University of Harakopio. 1999.
- Berndt, L., Fiestas de Ros de Ursinos, J.A., et al. "Les expériences méditerranéenes dans le traitement et l'élimination des eaux résiduaires des huileries d'olives". Tunis, 1996
- Borja Padilla R. "Depuración aerobia de las aguas de condensación del proceso de concentración térmica del alpechín". Grasas y Aceites, 42, 6, 422, 1991.
- Borsani, R. "Ultrafiltration plant for Olive vegetation waters by polymeric membrane batterie". Desalination, 108, 281, 1996.
- Cabrera, F. "The problem of the olive mill wastes in Spain: Treatment or recycling?" Ati VII Congresso Internazionale: Làpproccio Integrato della Microbiologia: Uomo, Territori, Ambiente. Vieste, Italia, 117, 1994.
- Cal Herrera, J.A. "El orujo de dos fases. Soluciones para un futuro residuo". Residuos, 43, 79-84, 1998.

- Cegarra, J. "Compostaje de desechos orgánicos y criterios de calidad del compost". Actas VII Congreso Colombiano de la Ciencia del Suelo. Bucara, Colombia, 1994.
- Cámara de la Fuente, M. "Gestión medioambiental y contabilidad. Una aplicación al sector del aceite de oliva". Ed. Diputación Provincial de Jaén. 1997
- Demicheli, M., Bontoux, L. "Survey on current activity on the valorization of byproducts from the olive oil industry". Informe Europeo EUR 16466 EN.
- Ehalotis C., Papadoupoulo, K. "Adaptation and population dynamics of azotobacter vinelandii during aerobic biological treatment of olive-mill wastewater" FEMS Microbiology Ecology, 30, 301, 1999.
- Fiestas, R. "The anaerobic digestion of wastewater from olive oil extraction". Anaerobic Digestion, Travemünde. 1981
- Fiestas Ros de Ursinos, J.A., Borja Padilla, R. "Vegetation water used as a fertiliser". Proceedings of International Symposium on Olive by-products valorisation. Sevilla, España. 65, 1991.
- Fiestas Ros de Ursinos, J.A., "Vegetation water used as a fertiliser". Proceedings of International Symposium on Olive by-products valorisation. Sevilla, España. 229, 1986.
- Flouri, F. Balis, C. "Efectos del alpechín líquido de las almazaras sobre la fertilidad del suelo". "Tratamiento de alpechines". Ed. Dirección General de Investigación y Extensión Agraria. 85, 1991.
- Galli, E. Passeti, F. "Olive-mill wastewater composting: microbiological aspects".
 Waste Management & Research, 15, 323-330, 1997.
- García Rodríguez. 'Eliminación y aprovechamiento agrícola del alpechín'. Actas Reunión Internacional sobre tratamiento de alpechines. Córdoba, España, 105, 1991.

- Hadmi, M. "Toxicity and Biodegradability of olive mill wastewater in batch anaerobic digestion". Bioprocess Engineering. Heft 8/79, 1993.
- Hermoso Fernández, et al. "Elaboración de aceite de oliva de calidad". Junta de Andalucía. Consejería de Agricultura y Pesca. Sevilla, 1991.
- Israilides, K. "Situación y perspectiva de los alpechines en Grecia". "Tratamiento de alpechines". Ed. Dirección General de Investigación y Extensión agraria. 21, 1991.
- Liberto, L. "Situación y perspectiva de los alpechines en Grecia". "Tratamiento de alpechines". Ed. Dirección General de Investigación y Extensión agraria. 11, 1991.
- López, R. Martínez Bordiú. "Soil properties after application of olive mill wastewater". Fresenious Envir. Bull., 5, 49-54, 1996.
- Paredes, C., Bernal, M.P., Roig, A., Cegarra, J. "Influence of the bulking agent on the degradation of olive-mill wastewater sludge during composting". International Biodeterioration & Biodegradation, 205-210, 1996
- Paredes, G. "Compostaje del alpechín. Una solución agrícola para la reducción de su impacto ambiental". CEBAS. CSIC. Murcia, 1997.
- Paredes, C., Segarra, J. "Composting of a mixture of orange and cotton industrial wastes and the influence of adding olive-mill wastewater". Proceedings ORBIT 99.
- Paredes, C., Segarra, J., Roig, A., "Characterisation of olive mill wastewater and its sludge for agricultural purposes". Biosource Technology, 67, 111, 1999.
- Pérez, J.D., Esteban, E., Gallardo-Lara, F., "Direct and delayed influence of vegetation water on calcium uptake by Crpos". Proceedings International Symposium on Olive by-products valorisation. Sevilla. España, 331.1986.

