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Energy valorization of solid residue from steam distillation of aromatic shrubs

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ABSTRACT

The interest for essential oils is increasing, alongside ongoing scientific research into distillation techniques. This process generates significant solid residue that could be revalorized as energy source. This study explores the energy recovery of the solid fraction produced during the distillation of three aromatic plants: *Cistus ladanifer, Juniperus communis* and *Rosmarinus officinalis*. Two conventional energy recovery technologies were considered and compared through an energy balance: solid biofuel production and biogas generation. In case of solid biofuels, the fractionation of biomass allowed for generation of three different qualities that meet the regulation standards of solid fuels, except for the dust fraction. According to the energy balance, the alternative use of these substrates for biogas production showed competitive production in case of *Cistus ladanifer* and *Juniperus communis,* while *Rosmarinus officinalis* biomass presented inhibition of the anaerobic digestion and null energy recovery.

1. Introduction

The increasing demand for essential oils leads to significant solid waste generation after industrial steam distillation. The important volume of solid waste material generated after extraction is a valuable energy resource that can reduce the external demand and carbon footprint of the essential oil generation processes. Some specific applications for reuse of solid distillation residue have been reported, such as the production of bio-oil (Abu Bakar et al., 2020), dietary supplementation on animals (Jeshari et al., 2016), biochar and absorbents production (Mediavilla et al., 2023) and gasification (Guo et al., 2013). However, the potential energy recovery through the most frequent process pathways applied to wastes, such production of solid fuels and biogas, has not been studied to the best of authors' knowledge.

Solid waste material produced after hydrodistillation has a high moisture content which depends on the initial moisture content of the biomass raw material and the conditions applied during the extraction. Values higher than 70 % have been reported in different species of shrubs (Alexandri et al., 2023). Consequently, in case of production of solid biofuels, wastes should be handled immediately or dried in order to avoid its enzymatic and microbial degradation (Skendi et al., 2023). After drying, a classification process, performed by a sieving and blowing process, allow to generate solid biofuels of different quality that can meet the standards of different purposes, such as residential or industrial sector (Telmo and Lousada, 2011). On the contrary, anaerobic digestion of the distillation wastes for biogas production can be directly applied without pretreatments in wet biomass. The anaerobic degradation is capable of converting complex lignocellulosic by-products into energy-rich biogas containing methane, carbon dioxide and trace amounts of other gases (García Álvaro et al., 2024). This alternative produces a standard fuel (methane) that can be easily used for heat, electricity generation, vehicle use or grid injection (García Álvaro et al., 2024). The lignocellulosic compounds present in the vegetable materials normally difficult the degradation by microorganisms and natural enzymes (Hashemi et al., 2021; Jin et al., 2022). Thus, biogas production with these kinds of materials presenting complex chemical structures of cellulose, hemicellulose and lignin requires a pretreatment stage to accelerate the first stage of hydrolysis (Karthikeyan et al., 2024; Zheng

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et al., 2014). Thermal pretreatments are commonly applied increasing the temperature of the raw materials by addition of steam at variable temperatures. In case of vegetable materials and agricultural wastes temperatures ranging between 110 and 220º C have proven to be highly effective increasing the final biogas production (Ferreira et al., 2013; Patowary and Baruah, 2018; Wang et al., 2023; Bittencourt et al., 2019; Montes and Rico, 2021). At this point it must be stressed that the hydrodistillation process applied to oil extraction entails the heating of the aromatic plants through the pass of a steam flow and subsequently the biomass subjected to the distillation process could be partially hydrolysed enhancing the subsequent anaerobic digestion process.

In this study the solid residue obtained after the distillation of three different aromatic plants (*Cistus ladanifer* L., *Juniperus communis* L. and *Rosmarinus officinalis* L.) have been studied as feedstock for the production of solid fuels after the classification of the different fractions. Since this process entails the drying, sieving and blowing of the residue with the consequent use of energy and time, direct conversion to biogas through anaerobic digestion of has been proposed and compared to the solid biofuel alternative through and energy balance. The main objective of the present work is to explore both energy valorization routes of the solid residue from steam distillation of aromatic shrubs; a) characterising as solid biofuel the residue of steam distillation of three different species (*C. ladanifer*, *J. communis* and *R. officinalis*) and b) carrying out a preliminary study on the production of a biogas from the anaerobic digestion of each material. Finally, an energy balance has been included showing the energy consumption and generation in each pathway, along with an assessment of the overall efficiency and sustainability.

2. MATERIALS AND METHODS

2.1. Source plant material

1000 kg of three different aromatic plants were manually collected in three wild environments of Spain. Branches with stem diameter below 50 mm were harvested with the objective of reproducing a pruning process in a plantation of these species. *C. ladanifer* was collected in Bustares, Guadalajara province (UTM coordinates: 30 T 495503 4553475) in October 2021. *J. communis* was harvested in Barriomartín, Soria province (UTM coordinates: 30 T 545081 4649553) in April 2021 collecting 50 % of male plants and 50 % of female plants; and finally, *R. officinalis* was harvested in Bonete, Albacete province (UTM coordinates: 30 T 478430; 4087843) in June 2021.

The biomass was divided into two batches which were crushed at 20 mm with a slow rotating single-shaft shredder (90 kW) described in (Bados et al., 2023) registering the weight of biomass, the shredding time and the energy consumed during the process. Afterwards, they were distilled in a steam distillation pilot plant. This plant has a 1.8 m^3 stainless steel still, a biomass boiler (Vulcano Sadeca, Mejorada del Campo, Spain) of 170 $kW_{thermal}$ that produces approximately 100 kg h^{-1} of 0.5 barg steam, a cooling system necessary for condensing the steam, and a glass Florentine flask used for separating the essential oil (lower density) from the hydrolate (higher density). Depending on the aromatic species, the distillation process had a length of 3.0 h with *C. ladanifer*, 2.5 h with *J. communis* and 1.5 h with *R. officinalis*, measured from the time the first drop of distillate fell. For defining the duration of the tests, the essential oil obtained every thirty minutes was weighed. The final length of the tests corresponded to the time when the quantity of essential oil separated in a period of thirty minutes was below 5 % of the total essential oil obtained throughout the process.

