Odours Prevention and Control in the Shell Waste Valorisation

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Abstract: Marine aquaculture and seafood processing industries in the northwestern coast of Spain generate significant amounts of shell waste that could be recovered in an environmental sound manner. Recent regulations and strategies on waste open up new opportunities to sustainable development through the management and the treatment of aquaculture materials, previously considered as waste. They encourage not only the application of environmental technologies, but also the recovery of waste and their use as raw materials in such a way that the consumption of resources is reduced and the sources of pollution can be minimized. This paper presents a plant dealing with mussel shell waste as input in its valorisation process, which is considered an eco-friendly solution to the problem of disposal of these products. In fact, it is a clear procedure to turn waste into a high value-added product like lime, a secondary but sustainable raw material with a market potential to be used in different applications. However, as a result of the thermal treatment of the shell waste, odour emissions to the atmosphere become a serious problem. The pollution caused by these odours is creating an environmental and social conflict between the industry and the population of the surrounding area. Accordingly, our work was aimed at identifying the sources of pollution to seek solutions and options for the abatement of odorous emissions from the installation.

Keywords: Shell byproducts, Waste management, Odour prevention and control, Life cycle

1. INTRODUCTION

In 2005, about 82% of the Spanish aquaculture production corresponded to Galicia (NW Spain), the leading mussel-producing region that represents the 98% of the total bivalve produced [1]. This is endorsed by more than 200,000 tons of mussels annually marketed, accounting for nearly a 40% at European level, and 16% of the worldwide production, only second to China [2]. Mussels farmed in floating nurseries are therefore the most important product of the sector, requiring neither input of nutrients nor control over its reproduction cycle thanks to the special conditions of the warm water temperatures and high primary production of the estuaries.

In this way, agro-food industries encompass a group of industrial activities aimed at transforming, manufacturing, preserving and canning foodstuffs, generally of raw vegetal or animal-natured materials. These industrial activities, as any other productive processes, show several features that have a great bearing on the environmental impacts they cause, as follows [3]:
- The exploitation of raw materials never achieves the 100%.
- The necessary auxiliary materials in the manufacturing process, which are not incorporated in the final product, turn them into waste when they do not gather the essential specifications for their usage.
- The specific operations of a productive process generate emissions.

This is the case of the marine aquaculture and seafood processing industries that fulfill the above conditions by generating a huge amount of shell waste that could be environmentally sound recovered. Accordingly, recent regulations and strategies on waste [4-6] point to new opportunities to sustainable development, since they promote the application of environmental technologies and the recovery of waste in such a way they could be exploited as resources. However this valorisation process is source of odours owing to their inherent features. On the other side the growing environmental awareness amongst the population in general, results in higher number of complaints which force to increase the environmental restrictions imposed by law. Odours emitted by food and waste valorisation industries are even more worrying the nearer the installations to the residential areas are located. Nuisance odours are result of an industrial process where the biological or chemical reactions give rise to odoriferous volatile organic compounds (VOCs) and are frequently accelerated by thermal treatments such as drying or calcination. Generally, the odour threshold in the surrounding area and the sensations it causes are very subjective.

For most of the European Union countries, the absence of specific regulations for odours is a common factor at local or regional level. However, the Integrated Pollution Prevention and Control, the so-called IPPC Directive [7], has established a framework of assessment and regulation for the most polluting industrial activities. The priority of this Directive is achieving a high level of protection of the environment taken as a whole, especially the prevention or, where not practicable, the reduction of pollutants, and thus avoiding the transference from one medium to another (air, water and land). Specific processes that fall
under the IPPC, like those carried out in plants for the treatment of animal by-products, are required to determine their impact on several criteria, including odour impact. The industrial sectors involved are encouraged to define ‘Best Available Techniques’ (BAT) and ‘Emission Limit Values’ (ELV) on a European level to achieve greater efficiency in environmental management and performance of these facilities.

