SMALLOPS
Nanoparticles for sustainability

VALORIZATION AND TREATMENT OF OLIVE POMACE AND VEGETABLE WATER

At Smallops, we have developed a technology that allows us to value both the olive oil and the alperujo. Thanks to our technology, we are able to valorize the alperujo by transforming it into iron nanoparticles encapsulated in carbon, called OPS. OPS have a high potential to be used in different environmental applications. In addition to nanoparticles, our technology makes it possible to produce biogas exclusively from these by-products.

1. WHAT IS OLIVE POMACE AND VEGETABLE WATER

The olive pomace is a by-product of the production of olive oil obtained in the process of centrifuging the olives in the mill. It is made up of parts of the olive (stone, pulp, water...), but it also contains traces of the olive oil. It has a more solid part that is the pomace and a somewhat more liquid part that is the vegetable water. Its properties include a high water content of 50-70%, a pH of 5.4 and a high organic matter content, since it has approximately 91%.

2. EVOLUTION OF TECHNOLOGY IN MILLS

Spain is the world's leading producer and exporter of olive oil, with an area dedicated to olives of approximately 2.5 million hectares. For this reason, the treatment of alperujo is key in the oil generation process.

There are currently around 1,828 olive oil producing entities, including cooperatives and private mills. Of these, 908 are cooperatives and 920 are private mills.

In the last 30-35 years, the oil extraction process in the oil mill has gone through various and very significant technological changes. Thus, from the traditional basket press, it has gone through continuous extraction by means of a three-phase decanter (obtaining; oil, pomace and olive oil), until in recent years the two-phase decanter (obtaining; oil and moist fatty pomace). and occasionally to the second centrifugation.

Until the years 70-80, the oil mills worked in 2 phases from which moist fatty pomace was obtained (60-70% humidity). In the 80s, the 3-phase one prevailed. Almost 50-100 kg of water was added for every 100 kg of olives and 50 kg of pomace was obtained with around 50% humidity and 4-5% fat content (richer), 80 kg of alpechín and 2 extra kg of virgin olive oil (AOV).

But at the end of the 90s, due to the great drought that occurred, it was changed back to 2 phases since this system does not require the addition of external water unlike the 3 phase system and, therefore, currently 85 -90% of the mills in Spain have this system. This system uses a maximum of 10% of water with respect to the input of olives and does not produce the problematic vegetable watern, although it does produce olive pomace (80 kg per 100 kg of olive) with 70% humidity and a fat content between 1.9-2.5% and AOV.

Consequently with the above, there has been a very significant change in the composition and in the form of presentation of the by-products originated in the mill and consequently those received by the extractor or pomace. Regardless of the fact that the changes described above have improved the process in the mill, the truth is that for the extractor, the new raw material has complicated its production process.

Since the implementation of the 2-phase system in the mills, the production of alperujo has grown exponentially. That is why in the 2018-2019 campaign the orujeras were collapsed due to the large amount of this by-product of the olive grove that they had to treat.

3. WHO IS IN CHARGE OF THE MANAGEMENT OF OLIVE POMACE?

Las orujeras u extractoras son las encargadas de valorizar este subproducto, del cual obtienen aceite de orujo, biomasas; hueso de aceituna y orujillo. Cabe mencionar que si no se asegura la valorización del subproducto, este es en sí mismo un residuo muy contaminante y problemático. De aquí el enorme y fundamental papel de las orujeras para el sector oleícola.

The Pomace oil producers are in charge of valorizing this by-product, from which they obtain pomace oil, biomass; olive bone and pomace. It is worth mentioning that if the recovery of the by-product is not ensured, this is in itself a highly polluting and problematic residue. Hence the enormous and fundamental role of the pomace for the olive sector.

3.1. HOW IS THE OLIVE POMACE TREATED?

There are two ways to treat the olive pomace in the pomace oil producers: In two or three phases.

In both ways, first the olive pomace is pitted, thus obtaining a very interesting biofuel (the olive pit). This must be turned over to separate unwanted pulp and inert remains and perform a subsequent drying. In this way, a biofuel of high quality and calorific value is obtained. Once the olive pomace is deboned, a horizontal centrifugation is applied:

HOW TO TREAT THE ALPERUJO IN 2 AND 3 PHASES?

In two phases: Most of the pomace oil producers in Spain work in 2 phases, so that they obtain, on the one hand, olive pomace oil (AOO) and, on the other hand, moist pomace, which must be dried for later use (mainly as biofuel).

The problem with working this way is that the watery part of the olive pomace (the vegetable water) remains in the pomace. Consequently, the pomace obtained is very humid. In addition, they have to be recirculated in the decanter by mixing it with pitted alperujo to take advantage of the heat of the pomace, so that the olive pomace enters the decanter less humid. In this way, the pomace obtained has less humidity, which benefits the drying part, obtaining thermal savings.