The biomass obtained after distillation followed two ways. On one hand, it was conditioned and characterised as solid biofuel and, on the other hand, it was used in anaerobic digestion tests.

2.2. Biomass conditioning to be used as solid biofuel and characterisation

The distilled biomass was stored indoors in a pile to be air dried. Periodic turning process up to a moisture content below 20 % (wet basis) was performed. Afterwards, it was divided into two batches which followed a sieving and blowing step, producing three different biomass fractions. The screener used was a gyratory reciprocating motion equipment (0.37 kW) with a sieve of 4 mm mesh, and it was fed with a belt conveyor and a rotary valve. The blowing process was carried out with a primary exhaust fan (1.5 kW) that produces a suction through the sieve and a secondary exhaust fan (11 kW) that assures the extraction of the clean air (Fig. 1). The time used for the tests and the energy consumed were registered.

After the sieving and blowing process, three different biomass fractions were obtained: (1) dust, which corresponds to the biomass separated by blowing, i.e. the lightest fraction; (2) the fine fraction, which is the particulate matter going through the 4 mm sieve; and (3) the coarse fraction, which is the particulate matter with size higher than the sieve mesh. All the biomass fractions were weighed, and five subsamples were taken from moving material at the three different outlets (dust, fine and coarse fractions) following the standard ISO 21945:2020 (Solid biofuels. Simplified sampling method for small scale applications).

Three final samples were achieved by blending the five subsamples of each biomass fraction, which were analysed as solid biofuel at CEDER-CIEMAT Biomass Characterisation Laboratory (Lubia, Soria, Spain). Moisture, ash, N, S and Cl contents, calorific value and minor elements were determined following well-accepted analytical methods and standards. Thus, to prepare the analytical sample, ISO 14780:2017 was used. The moisture and ash contents were determined following ISO 18134–2:2017 and ISO 18122:2015 standards respectively. To analyse N, S and Cl contents, the standards ISO 16948:2015 (N), and ISO 16994:2016 (S and Cl) were used. Finally, for determining the heating value, ISO 18125:2017 was followed, and for analysing the minor elements ISO 16968:2015 was utilised.

Moreover, in order to know the leaf mass of the three species tested and the quantity of clean wood (i.e. wood without bark) contained in the different fractions, two different tests were carried out. For analysing the leaf mass, three original samples of five branches per species were air-dried until the shredding process was initiated. At that moment, leaves were manually separated and weighed to calculate their percentage regarding the total biomass. Concerning the wood content, a separation of wood based on the physical aspect of the samples was performed. A sample of 50 g was selected and, after a separation carried out with tweezers, the two fractions obtained (wood and rest) were

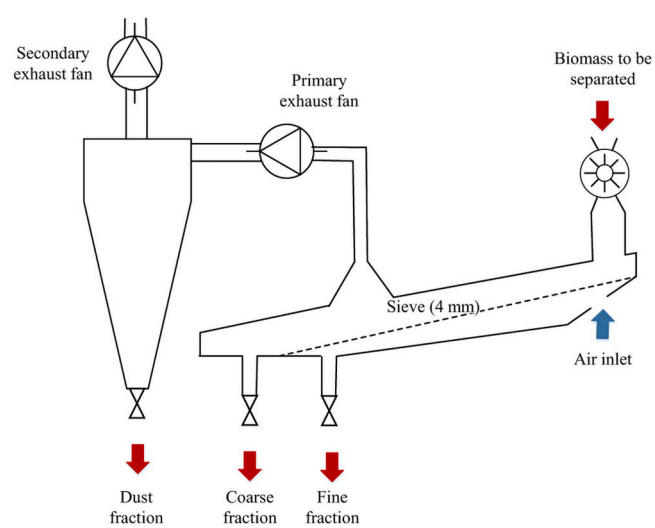

Fig. 1. Scheme of the equipment used for the sieving and blowing step. The crushed biomass is fed to the screener through a rotary valve. Then, the biomass is separated with a sieve of 4 mm using a gyratory reciprocating motion. At the same time, the lightest particles are suctioned by a primary exhaust fan to a cyclone which separates them from the suction air.

weighed for calculating the percentage of wood in the samples.

2.3. Anaerobic digestion tests and biomass and gas analysis

The anaerobic digestion process was developed using wet distilled biomasses with a particle size of less than 1 mm as substrate, and a basic mechanical pre-treatment with a grinder was conducted. The experiment was set up using serological bottles with substrate and inoculum mixed in a 1:1 ratio in terms of volatile solids. Each biological reactor had a working volume of 70 mL, with an additional 50 mL of head space provided for biogas accumulation. To prevent pH fluctuations, 0.3 g of calcium carbonate ($CaCO_3$) was added as a buffer to each bottle. In addition, to establish anaerobic conditions, the reactors were purged with nitrogen gas and sealed with septum rubber and aluminium crimps.

Anaerobic digestion was carried out in an incubator (Hotcold-GL, Selecta, Barcelona, Spain) at 35±1 °C equipped with an orbital shaker (Rotabit, Selecta), following the protocol of the biochemical methanogenic potential (BMP) experiments stablish by Holliger et al., (2016) and performed in triplicate (Fig. 2). The inoculum used to initiate the assays was obtained from the anaerobic digester facility of the Wastewater Treatment Plant (WTP) of Soria (Spain) and had a preparation period of 4 weeks at laboratory conditions before the experiment begin at 35±1 °C. The daily quantification of biogas generation was measured through a water displacement technique by subtracting the endogenous production from the inoculum with a blank assay and biogas composition in terms of methane, carbon dioxide and hydrogen sulfide was determined with a gas analyser (GeoTech Biogas 5000, Leamington Spa, UK).

