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Innovative circular processes for bivalve shells valorisation

Martiña Ferreira, Diego Méndez & Leticia Regueiro
ANFACO-CECOPESCA

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First of all, hello to everyone and welcome to this unit coordinated by Anfaco, and produced by Martiña Ferreira, Diego Méndez and Leticia Regueiro.

In this unit the main objective is to explain the possibilities for bivalve shells within the concept of the circular economy and particularly present the work carried out under the GAIN project.

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Part 1: Shellfish production and mineral by-products, especially calcium

Innovative circular processes for bivalve shells valorisation

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In Part 1 we briefly introduce the production of bivalve shells, the quantities generated around the word and specifically the main countries where they are produced in Europe. We then look at their primary use as a source of minerals, especially calcium.

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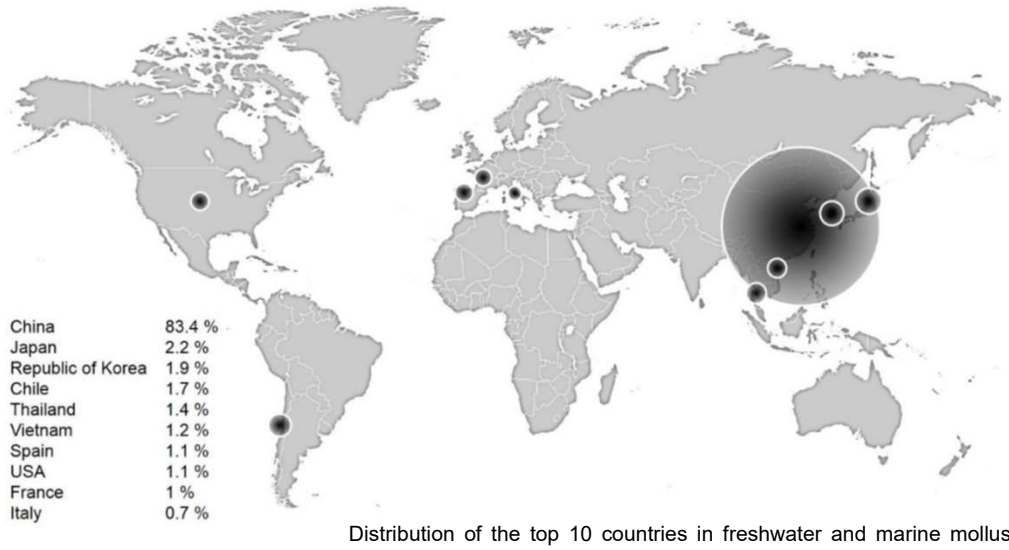

Distribution of the top 10 countries in freshwater and marine mollusc aquaculture production, representing 95.7% of the total global production by live weight

Here you can see the current distribution of the marine and freshwater mollusc production in the top ten countries, that represents almost the 96% of the total World production.

Regarding the European situation, you can see that only three countries are highlighted, Spain, France and Italy. The contribution is low compared to that of Asia, but they are not negligible in the regional and environmental contexts.

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The main European producing **countries are Spain, based on mussel farming**, followed by **France (oysters) and Italy (clams)**. These three countries accounted for 73.8% of the total European aquaculture mollusc production in 2016 (Eurostat, 2018).

Spanish mussel sector produces an average of 267,000 t per year (**45% of EU mussel production**), with an estimated first sale value of 124.9 M€. Galicia account around 97% of this production (3,337 production units distributed in 47 cultivation areas). Rafts are the mussel farming system commonly used in Galicia. They are floating wood structures anchored to the bottom. Mussels are grown in hanging ropes, maximum 500 per raft. Each raft yields between 100 and 150 t per year, depending on the production cycle and commercial objective.

Around 30 to 40% of the total harvest weight are the shells, so in Galicia, there are around 90,000 tonnes of mussel shell discards per year. In France, more than 56,000 t of oyster shells are generated which represent 75% of the biomass of harvested oysters.

Looking deeper at the European production, the main products by country are mussels in Spain, oysters in France and clams in Italy.
According to 2016 data, these three countries accounted for 73.8% of total European aquaculture mollusc production.
Specifically in Spain, the mussel sector produces around 267 thousand tonnes per year, that means around 45% of the total European mussel production. The estimated market value of this product is around 125 million Euros.

The Galician region in Northwest Spain produces more than 97% of this production in 47 cultivation areas with around 3,337 production units.
The production units are normally rafts, which is the most common farming system applied in the Galicia region.
These rafts consist of floating wood structures anchored to the bottom. The mussels are grown on hanging ropes, that are a maximum of 500 per raft.
The production capacity of each raft is around 100 to 150 tonnes per year, but it depends on the production cycle and also on the commercial objective.
Around 30 to 40% of the total harvest weight are the shells, so in Galacia, there are around 90,000 tonnes of mussel shell discards per year. Similarly, France generates more than 56,000 tonnes of oyster shells representing 75% of the biomass harvested.