- Pompei, C., Codovilli, F., "Risultari preliminari sul trattamento di separazione delle acque di vegetazioni delle olive per osmosi inversa". Scienza e Technologia degli Alimenti, 363, 1974.
- Proietti, P., Catechini, A., "Influenza delle acque reflue di frantoi oleari su olivi in in vaso e in campo. Inf. Agrario. 45.87.1988.
- Ramos-Cormenzana, A., "Antimicrobial activity of olive mill wastewater and biotransformed olive oil mill wastewater". International Biodeterioration & biodegradation, 283-290. 1996.
- Saviozzi, A., Roffaldi, R., "Efficti dello Spandimento di Acque di vegetazione sul teereno agrario". Agrochimica, 35, 1991.
- Steegmans, R., Frageman, H. 'Optimierung der anaeroben Verfahrenstechmik zur Reinigung von Organisch Hochverschmutzt Abwässern aus der Olivenölgewinnung Oswaltz-Schuzule-Stiftung", Forschungsberitch AZ 101/81
- Torres Martín, M., Zamora Alonso, M.A., "Aspectos a considerar en el empleo del alpechín como fertilizante II. Ensayos en maceta.". Anales de Edafología y Agrobiología, 39, 1379, 1980.
- Visiolo, F. Romani, A. "Antioxidant and other biological activities of olive mill wastewater". J. Agric. Food Chemi. 47, 3397, 1999.
- Informe CARTIF-TRAINALBA. 'Problemática de los residuos sólidos y líquidos que producen las almazaras, según los diferentes sistemas de extracción de aceite de oliva virgen".
- "Situación Olivarera en Europa". MERCACEI, Oct. 1999
- Informes anuales (1997 1999) de Progreso del Proyecto Europeo FAIR-CT96-1420 "Improvements of treatments and validation of the liquid-solid waste from the two-phases olive oil extraction" (IMPROLIVE)

IV.- Patents

- GR871461 PROCESS FOR THE INTEGRAL USE OF OLIVE VEGETATION LIQUORS AND OTHER AGROINDUSTRIAL WASTE LIQUORS BY MIXING WITH OLIVE HUSKS
- US5801127 OLIVE PULP ADDITIVE IN DRILLING OPERATIONS
- WO9807337 OIL-PRESS WITH MILD CRACKING OF OLIVE-CROP AND WASHING OF OLIVE-MASS WITH WASTE OLIVE WATER
- WO9728089 METHOD OF EXTRACTION OF OLIVE PASTE FROM VEGETABLE WATER AND ITS USE AS FOODSTUFF
- US4663174 METHOD OF STUFFING PITTED OLIVES WITH ANCHOVIES
- US3975270 PROCESS FOR RECOVERYING USABLE OLIVE-PROCESSING LIQUOR FROM OLIVE-PROCESSING WASTE SOLUTION
- GB2272903 PACKAGING MEMBER
- GB623082 NO TITLE AVAILABLE
- GB607721 NO TITLE AVAILABLE
- GB565772 NO TITLE AVAILABLE
- GB487855 NO TITLE AVAILABLE
- GB473615 NO TITLE AVAILABLE
- GB464211 NO TITLE AVAILABLE
- GB423669 NO TITLE AVAILABLE
- GB421718 NO TITLE AVAILABLE
- GB421117 NO TITLE AVAILABLE
- GB407066 NO TITLE AVAILABLE
- GB395340 NO TITLE AVAILABLE
- GB378383 NO TITLE AVAILABLE
- GB369915 NO TITLE AVAILABLE
- GB366911 NO TITLE AVAILABLE