Six parallel experiments were conducted including the following combinations of controls (raw biomass without distillation) and treatments (distilled biomass) for each species: (1) *C. ladanifer*-distilled, (2) *C. ladanifer*-Control, (3) *J. communis*-distilled, (4) *J. communis*-Control, (5) *R. officinalis*-distilled, and (6) *R. officinalis*-Control.

The lignocellulosic components, including cellulose, hemicellulose and lignin, present in both the pre- and post-distillation treatment samples were examined following the lignocellulosic biomass analysis protocols developed by the National Renewable Energy Laboratory. This procedure employs a two-stage sulfuric acid hydrolysis to fractionate the biomass into forms that are more easily quantified and measured. The resulting hydrolysis solutions are analyzed to determine the carbohydrate and lignin content of the original biomass sample using high-performance liquid chromatography (HPLC) (NREL, 2005, 2008, 2012).

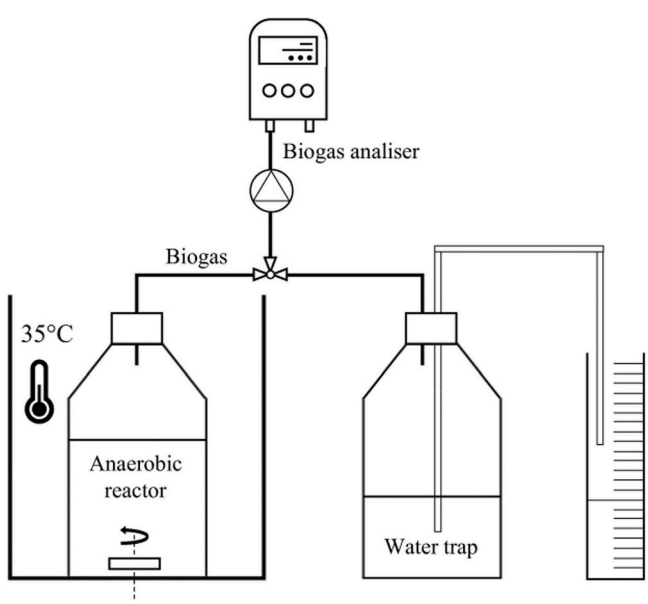

Fig. 2. Experimental setup to assess the biochemical methane potential (BMP). In a temperature-regulated environment (under mesophilic temperature of 35 °C) a fermenter flask with a mix of inoculum and feedstock (*C. ladanifer, J. communis* and *R. officinalis*) is set up. The biogas produced passes through a three-way valve to a bottle of water solution and is measured by water displacement. Changing the position of the three-way valve the biogas composition could be measured by a biogas analyser.

2.4. Energy balance in biomass valorization processes

The energy balance resulting from converting biomass feedstocks into solid biofuels and biogas is the key evaluation of the overall sustainability and viability of both routes. In this section, the energy produced and consumed during the solid biofuel resuling from the processing of *C. ladanifer, J. communis* and *R. officinalis* biomasses after distillation was evaluated. Same scenario was calculated for anaerobic digestion of the byproducts to generate biogas. By analysing the energy inputs and outputs of each valorisation pathway, the net energy outcome was calculated and the opportunities to optimize the energy efficiency of both conversion routes were identified. Both scenarios are shown in Fig. 3.

Considering 1 ton of distilled biomass, the net energy balance of the combustion processes ($E_{Balance\ Comb}$) and the anaerobic digestion ($E_{Balance\ AD}$) was calculated as the difference between the energy produced and the energy consumed with the intermediate steps in Eqs 1-6.

$$E_{Balance\ Comb}\left(\frac{MJ}{t}\right) = E_{Generation(Comb)}\left(\frac{MJ}{t}\right) - E_{Consumption(PreT+Comb)}\left(\frac{MJ}{t}\right) \quad (1)$$

$$E_{Balance\ AD}\left(\frac{MJ}{t}\right) = E_{Generation(CH_4)}\left(\frac{MJ}{t}\right) - E_{Consumption(PreT+AD)}\left(\frac{MJ}{t}\right) \quad (2)$$

where $E_{Generation\ (Comb)}$ is the energy produced in the solid biomass combustion and the AD and $E_{Consumption\ (PreT+C)}$ is the energy consumed including the pretreatments.

$$E_{Generation(CH_4)}\left(\frac{MJ}{t}\right) = CH_4P\left(\frac{m^3CH_4}{tVS}\right) * VS\left(\frac{tVS}{t}\right) * CV\left(\frac{MJ}{m^3CH_4}\right) \quad (3)$$

Where CH_4P is the experimental methane production per ton of substrate calculated, *VS* is the volatile solids of the substrate and *CV* the calorific value of the methane of 36 MJ/ m^3 CH_4.

$$E_{Consumption(PreT+AD)}\left(\frac{MJ}{t}\right) = E_{(Miller)}\left(\frac{MJ}{t}\right) + E_{(AD)}\left(\frac{MJ}{t}\right) \quad (4)$$

where E_{Miller} is the energy consumed in the mechanical pretreatment of cutting the substrate to 1 mm size with experimental values between 324 and 424 MJ• t^{-1} depending on the biomass specie and E_{AD} is the energy consumed in the anaerobic digester process operation considering 2.3 MJ/m^3 CH_4 produced (Deublein and Steinhauser, 2011; Ranieri et al., 2021)

$$E_{Generation(Comb)}\left(\frac{MJ}{t}\right) = DM\left(\frac{tDM}{t}\right) * CF\left(\frac{tCFL}{tDM}\right) * LHV\left(\frac{MJ}{tCFL}\right) \quad (5)$$

Where *DM* is the dry matter, *CF* is the coarse fraction selected for combusting and *LHV* is the experimental lower heating value the biomasses calculated.