The shell, as part of an animal or product of animal origin not intended for human consumption, is considered a by-product, a category 3 material, as far as section j of article 6 is concerned according to Animal By-products Regulation [8]. Consequently, their treatment has to comply with the specific provisions imposed by this law to this kind of material.

In this work, we show the valorisation process of mussel shells carried out in a plant in Galicia (NW Spain) and the measures applied for odour prevention and control.

2. CASE STUDY

The installation under study, Calizas Marinas, S.A., is a shell valorisation plant that extracts calcium carbonate from mussel shells or other seashells by a thermal treatment to obtain commercial value-added products for using in diverse applications. The plant, whose theoretical capacity is around 80,000 tons a year, is strategically located in Galicia, near the estuary of Arousa, in the northwestern coast of Spain to absorb the significant amounts of shell waste generated by the production centres located in the coastal areas of the region (Fig. 1). It is placed in an industrial park taking up an area of 21,450 m². The built-up surface accounts for 5,120 m², where the production plant has 4,150 m² and eleven-meter high.

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The shell is produced as a rejected material in different marine aquaculture activities and seafood processing industries such as production companies, mollusc purification and boiling facilities and, canneries. For the particular case of the mussel, the shell roughly represents between 31-33% of the total weight for this kind of molluscs used in the canning and processing installations aforementioned [9, 10]. The shell is a composite biomaterial, for which the mineral phase, calcium carbonate, accounts for 95 to 99% per weight, whilst the remaining 1-5% represents organic matter [11]. This abundance of calcium carbonate in the shells can be exploited to be used for a wide range of applications.

3.2. Description of the valorisation process

A general flowsheet of the valorisation process is shown in Fig. 2 as part of the mussel shell life cycle since the harvesting of the raw materials (blue mussels) in floating nurseries to the processing step in diverse production centres, where the rejected shell is turned into a valuable by-product used as input in this process. The valorisation process carried out in the Calizas Marinas plant can be divided in several stages as follows:

Preliminary operations. This is the first stage of the valorisation process, consisting in the reception and unloading of the raw materials, in addition to those operations involving the elimination of salt and mud contained in the shells and the storage prior to their processing.

Reception and storage. Mussel shells are transported from mussel-processing plants by truck to the installation. Once accepted, the trucks unload the shell in two reception hoppers placed at ground level to facilitate this operation where the material remains until to be processed the same day.

Washing and dripping. This step consists in cleaning the shell with freshwater to reduce the salt content of the final product, avoid the wear of the equipment by corrosion and obtain a more concentrated product of CaCO₃. Therefore, it is very demanding on water, about 80-90% of the total water consumption inside the installation. This activity is carried out in two rotary washing machines operating countercurrently to increase the performance of the salt extraction. Afterwards there is a shaker draining rack to remove the water dragged by the product. Then, waste waters and mud waste go to the on-site waste-water treatment plant (WWTP) where they undergo a physicochemical treatment.

Storage. The washed material completes its dripping in stainless steel silos that are loaded by gravity and unloaded by a vibrating system to favour the thermal treatment. The washed shells stay here at most for three days. The leachates generated here are channeled to the WWTP for its treatment.

Processing. It involves the thermal treatment of the shells and the subsequent cooling of the dead-burned material.

Calcination. The calcination takes place in a rotary kiln, which receives the material stored in silos by a dosing machine to regulate its input. Nowadays, the plant achieves a production capacity during of 18 tons per hour, with a product output of around 70-80%. The kiln has 17 meters long and 2.5/3.0 meters in diameter. The residence time of the material depends on the spin velocity of the kiln. It is about 20-30 minutes if the kiln is rotated 2
times per minute. Four thermocouples (T1-T4) register and monitor the temperature in different sections inside the kiln. Besides, to assure good combustion temperatures, there is a set temperature so if the temperature falls, the calcination operation is automatically halted. The sections in which the kiln is divided and the temperatures attained during the calcination of the mussel shells are reflected in Fig 3. The flux of gases and the material inside the kiln go countercurrently, so the energy efficiency of the unit is increased, allowing the integration of two operations: drying and calcining in a single piece of equipment. Drying is at 190ºC for eighteen minutes, while calcination at 500ºC takes fifteen minutes. In this way, several phases take place during the thermal treatment inside the kiln as follows:
- Between 100-140ºC an endothermic process related to water removal.
- Between 250-410ºC an exothermic process associated to the most volatile organic matter.
- Between 500-540ºC, another exothermic process corresponding to the most resistant organic matter.