- GB364104 NO TITLE AVAILABLE
- GB362402 NO TITLE AVAILABLE
- GB360938 NO TITLE AVAILABLE
- GB120049 NO TITLE AVAILABLE
- GB113181 NO TITLE AVAILABLE
- FR2715590 NO TITLE AVAILABLE
- WO9605145 THE WAY OF DISPOSAL OF WASTE FROM OLIVE OIL PRODUCTION
- WO9412576 ORGANIC MATERIAL FORMED FROM COIR DUST
- WO9211206 PROCESS AND PLANT FOR PURIFICATION OF AGRICULTURAL WASTE MATERIAL
- EP0722425 THE WAY OF DISPOSAL OF WASTE FROM OLIVE OIL PRODUCTION
- EP0557758 PROCEDURE FOR THE PURIFICATION AND DEVELOPMENT OF LIQUID AND SOLID WASTE RPODUCT PRODUCED BY OIL MILL
- EP0557758 PROCESS FOR PRODUCING OLIVE OIL
- EP0451430 PLANT TO DEPOLLUTE WASTEWATER, PARTICULARLY WATER FROM OLIVE CRUSHERS.
- DE19548621 NO TITLE AVAILABLE
- DE4210413 MEMBRANE FILTER FOR SEPARATION OF POLY-DISPERSIONS INTO CONTINUOUS AND DISPERSED PHASES – IS A BONDED POWDER MASS ON A CARRIER SUPPORT GRID PROVI
- CZ9401911 PROCESS OF DISPOSING WASTE FROM THE PRODUCTION OF OLIVE OIL
- CZ280400 PROCESS OF DISPOSING WASTE FROM THE PRODUCTION OF OLIVE OIL

APENDIX II: FOTOGRAPHIES



3 phases spent olives. Typical landscape in Greece in the collecting period (November – February)



Spent olives without stone



Fresh pasty spent olives



Draining waters

Degreased spent olives



Stone after the stoned process



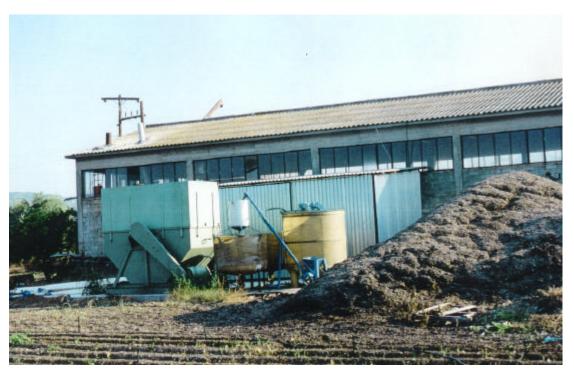
Vegetable wastes of olives cleaning process



Vegetable water tank



Sprayer



Pilot plant for the transformation of vegetable water into liquid fertiliser in Romanos, Messina (Greece)



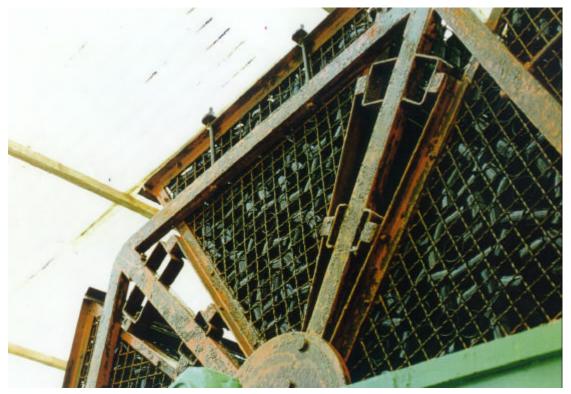
Co-composting plant of spent olives mixed with vegetable water



General view of a composting plant in Kalamata (Greece).



Bio-wheel system to transform vegetable water into a liquid with fertilisation properties (Romanos, Messinia, Greece)



The same plant . PVC elements. Rotation speed: 8 rpm



Rotational reactor to transform vegetable water into fertiliser



Kalamata plant, Greece (Life project 1995). Rotational speed : 6 rpm. Lineal speed: 1.8 m/min. Tank length : 25 m. Capacity : 100 m³



Reservoir system used in Greece to storage/evaporate vegetable water



Dry spent olives installation



Thermal concentration of vegetable waters installation of Trainalba, SA Flocculation –decantation (first photo) Boiler and evaporator (second photo)



La Gineta plant (Albacete) - Dryers



"La Gineta" plant (Albacete - España) - Composting



Dryer



"La Gineta" plant (Albacete – España) Separation equipment of the stones from the spent olives



Spent olives tanks and extraction by an endless screw



Oleícola El Tejar – Vetejar General view



Oleícola El Tejar – Vetejar Electric cogeneration plant



Oleícola El Tejar – Vetejar Activated carbon manufacturing



Oleícola El Tejar – Vetejar Extraction and cogeneration plants general view