$$E_{Consumption(PreT+Comb)}\left(\frac{MJ}{t}\right) = E_{(Siev+Blow)}\left(\frac{MJ}{t}\right) + E_{(Comb)}\left(\frac{MJ}{t}\right) \quad (6)$$

where $E_{Sieving+Blowing}$ is the energy consumed in the pretreatment for biomass fractions separation with experimental values between 150 and 360 MJ• t^{-1} depending on the biomass specie and E_{Comb} is the energy consumed in the process considering the biomass transportation and handling representing a 5 % of the energy produced (Rentizelas et al.,

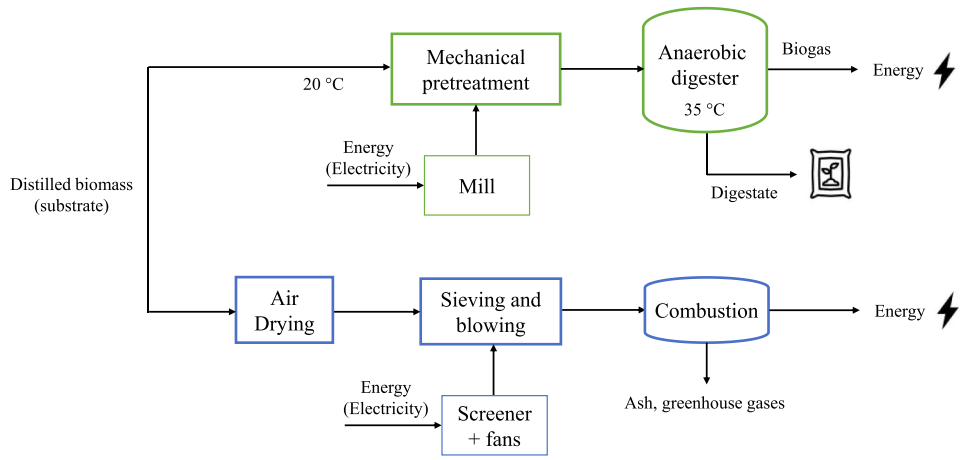

Fig. 3. Energy flow diagram configuration.

2009).

3. Results and discussion

The integration of solid residues obtained after aromatic plant distillation into the essential oil production process can reduce the external demand of energy. For this purpose, two mature technologies of energy recovery (solid biofuel and biogas) were tested and compared by means of an energy balance. In case of solid fuels, three different fractions have been considered for this quality.

3.1. Biomass conditioning to be used as solid biofuel

Distilled biomass was air dried and a sieving and blowing process was performed obtaining three different fractions: coarse, fine and dust (see Fig. 4). These fractions were weighed and the quantity of wood in the resulting material was determined (Table 1). In general, more than 50 % of the distilled material, which underwent a sieving and a blowing process, was separated in the fine fraction and 34.8–42.0 % was obtained in the coarse fraction. On the contrary, the dust fraction included a much lower percentage of the initial biomass (1.3–11.3 %). It must be noticed that the finest fractions (i.e. fine and dust) contained a higher quantity of leaves and bark than the coarse fraction (Fig. 3), and this fact can be seen in the wood content measured in the different fractions. The results were homogeneous among the three species tested since the fraction with the highest wood content was the coarse one, while the fraction with the lowest content was the dust one.

Comparing the different species and taking into account the values of the leaf mass included in Table 1, it can be observed that the higher the leaf mass, the higher the dust fraction and the lower the coarse fraction. Consequently, in *J. communis*, with a leaf mass of 53.9 %, 11.3 % of the total biomass was separated in the dust fraction, while in *C. ladanifer*, whose leaf mass is 25.4 %, the dust fraction contained 1.3 % of the total biomass. *R. officinalis* showed an intermediate result, with 7.8 % of dust fraction and 42.6 % of leaf mass.

3.2. Characterisation of biomass fractions as solid biofuels: comparison with ISO 17225–9:2021

In order to know the suitability of the three different biomass fractions to produce solid biofuels, the samples obtained were analysed and compared with the limits established by the standard ISO 17225–9:2021 (Solid biofuels. Fuel specifications and classes. Part 9: Graded hog fuel and wood chips for industrial use). The analysis results can be seen in Table 2.

The species analysed exhibited the same general trend with regard to the ash, N and S contents, with the lowest values in the coarse fraction, followed by the fine fraction and finally the dust fraction. Moreover, the Cl content was similar in the three fractions analysed. This trend could be related to the wood, leaves and bark contained in the fractions, since the contents of ash, N and S tend to be higher in bark and leaves, (which are the main components in the fine and dust fractions) compared to wood (which is the main component in the coarse fraction), while the content of Cl is often similar in all of them (Monti et al., 2008; Obernberger et al., 2006). Considering the limit values established by the ISO 17225–9:2021, the ash, N, S and Cl contents did not seem to be a limiting factor for using the coarse and fine fractions as solid biofuels. Furthermore, the coarse fraction of the three species fulfilled the limits established for these parameters in the highest quality class established by the above-mentioned ISO standard. On the contrary, the ash content of the dust fraction of *C. ladanifer* and *R. officinalis* could be limiting for its use, since the values analysed exceeded the maximum limit specified by the ISO standard (11.4 % and 9.0 % versus 7.0 %).