Another problem with working in 2 phases is that, as the pomace is constantly recirculating, the pomace has less processing capacity than those that work in 3 phases.

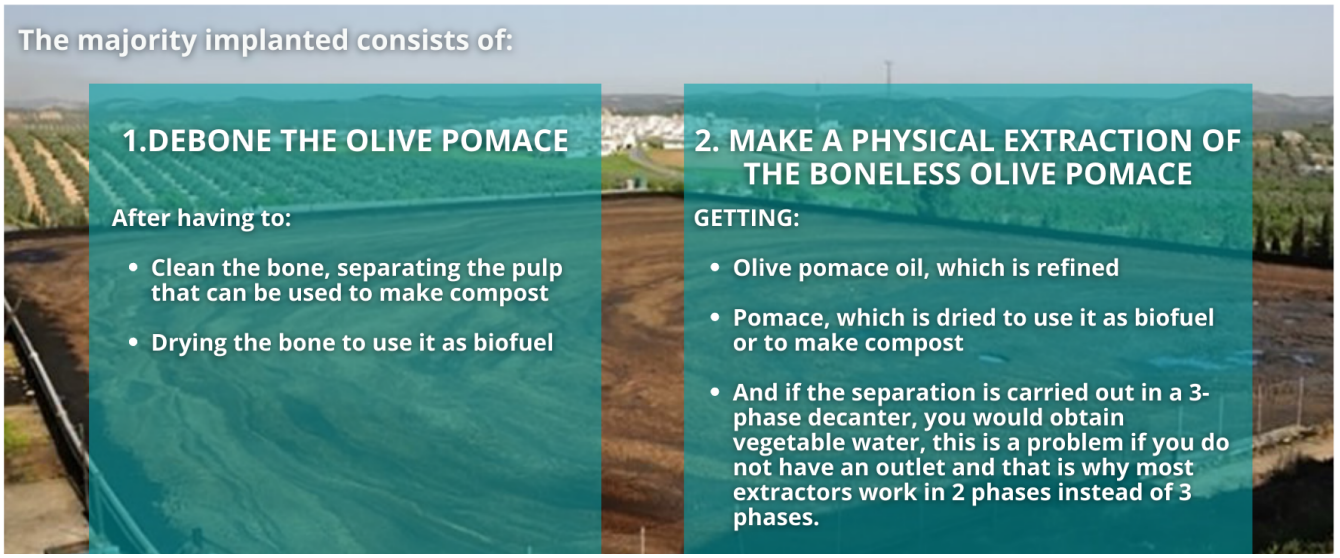
In three phases: Very few pomace oil producers have this system implanted. One of them is Troil Vegas Altas located in Valdetorres, Badajoz. What the orujeras obtain by working in three phases is AOO, olive pomace and vegetable water. In a few words, **the main difference with the two-phase** method is that they divide the Olive pomace into vegetable water (the liquid part) and pomace (the solid part). This means that the pomace has less humidity than what is obtained in the two-phase system.

Consequently, it has greater processing capacity since it is not necessary to recirculate it in the decanter. They also get several avenues of income.

In addition, through both treatment systems, olive pomace oil is obtained, which the pomace makers sell to refiners or refine it themselves for subsequent marketing.

It is evident that the processing of olive pomace is an important link in the value chain of the olive oil sector, since it allows the by-products of the process to be valued, which currently represents a cost for the oil mills and damages the environment.

3.2. EN RESUMEN



4. NEW METHOD OF TREATMENT OF VEGETABLE WATER AND OLIVE POMACE

4.1. CIRCULAR BIOECONOMY AND ZERO WASTE

Smallops makes available to pomace oil producers and oil mills a treatment through which we are able to get more out of the olive pomace and obtain new income in an environmentally sustainable way.

Benefits for pomace oil producers:

1. **Dar salida al excedente de alperujo:** Resolver la problemática de acumulación de alperujo dando una salida recurrente al residuo mediante un método innovador.

2. **Dispose of surplus of olive pomace:** Solve the problem of accumulation of alperujo by giving a recurring outlet for the residue through an innovative method.
    a. **New product for sale from olive pomace:** Production of iron nanoparticles (OPS) from vegetable water with different environmental applications for sale and/or self-consumption in the biogas plant. Smallops will handle the production and sale of OPS.
    b. Biogas production exclusively through olive pomace:
        i. Sustainable treatment that eliminates 84% of polyphenols, which cause the inhibition of anaerobic digestion.
        ii. Greater energy use of the residue: Thanks to the addition of OPS in the biodigester together with the olive pomace, the polyphenol load of the material is reduced by 24%, which allows the generation of biogas, for self-consumption or its sale.
            1. The addition of OPS in the process will allow, on the one hand, an increase in production, obtaining a greater quantity and quality of energy for the operation of the machinery and/or injection into the electrical network. On the other hand, it favors the plant towards the establishment of biogas as a reliable energy source. All this because biogas production will be more constant and homogeneous, in addition to being of higher quality and maximizing its production.
        iii. Generate savings in operating costs of olive pomace treatment thanks to the use of thermal energy created in the biogas generation process for self-consumption.
        iv. Obtaining an organic amendment (fertilizer) class A that complies with RD 999/2017 to use in the olive trees themselves or for sale.