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At present, around 500,000 t per year of mussels are produced in Europe, of which around 45% comes from Galicia. The canning industry is very relevant in this region and annually produces around 35,000 tonnes of shells as by-products which at present are sent to waste managers for the valorisation, normally throughout incineration or directly to landfill.

The shell is a composite biomaterial, for which the mineral phase, calcium carbonate, accounts for 95 to 99% by weight, whilst the remaining 1-5% represents organic matter. This abundance of calcium carbonate in the shells can be exploited for a wide range of applications.

In Galicia, due to the high shells production, an opportunity arose for a company to valorize them. This came in the form of the company Calizas Marinas, a company producing construction materials. They invested in a plant that extracts calcium carbonate from mussel shells or other seashells by a thermal treatment.

Considering that in Europe. mussel production is around 550 Mt per year, of which around 45% comes from Galicia. The canning industry is very relevant in this region and annually produces around 35,000 tonnes of shells as by-products which at present are sent to waste managers for valorisation throughout incineration or disposal via landfill. The shell is a composite biomaterial, for which the mineral phase, calcium carbonate, accounts for 95 to 99% by weight, whilst the remaining 1-5% comprises organic matter. This abundance of calcium carbonate in the shells can be exploited and used for a wide range of applications.

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The main objective of Calizas marinas, commonly called Calizamar, is to obtain commercial value-added products for use in diverse applications. The plant, which has a capacity of around 80,000 tons a year, is strategically located in Galicia, and able to absorb the significant amounts of shell waste generated by the companies in this area.

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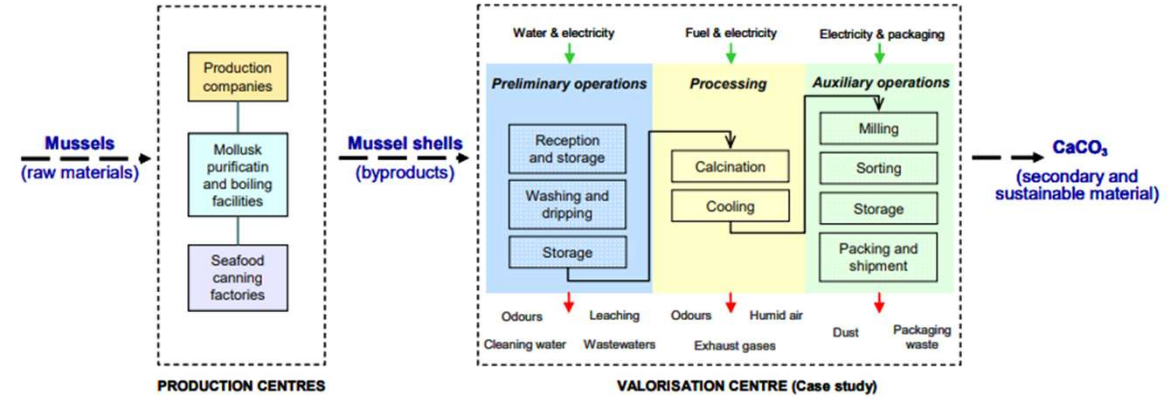
CALIZAMAR



Proceedings of International Symposium on EcoTopia Science 2007, ISETS07 (2007)

The Calizamar valorisation process consists of three steps:
Firstly, the preliminary operations. This involves the reception and unloading of the raw materials, the elimination of salt and mud contained in the shells and storage prior to further processing.
The second step involves the thermal treatment of the shells and the subsequent cooling of the dead-burned material.
The final step is auxiliary operations such as milling and sorting that prepare the final product for marketing. Other operations are the final product storage and its packing and shipment as orders are received.

However this solution that appears to be so good for the byproducts in our area was not working properly for two reasons.
The first one related to the odour. Odours emitted by food and waste valorisation industries (mainly due to volatile organic compounds) are frequently accelerated by thermal treatments such as drying or calcination. Despite efforts carried out over the years to improve the production process to prevent and/or control the environmental impacts derived from shell valorisation, the number of complaints was high.

The other reason is related to the price, since the final product is too low in value to

support all operating costs of the plant. These two factors led to the closure of the plant.

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ABONOMAR

Another company valorising mollsc shells for their calcium is Abonomar, which started in 1989.