In general, a low ash content entails less frequent ash removal in

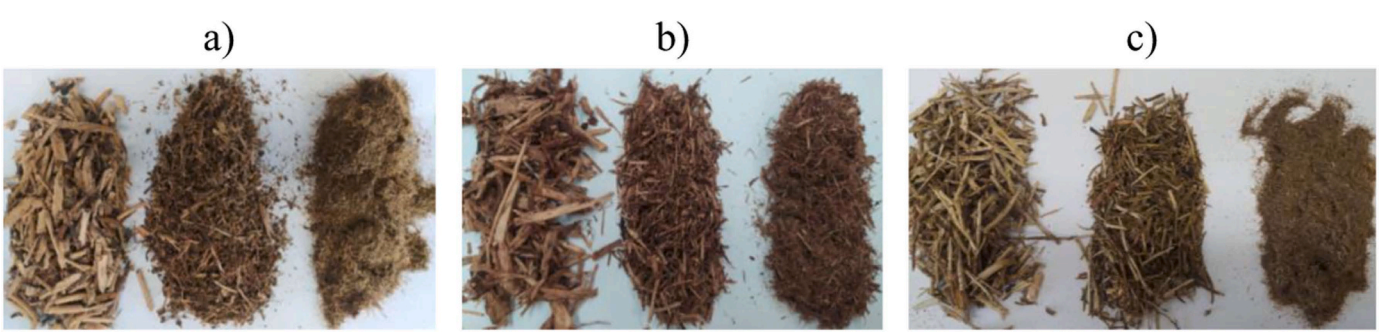

Fig. 4. Fractions of a) *C. ladanifer,* b) *J. communis* and c) *R. officinalis* after the sieving and blowing process.

Table 1
Results of the sieving and blowing process, expressed in weight %, wet basis.

Species		Coarse fraction			Fine fraction			Dust fraction		
	% leaf mass	MC	% of the total	% of wood	MC	% of the total	% of wood	MC	% of the total	% of wood
C. ladanifer	25.4	18.6	41.4	94.8	18.2	57.3	13.8	15.4	1.3	0.1
J. communis	53.9	10.9	34.8	75.0	10.9	53.9	14.5	9.0	11.3	0.5
R. officinalis	42.6	10.1	42.0	95.9	9.3	50.1	16.9	8.7	7.8	0.2

MC: moisture content expressed in weight %, wet basis

Table 2
Composition and calorific value of the *C. ladanifer, J. communis* and *R. officinalis* fractions.

Property	Coarse fraction			Fine fraction			Dust fraction		
	C. ladanifer	*J. communis*	*R. officinalis*	*C. ladanifer*	*J. communis*	*R. officinalis*	*C. ladanifer*	*J. communis*	*R. officinalis*
Ash (wt% d.b)	2.7	2.2	1.9	4.6	4.7	6.5	11.4	5.9	9.0
LHV (MJ/kg, d.b.)	17.96	18.36	18.82	18.39	18.76	19.98	18.51	19.08	18.97
N (wt% d.b)	0.29	0.41	0.43	0.46	0.93	0.85	1.07	0.91	0.98
S (wt% d.b)	0.04	0.04	0.04	0.05	0.06	0.08	0.08	0.07	0.09
Cl (wt% d.b)	0.02	0.03	0.03	0.03	0.03	0.04	0.03	0.04	0.03
As (mg/kg, d.b.)	<0.10	<0.20	<0.20	<0.10	<0.20	<0.20	0.38	<0.20	0.57
Cd (mg/kg, d.b.)	0.29	<0.10	<0.10	0.40	<0.10	<0.10	0.73	0.11	<0.10
Cr (mg/kg, d.b.)	<1.0	<1.0	2.6	<1.0	1.2	2.7	4.6	3.7	5.2
Cu (mg/kg, d.b.)	1.5	2	3.6	2.1	2	5.6	6.7	4.9	9.3
Hg (mg/kg, d.b.)	0.002	0.014	0.01	0.004	0.004	0.017	0.013	0.015	0.029
Ni (mg/kg, d.b.)	<1.0	1.1	1.2	<1.0	1.3	1.5	1.8	2.6	2.9
Pb (mg/kg, d.b.)	1.2	<1.0	<1.0	1.3	<1.0	<1.0	4.8	1	3
Zn (mg/kg, d.b.)	9.1	13	7.1	16	12	17	43	28	24
Classification according to ISO 17225–9:2021	I1	I1	I1	I2	I2	I4	Out of the established classes	I3	Out of the established classes

LHV: low heating value; wt%: weight %; d.b.: dry basis,

combustion equipment. However, ash composition and combustion parameters determine the slagging and fouling behaviour of biomass and also the particulate matter emission. In this sense, although the ash content of the species studied is in line with shrub biomass studied in a previous work (Mediavilla et al., 2017), it is necessary to know the ash composition to predict the combustion behaviour of these biomass materials, and to perform combustion tests to know their real behaviour, which will also depend on the combustion device and the operating conditions.

N, S and Cl contents influence gaseous pollutant emissions and S and Cl the deposition of ash on combustion device surface. However, the interaction between fuel and combustion parameters makes difficult to predict emissions and deposition from the concentration of these atoms in the biomass (Robbins et al., 2012).

Comparing the analysed values with those corresponding to milled pine used as reference fuel for industrial boilers in a previous work (Mediavilla et al., 2017) in general, *C. ladanifer*, *J. communis* and *R. officinalis* show higher ash and N contents, since milled pine showed 0.7 % and 0.09 % respectively. With regard to the S content, similar values to the content in the pine (0.03 %) are observed in the coarse fractions. Nevertheless, the S content in the fine and dust fractions is higher than in pine. Concerning the Cl content, values in line with milled pine (0.02 %) are observed.

Calorific value is not a limiting property in the case of the ISO 17225–9:2021, but its value has to be declared. Comparing the values analysed in this study with other values obtained in a previous work performed with shrub biomass (Mediavilla et al., 2020), all the fractions showed similar values to those obtained with shrub biomass and similar or even higher values than milled pine used as industrial biomass fuel reference (Mediavilla et al., 2017).

As far as the minor elements were concerned, we observed the same trend than that with ash, N and S contents, that is, with the highest values in the dust fraction, followed by the fine fraction and, finally, the coarse one, as was expected from the bark and leaves content in the different fractions (see wood content in Table 1) (Naveed et al., 2023; Obernberger et al., 2006). Moreover, even in the dust fraction, the values analysed were below the limits established by the ISO standard for the most restrictive class.