The maximum temperature reached in the kiln is 600ºC, because temperatures above the range of 700-900ºC are linked to the calcium carbonate disintegration into calcium oxide and carbon dioxide.

Cooling. The calcined material must be cooled from temperatures of 500-600ºC to 60ºC since the milling equipment does not withstand such higher temperatures. This cooling process takes place in two steps by means of a thinly-dispersed water injection that achieves a decrease of temperature from 500-600ºC to 170-190ºC due to the induced effect of water evaporation and by air refrigeration, that complete the reduction of the temperature from 170-190ºC to 60ºC. This allows the elimination of any residual moisture at the same time. As the material is cooled, a screw moves it forward the bucket-conveyor belt that feeds the milling equipment.

Auxiliary operations. In this stage, additional operations such as milling and sorting that prepare the final product for its marketing take place. Other operations are the final product storage and its packing and shipment.

Milling and sorting. Milling is aimed at crushing the shell to obtain different sizes of grain, giving an appropriate granulometry to the product to satisfy market requirements. So, once cooled to a temperature below 60ºC and moisture-free, the calcined shell goes to the milling unit. Thus, several products with purity levels of 90-95% in CaCO₃ and different sizes of particle that will determine its industrial application are obtained. The different operations that can be carried out are grinding, screening and micronizing. The particulate size obtained is reflected in Table 1.

![Fig. 2: Flowsheet for the mussel shell life cycle](image)

![Fig. 3: Rotary kiln of Calizamar. The four thermocouples indicate the following temperatures: T1 (125-250ºC), T2 (225-250ºC), T3 (300-325ºC) and T4 (475-500ºC).](image)

Table 1. Particle size with respect to milling operations

<table>
<thead>
<tr>
<th>Milling operations</th>
<th>Particle size (diameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td>0-8 mm</td>
</tr>
<tr>
<td>Screening</td>
<td>&lt; 2 mm</td>
</tr>
<tr>
<td>Micronizing</td>
<td>&lt; 63 µm</td>
</tr>
</tbody>
</table>

Storage. The sorted fractions of the final products are stored in three adjustable hoppers according to its size.

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PRODUCTION CENTRES

Mussels (raw materials) → Mollusk purificatin and boiling facilities → Seafood canning factories

VALORISATION CENTRE (Case study)

Fig. 2: Flowsheet for the mussel shell life cycle
grain. From them, the products can be stored either in two enclosed warehouses or in silos depending on the final use of the product or the packaging format in which it is marketed.

**Packing and shipment.** The final products are packaged in bulk (tanks or containers) or big bags of 35 kg and 1 tons, and shipped off for sale.

### 3.3. Identification of odorous sources

After analyzing the valorisation process performed in the plant, several sources of odour emissions were identified as potential problem steps, as stated below:

i. Transport of raw materials, mussel shells, from the production centres to the valorisation plant.

ii. Initial storage of the shell prior to its processing.

iii. Thermal treatment (drying and calcination operations).

iv. Leachates from the washing and dripping operations and the WWTP where these effluents are treated.

The odorous emissions are mainly caused by the release of VOCs during the decomposition of the organic fraction existing in the shell, as well as during the calcination step. Other sources are those related to the operation of the WWTP.