Patented system for shell valorisation

Use for fertiliser and poultry feed purposes (OSTRAGRIT)

Fertiliser for vineyards: industrial symbiosis in Rías Baixas


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Another company located in Galicia and involved in shell recycling and valorisation is Abonomar.
This is a company located in Arousa Island (Pontevedra) that was created in 1989 and whose main business is related to the use of shells for fertiliser or livestock purpose. They have a patented system for shells valorisation and reuse.
Regarding fertiliser they use waste shells in a product with a composition of: 5% Nitrogen, 10% Phosphorus, 15% Potash, 18% Calcium, 1% Magnesium and trace elements. It is low in Chlorine and provides gradual release and slow solubility of the nutrients. It is indicated for fertilization of the following applications: Forestry, fruit trees, ornamental species and vineyards.

This is a good example of industrial symbiosis, which is an instrument encompassed under the paradigm of the economy circular that promotes sustainable growth and increased efficiency of resource use. It involves the establishment of exchange synergies and material use between industries in order to produce a beneficial relationship for the industries involved. In this case the cannery industry and wine industry could be a good example.

Their livestock product is OSTRAGRIT, which is a Natural Grit for use in poultry feed,

based on 100% crushed mollusc shell, containing 12 natural minerals. Its composition includes a high content of Calcium with other active elements that awaken the appetite of poultry due to its organic origin. It is an excellent complement to the bird's diet, providing a correct level of calcium and avoiding mineral deficiencies that cause alterations in development, growth and reproduction. Its different components are essential for optimal digestion, increasing the efficiency of the feed breakdown so that all the nutritional elements can be perfectly assimilated. The oyster shells are ground into different grain types to adapt to the different types of birds.

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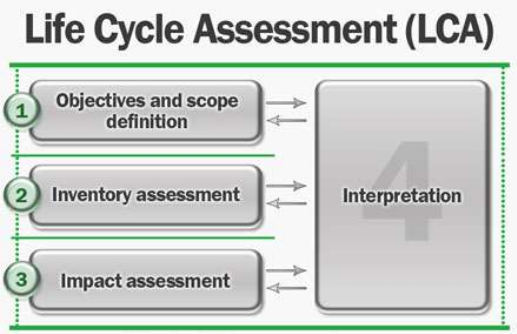
Environmental aspects: is valorisation sustainable?

Calcined shells have been advocated as potential CO_2 sorbents.

They performed a life cycle assesment on calcium oxide derived from waste of oyster shells from Eastern Taiwan (*Crassostrea angulate*).

As a CO_2 sorbent, waste shells were determined to be a more sustainable starting medium in calcium oxide production when compared to mined limestone in terms of carbon dioxide emissions. Although waste reutilization is a step in the right direction in any process, the calcination process itself was not considered, and it is the authors' opinion that calcination will remain an inherently unsustainable process regardless of the calcium carbonate source.



Main steps in the assessment process.

Wang et al 2014.
https://doi.org/10.1016/j.jhazmat.2014.01.026

Considering the environmental impacts of valorisation, we should ask if the valorisation process itself is sustainable.
Few studies have considered that point.
According to Wang and co-workers, the calcined shells have been advocated as potential carbon dioxide sorbents.
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Type of application	Processing required	Quantity sold	Selling price (as of June 2017)
Poultry feed	Heat treated, crushed	1 kg – 25 kg	0.4€ - 3€ per kg
Pet bird nutrition	Heat treated, crushed	440 g – 2.5 kg	0.6€ - 7€ per kg
Bio-filter medium	Heat treated, crushed	600 kg – 1000 kg	0.4€ - 0.5€ per kg
Aquarium/pond pH buffer	Heat treated, crushed, chlorine washed	5 kg	4€ per kg
Soil liming	Heat treated, powdered	22.7 kg	0.4€ - 0.6€ per kg
Shell aggregates	Whole shell, dried	250 kg – 1000 kg	0.3€ - 0.9€ per kg
Shell aggregates	Dried, crushed	15 kg – 1000 kg	0.3€ - 3€ per kg

https://zenodo.org/record/2662011/files/Shell_Waste_Report.pdf?download=1

On this slide you can see different products derived from mollusc shells, the typical quantity sold per order and sales price per kilogram in 2017.
The best price is related to pH buffer for aquariums or ponds, however the process required is more complex since it consists in crushing, heating and chlorine treatments. It may also be more limited in terms of market volume.
The other prices are more similar and mainly linked to the processing required. They oscillate between 0,3 to 1 Euro per kilogram, but for poultry feed or pet bird nutrition it can reach 3 to 7€ per kilogram.

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End of Part 1
Thank you for you attention

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This is the end of Part 1. You can continue learning more about mollusc shell valorisation in Part 2.