The classification of the biomass within one class or another can determine the type of combustion equipment to be used. Moreover, the coarse fraction corresponding to *R. officinalis* could be even used to produce pellets for domestic use, since its ash, S, N, Cl and minor elements contents were lower than the limits considered by the ISO 17225–2:2021 (Solid biofuels. Fuel specifications and classes. Part 2: graded wood pellets) in the B class.

3.3. Biogas production

3.3.1. Effect of the thermal treatment on the generation of biogas

Following the BMP methodology, biogas production data were obtained from the raw biomass of the three substrates studied before and after being distilled, with the aim of studying the influence of the distillation as thermal pretreatment. Fig. 5 shows the daily and cumulative biogas production over the 50 days of biodegradation. Large differences in biogas production have been observed in the different substrates and distillation acted as an effective thermal pretreatment increasing total biogas production and rates of degradation.

When *R. officinalis* was used as substrate, the biogas production was practically null in the whole trial (Fig. 5c). This effect might be attributed to the accumulation of inhibitory substances within the process, hindering methanogenic activity. *R. officinalis* contains a high concentration of phenolic compounds, notably rosmarinic acid and other caffeic acid derivatives (Jordán et al., 2013; Ribeiro et al., 2016). These compounds are known for their potent antioxidant and antimicrobial properties leading to biogas production inhibition. In parallel this specie is also rich in various terpenoids, including α-pinene, camphene, borneol, and camphor, contribute to the plant's characteristic aroma but also with a notable antimicrobial activity (Shen et al., 2023; Spréa et al., 2024). Previous studies have shown that phenolic acids and terpenoids compounds have the potential effect of anaerobic digestion inhibition

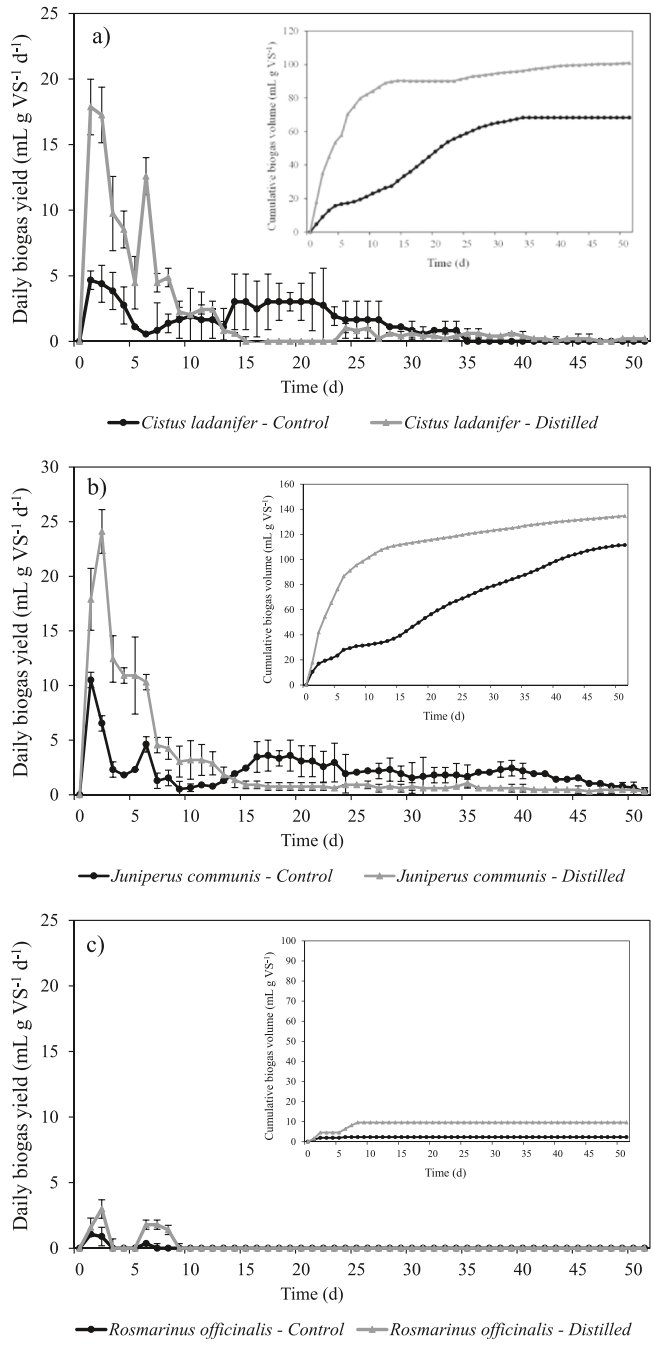

Fig. 5. Cumulative and daily biomethane generation from the anaerobic digestion of *C. ladanifer, J. communis* and *R. officinalis biomass* raw (Control) and biomass distilled along the experiment.

(Chapleur et al., 2016; Mikucka and Zielinska, 2022; Wikandari et al., 2013).

Conversely, for the other two substrates (*C. ladanifer* and *J. communis*; Figs. 3a and 5b), the trend was different as biogas generation was recorded from the first days of the trial with the highest levels of production observed within the first ten days. In these cases, the trials with distilled biomass exceeded the production of 15 mL biogas per gram of volatile solids per day. From day 10 onwards, the biogas production from the distilled biomasses gradually decreased primarily attributed to the diminishing availability of convertible organic content. Ultimately, the cumulative production amounted 135 and 101 mL biogas per gram of volatile solids (VS) for the *J. communis* and *C. ladanifer* distilled trials, respectively.

In contrast, the control trials (raw biomass without distillation) exhibited a considerable reduced biogas production, sustaining higher levels throughout the first 10 days, always below 10 mL biomethane g VS^{-1} (Figs. 3a and 3b) Subsequently, it transitioned into a stationary phase of production, generating between 0 and 5 mL of biomethane (mL• g VS^{-1}•d^{-1}) until the end of the experiment resulting in cumulative production of 111 and 68 mL of biogas per gram of volatile solids for *J. communis* and *C. ladanifer,* respectively.