### 3.4. Characterization of the emitted gases

The gases emitted coming out of the kiln during the valorisation process in this case study show the following features:

- **Volume of flow:** 14,000 Nm³/h
- **Temperature:** 130-150 ºC
- **Moisture:** 17% (vol.)
- **VOCs (as TOC) concentration:** 650 mg/Nm³

In spite of being hardly detectable concentrations of organic substances, the released gases are aggressive olfactory emissions of an intense and unpleasant smell and high temperatures.

By taking into account the features of the residual gas to be treated and the process performed; several measures applied in the plant will be studied in detail to determine their feasibility.

### 4. RESULTS AND DISCUSSION

#### 4.1. Results

Despite diverse technologies to control odour nuisances have been developed or improved [12], the best method to manage this type of emissions is the elimination of the odorous component before its formation, thus avoiding a further treatment of the waste gas stream. Nonetheless, most of the waste valorisation installations can not have an exhaustive control over all the VOCs emitted during their processes.

The measures and alternatives to be considered in order to prevent and/or limit the odours in the installation are the following described here.

**Transport of raw materials**

The transport of raw materials from the production centres to the valorisation plant, Calizas Marinas, S.A., is a step in the process with a strong influence in the emission of odours. A key parameter to consider is the shell lifetime at the time of collecting, because it has a remarkable importance in the degradation state of the waste, made up of the shell and other parts of the mussel. The flesh attached to the shell has a highly perishable nature and generally requires either rapid storage and containment or quick processing to avoid decomposition and, consequently, odour emission and dispersal of pathogens. The processing of shell with minimum delay may prevent or minimize waste and odour problems during storage and processing, which could otherwise develop due to their decomposition over time. Fig. 4 shows the state in which mussel shells arrive to the installation with flesh and mud attached. Other parameters to take into account are the climatic conditions (sunny and hot weather favours faster reactions), as well as the cleaning of the vehicles and the time the shell stays stored in the production centres, specially in the case of smaller plants and when the production of shells is lower, such as at the beginning and at the end of the mussel campaign.

![Fig. 4: Detail of mussel shells received in the plant.](image)

The measures to consider in this step are as follows:

- Collect the shells as soon as possible after their production. This is possible due to the strategic position of the case study near the production centres as seen in Fig. 1, so the shell arrives to the plant within 48 hours past its rejection.
- The transport should be done in hermetically sealed containers to prevent the emission of liquid effluents. The waste should be saved in dry conditions whenever is possible to avoid increasing odour problems.
- Containers, receptacles and vehicles used for transporting unprocessed material must be cleaned in a designed area.

**Initial storage of the shell prior to its processing**

The measures to consider in this step are as follows:

- The shells must be processed immediately after their arrival to the plant, otherwise stored properly until processed in enclosed buildings with sealed hoppers to avoid the emissions outside the facilities. In the plant, the maximum storage time in the hoppers is the same day they are received to avoid the decomposition of the remaining flesh attached to the shells.
- By far, the shells are stored in silos for three days after have been washed to avoid fermentation processes and the release of odours. But if fermentation occurred, the shells should be washed to control the achievable temperatures (up to 70ºC).
- The ground of the storage facilities should be waterproof and extraction systems should be installed to collect residual gases for further treatment.
- Installations and equipment must be regularly cleaned and disinfected.