Benefits for oil mills:

1. **Dispose of the alperujo generated in situ:** Solve the olive pomace management problem by providing a recurring outlet for the waste using an innovative method in your own facilities.
    a. Waste transport costs are eliminated due to its management: You will not have to pay for the management of the alperujo when treating it on site at your facilities.
    b. **Production of iron nanoparticles (OPS) from vegetable water** with different environmental applications for sale and/or self-consumption in the biogas plant. Smallops will handle the production and sale of OPS.
    c. Biogas production exclusively through olive pomace:
        i. Sustainable treatment that eliminates 84% of polyphenols, which cause the inhibition of anaerobic digestion.

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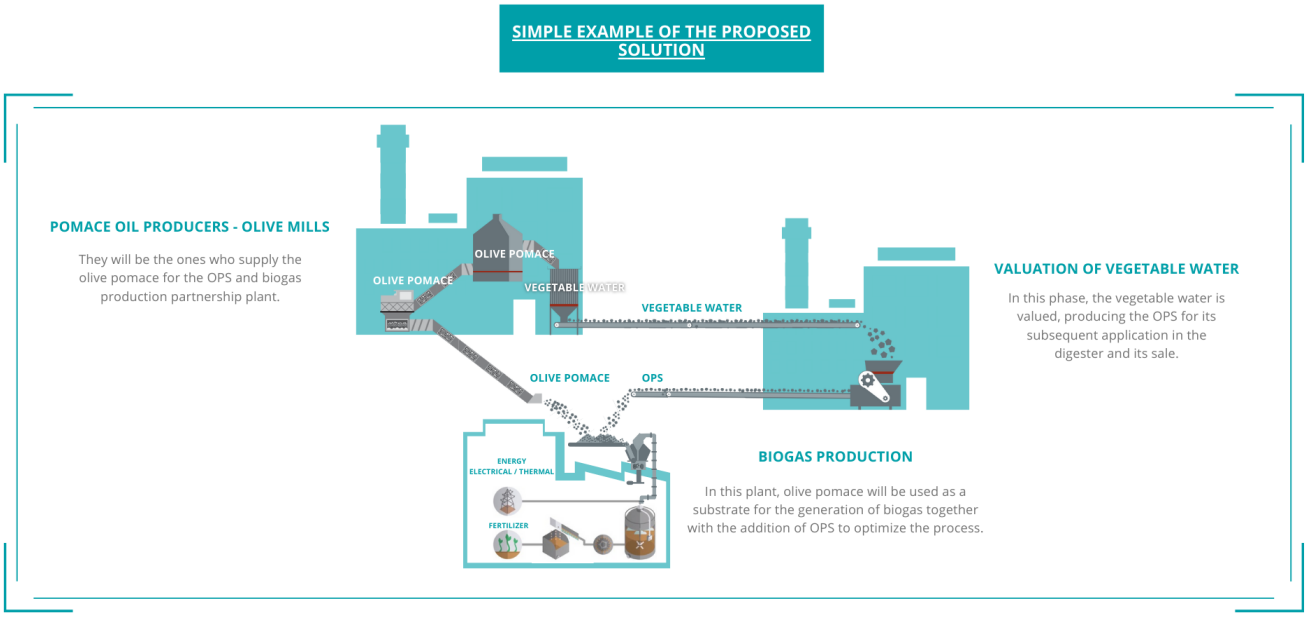
In summary

Con nuestra tecnología obtenemos biogás exclusivamente a partir de alperujo y alpechín. Tratamos los residuos y subproductos de forma que obtenemos un biogás con excelentes rendimientos. Además, logramos un digestato susceptible de emplearse como fertilizante en los olivos, entre otros cultivos.

With our technology we obtain biogas exclusively from olive pomace and vegetable water. We treat waste and by-products in such a way that we obtain biogas with excellent yields. In addition, we achieve a digestate that can be used as a fertilizer in olive trees, among other crops.

And we don't just make biogas! **With our treatment we managed to produce iron nanoparticles encapsulated in carbon.** A product with different applications such as water treatment or the improvement of biogas production.