The AD of lignocellulosic species has been extensively studied in agricultural and forestry wastes, but few experiences have been reported in the shrub species used as feedstock for the essential oil production. Triolo et al., (2012) reported methane yields of 165 mL CH_4/g VS for oval-leaved privet (*Ligustrum ovalifolium*) and 187 mL CH_4• g VS^{-1} for black chokeberry (*Aronia melanocarpa*). Nizami and Murphy, (2010) and Prochnow et al., (2009) investigated grassland silages from diverse species, observing a wide range of 150–500 mL CH_4• g VS^{-1}. Corno et al., (2014) documented 262 mL CH_4• g VS^{-1} for giant cane (*Arundo donax*). Additional studies have examined the biogas production of tree species that can be managed as shrub plantations such as *Betula* sp, *Platanus* sp, *Salix* sp. and *Populus* sp, with productions between 130 and 300 mL CH_4• g VS^{-1} (Chynoweth et al., 1993; Triolo et al., 2012). Finally, biogas production values for other lignocellulosic biomasses such as cereal straw or agricultural residues typically range between 150 and 400 mL g VS^{-1}. (Alvaro et al., 2023; Kainthola et al., 2019; Mohammad Rahmani et al., 2022; Naik et al., 2021; Sawatdeenarunat et al., 2015).

Regarding the composition of the biogas in each trial, the experiments involving *J. communis* and *C. ladanifer* were comparable, with methane content exceeding 50 % (Fig. 6). However, for the trials with *R. officinalis*, it was evident that the biogas produced had a low methane content, indicating incomplete anaerobic digestion likely due to inhibitions occurring during the process stages, as consequence of the presence of inhibitors such as phenolic acids and terpenoids. The quality and calorific value of biogas in the subsequent energy recovery stage directly rely on its composition. For substrates with a lignocellulosic structure, which have a high carbohydrate content, the average biogas composition is approximately 50 % methane content (Rasi et al., 2007; Schnürer, 2016).

3.3.2. Lignocellulose components decomposition

In order to determine the breakdown of the lignocellulose fraction during the distillation process the variations in the chemical composition of the different samples in terms of cellulose, hemicellulose and lignin content were analysed (Table 3). The performance of *C. ladanifer* and *J. communis* substrates exhibited a similar pattern, with a decrease in the cellulose and hemicellulose content between raw samples (control) and the samples obtained after distillation (Table 2). It must be

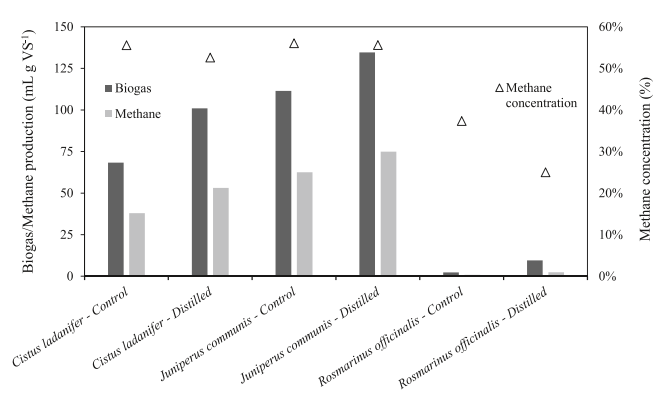

Fig. 6. Biogas (dark grey bars) and methane (ligh grey bars) total production from the anaerobic digestion of *C. ladanifer, J. communis* and *R. officinalis biomass* raw (Control) and biomass distilled, and the methane concentration obtained (triangles) in each experiment.

Table 3
Structural composition of raw and distilled substrates *C. ladanifer, J. communis* and *R. officinalis* in terms of cellulose, hemicellulose -divided in xilan, galactan, arabinan and mannan, lignin -divided in insoluble and soluble acids- and ashes percentage content.

Component	*J. communis - Control*	*J. communis - Distilled*	*C. ladanifer - Control*	*C. ladanifer - Distilled*	*R. officinalis - Control*	*R. officinalis - Distilled*
Cellulose (%)	18.56 ± 0.46	14.71 ± 0.37	17.27 ± 0.26	12.03 ± 0.20	17.40 ± 0.30	16.90 ± 0.16
Hemicellulose (%)	13.69 ± 0.40	9.59 ± 0.42	15.80 ± 0.34	11.49 ± 0.69	11.20 ± 0.10	10.10 ± 0.16
Xilan	4.18 ± 0.22	2.49 ± 0.16	9.62 ± 0.17	6.45 ± 0.87	8.10 ± 0.04	7.30 ± 0.14
Galactan	2.88 ± 0.03	2.47 ± 0.16	2.56 ± 0.10	2.59 ± 0.06	1.00 ± 0.04	1.00 ± 0.01
Arabinan	3.56 ± 0.15	1.85 ± 0.06	2.94 ± 0.20	1.34 ± 0.07	0.08 ± 0.03	0.70 ± 0.01
Mannan	3.07 ± 0.36	2.78 ± 0.21	0.68 ± 0.05	1.11 ± 0.02	1.3 ± 0.03	1.10 ± 0.02
Lignin (%)	44.54 ± 0.74	57.39 ± 0.37	38.37 ± 0.37	51.18 ± 0.22	31.40 ± 0.18	32.80 ± 0.04
Insoluble Acid	41.70 ± 0.79	54.49 ± 0.42	33.57 ± 0.47	46.64 ± 0.24	30.20 ± 0.19	31.50 ± 0.60
Soluble Acid	2.84 ± 0.46	2.90 ± 0.04	4.80 ± 0.06	4.54 ± 0.07	1.20 ± 0.03	1.30 ± 0.35
Ashes (%)	4.74 ± 0.46	6.61 ± 0.12	5.04 ± 0.42	7.21 ± 0.21	5.60 ± 0.01	6.20 ± 0.10

noted that this result was expected as exposure to high temperatures affects the solubility of these compounds as previous studies indicate (Patowary and Baruah, 2018; Rajput et al., 2018) e. The recorded degradation of hemicellulose was 30 % and 27 % for *J. communis* and *C. ladanifer*, respectively, while cellulose degradation was 21 % and 30 %. In contrast, in the case of *R. officinalis*, the degradation was significantly lower in comparison with a 10 % of the hemicellulose and 3 % of the cellulose degraded. This fact can be attributed to the distillation time for *R. officinalis* being half the duration compared to the other species, as mentioned in Section 2.1.