**Thermal treatment**

The measures to consider in this step are as follows:
- The shell must be placed straight in the kiln without direct handling in order to prevent opening during loading operations and favor the release of residual gases. As indicated in the process description, the input of shell to the kiln is done and regulated by a dosing machine.
- Control the temperature up to 850°C ensuring that is maintained at all times during operation and as long as unburned material is inside.
- The gas resulting from the process is raised and controlled conditions to a temperature of 850°C for two seconds. As previously explained, the temperatures inside the combustion chamber achieved this figure.
- When inherently malodorous substances are produced during the calcination of the shell, pass the low intensity/high volume gases through abatement equipment, such as biofilter or oxidizer to clean the emission where odour prevention is not reasonably practicable. There are several devices to treat VOCs emissions that should be considered to collect the waste gas stream by an extraction system prior to the end of pipe treatment. They are divided into recovery techniques, such as membrane separation, condensation, adsorption and wet scrubbers for gas removal and, abatement techniques such as biofiltration, bioscrubbing, biotrickling, thermal or catalytic oxidation and flaring [13]. The technique chosen by the plant of Calizas Marinas, S.A. is a regenerative oxidizer (Fig. 5), given the nature of the waste gas stream from the kiln. Besides its content in organic substances (carbon monoxide, VOCs and others), the existence of ashes made necessary a bag filter prior to the abatement equipment to firstly scrub the exhaust gases. In this way both equipments assure not only the removal of particulate matter from the gaseous stream (less than 10 mg/Nm³), but also the destruction of any existing VOCs at temperatures of 800-1,000°C inside the combustion chamber (efficiency higher than 95%). At present, the postcombustion equipment has proven its efficiency because the level of TOC emitted to the atmosphere is around 20-23 mg/Nm³.

In addition, olfactometric assessment and testing has been carried out in the plant this year to determine odour nuisances and the involved compounds, showing the above most representative species indicated in Table 2. Odour concentration made by dynamic olfactometry results in 96,755 (uoE/m³).

**Table 2. Inorganic and organic compounds in the outlet gas stream from the thermal oxidizer**

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration [mg/Nm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1 Dichloroethene</td>
<td>3.27</td>
</tr>
<tr>
<td>Trans-1,2 Dichloroethene</td>
<td>23.50</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.93</td>
</tr>
<tr>
<td>Toluene</td>
<td>17.90</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>5.64</td>
</tr>
<tr>
<td>Xylenes</td>
<td>7.44</td>
</tr>
<tr>
<td>Mercaptans (2)</td>
<td>52.30</td>
</tr>
<tr>
<td>Sulphhydric</td>
<td>&lt;20.90</td>
</tr>
<tr>
<td>Ammonia</td>
<td>634.00</td>
</tr>
</tbody>
</table>

(1) Sample analyzed in nalophan bag (5 L) and subsequent analysis by TD-GC-MS (thermal desorption + gas chromatography joined to mass spectrometry), except for mercaptans.

(2) Sample analyzed by Dräger colorimetric tubes.

**Waste water treatment plant**

The measures to consider in this step are as follows:
- Prevent waste water stagnation by laying the pipelines related to the WWTP with a certain inclination.
- Subject the leachates and the effluents to a biological treatment process, anyway aerobic or anaerobic ones. At present, the treatment carried out in the plant consists of a physicochemical treatment, with screening of solids, homogenization and dissolved air flotation, where the flocculation-coagulation processes take place. Once the flocculates are separated, they pass to a sludge pit and then they are thickened and dewatered in a centrifuge. But taking into account, this is not the most suitable treatment according to the high organic loaded wastewaters and the discharge limits do not totally comply with the permissible values, the board has just considered adding a biological stage of nitrification-denitrification for further treatment of waste waters. Currently this stage is starting up and no data is available, but they hope to meet the allowable discharge limits. At the same time, water consumption for the most water-demanding step, the washing of shells, is minimized because cleaned water is recirculated to this operation.

5. CONCLUDING REMARKS

Calizas Marinas, S.A. is a pioneering industrial activity on thermal valorisation of mussel shells reutilizing wastes as resources. This makes every unexpected technical fault is faced up to without any previous background. Therefore, the organization is source of new experiences regarding technological development.

Most of the measures have just been implemented by the installation and other have to improve the conditions in which they are applied.

Getting the environmental permit required to operate
according to the provisions of the IPPC is a driving force to audit and monitor odour emissions, reduce their generation to the surrounding area by means of the aforementioned measures and best environmental practices and upgrade the operating conditions of the equipment and the facilities. Nevertheless, despite the efforts carried out over the years in order to improve the productive process, hard work is still going to be addressed to prevent and/or control the environmental impacts derived from shell valorisation.

REFERENCES