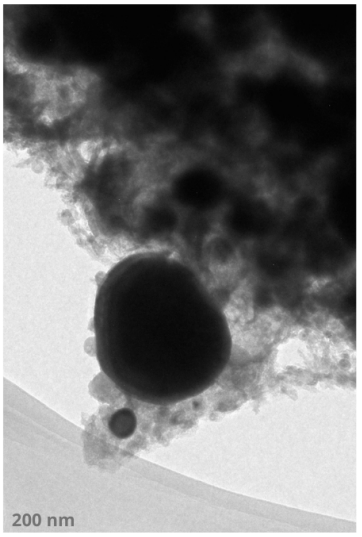


4.2. NANOPARTICLES FROM OLIVE POMACE

OPS: Nanoparticles of zero valent iron encapsulated in carbon from vegetable water

1. First the olive pomace is boned
2. Then the olive pomace oil is extracted by means of a 3-phase decanter, obtaining in turn olive pomace and vegetable water

We can use this vegetable water in the HTC reactor directly or condition it



4.2.1. WHAT IS HYDROTHERMAL CARBONIZATION (HTC)?

Hydrothermal carbonization is a **thermochemical process** that consists of subjecting moist biomass to moderate temperatures (180-260°C) under certain conditions, converting the biomass into a solid carbon-like compound called biochar.

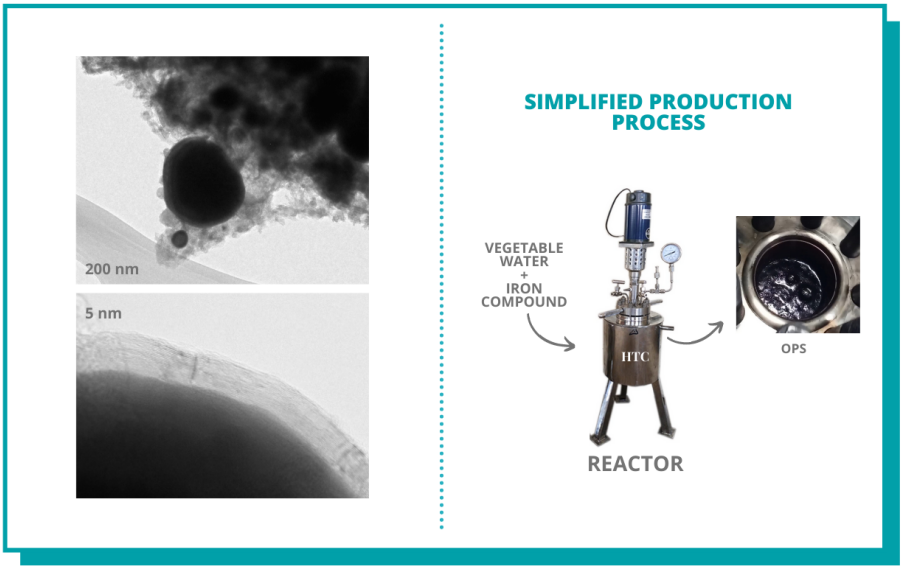
The various compounds are modified by reactions in series and in parallel such as:
- hydrolysis
- dehydration
- decarboxylation

→

As a result, it generates:
- an organic liquid fraction that is rich in sugars, carboxylic acids, among other easily degradable compounds (15-20% of the input biomass carbon);
- a lignite-like product (biochar, 75-80% of input carbon);
- a very small amount of gases (5-10% of the input carbon).

OPS contain on average 2.5% zero valent iron (ZVI), 44.5% total iron and 55.5% carbon. OPS are magnetic and have a mean size of 150 nm, a surface area of 14.7 m2/g, an external surface area of 3.864 m2/g, an internal surface area of 11 m2/g, a micropore volume of 0.004 cc/g and a total pore volume of 0.0696 cc/g.

If an activation process is applied to them, these values can be improved, such as obtaining a surface area of 190 m2/g and 10% ZVI.

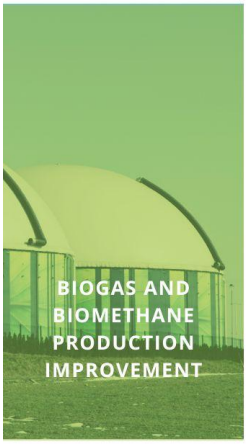


Oxidation and reduction reactions:

- Iron is reduced to its zero valent state.
- Around it, various layers of carbon are deposited together with iron ions.

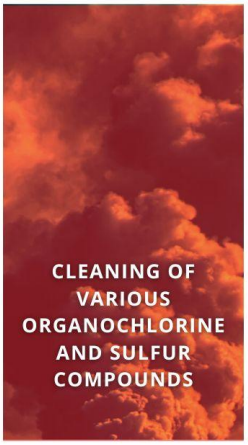
4.2.2. OPS APPLICATIONS

Smallops OPS offer different competitive advantages to different sectors:



BIOGAS

WATER TREATMENT



TREATMENT OF GAS STREAMS

FERTILIZER

NEW MATERIALS

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