Distillation accelerated the hydrolysis rate of cellulose and hemicellulose, resulting in a positive effect on anaerobic digestion with increased biogas production. Conversely, the lignin degradation rate followed an opposite trend, probably due to the formation of pseudo-lignin under extreme conditions or the development of cross-linked compounds resulting from reactions involving sugars released during the hydrolysis of the hemicellulosic fraction (Nelson et al., 2011). Furthermore, as previous studies indicated, a more intense treatment of lignocellulosic biomass, characterized by elevated temperatures or prolonged exposure durations, could result in reduced methane yields. This is attributed to lignin decomposition, potentially releasing phenolic and heterocyclic compounds (Li et al., 2023; Yadav and Vivekanand, 2021). These compounds could also interfere the activity of fermenting microorganisms during the anaerobic digestion process (Hendriks and Zeeman, 2009).

3.4. Energy balance in biomass valorization processes

The energy balance of the two forms of energy recovery (solid biofuel and biogas) was evaluated with the configuration described in Section 2.4. Calculations based on the processing of one tonne of distilled biomass are presented in Table 4 where the main results of the study are presented.

The final balance energy in the processes showed a higher potential production through the combustion with values of 4507.8 MJ/t for the *J. communis,* 4507.8 MJ/t for the *C. ladanifer* and 5224.1 MJ/t for *R. officinalis.* On the other hand, the anaerobic digestion pathway of *C. ladanifer* produced 1265.7 MJ/t and *J. communis* 2029.5 MJ/t, respectively. These results evidenced that the direct combustion is more efficient considering the energy balance. However, other factors such as environmental impact, emissions, and resource availability must also be considered when determining the most sustainable biomass valorisation pathway. As this point, it should be noted that although the biogas route yielded a limited value compared to solid fuels pathway (between 25 % and 45 %, for *C. ladanifer* and *J. communis*, respectively), methane is considered and "drop in" fuel completely interchangeable with fossil natural gas. In this sense, distillation by-products of both shrubs can be potentially considered as co-substrates for biogas generation with a competitive methane yield, similar to other lignocellulosic wastes. Finally, that is not the case of *R. officinalis* that should be rejected due to the presence of inhibitors of the methanogenesis.

Future research on the energy valorization of biomass distilled from shrubs such should focus on several key areas. Firstly, it is essential to achieve a real integration of heat expenditure in the hydrodistillation process with the heat input provided by the two types of fuels. This will allow for a more comprehensive understanding of the energy balance and efficiency of these valorization pathway. Secondly, expanding the scope of studies to include a broader range of species will provide a more comprehensive understanding of the potential biomass resources available for energy production and scalability of these valorization approaches. Lastly, exploring the potential of co-digestion with other substrates can enhance the efficiency and yield of anaerobic digestion processes and analysing the presence of inhibitors.

4. CONCLUSIONS

The quality of biomass and biogas derived from distillation residue of three aromatic plant species (*C.ladanifer, J.communis,* and *R.officinalis*)

Table 4
Energy balance results considering a ton of *C. ladanifer, J. communis*, and *R. officinalis* distilled biomass as a solid biofuel for combustion or biogas from an anaerobic digestion process.

	Combustion		Energy generation		Energy consumption		Energy balance
Sample	Dry matter (%)	Coarse fraction	MJ/kg (db)	Energy (MJ/t)	Sieving and blowing (MJ/t)	Combustion process (MJ/t)	Energy (MJ/t)
C. ladanifer	81.4	41.4	17.96	5447.2	150.4	272.4	5024.5
J. communis	89.1	34.8	18.36	5123.6	359.6	256.2	4507.8
R. officinalis	79.9	42	18.82	5684.1	175.7	284.2	5224.1
	Anaerobic digestion		**Energy generation**		**Energy consumption**		**Energy balance**
Sample	Dry matter (%)	Volatile solids	Methane yield (m^3 CH_4/t VS)	Energy (MJ/t)	Miller (MJ/t)	AD process (MJ/t)	Energy (MJ/t)
C. ladanifer	58.3	94.9	53.1	1814.1	426.1	122.3	1265.7
J. communis	73.9	96.3	74.9	2596.6	394.6	172.6	2029.5
R. officinalis	59.9	88.3	-	-	324.5	-	-

was investigated. Findings showed that the coarse fraction, termed Class I1 by ISO 17225–9:2021, from all species, offers high-quality biomass for combustion, while fine fractions are of lower quality, they have potential for energy recovery. Dust fractions, with more bark content, have the lowest quality and only *J. communis* wastes meets ISO standards. Direct anaerobic digestion of post-distillation biomass produces biogas, with *C.ladanifer* and *J.communis* showing notable biomethane production with a total energy recovery between 25 % and 45 %, compared to solid fuel route. However, anaerobic digestion of *R. officinalis* biomass (distilled and not) was tentatively hindered by terpenoids and phenolic compounds. The present study demonstrates the potential of utilizing solid residues after essential oil extraction as energy resources.

CRediT authorship contribution statement

Irene Mediavilla: Writing – review & editing, Data curation, Conceptualization. **Alfonso García Álvaro:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Ignacio de Godos Crespo:** Writing – review & editing, Funding acquisition, Conceptualization. **César Ruiz Palomar:** Writing – original draft, Methodology. **Luis Saúl Esteban:** Writing – review & editing, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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