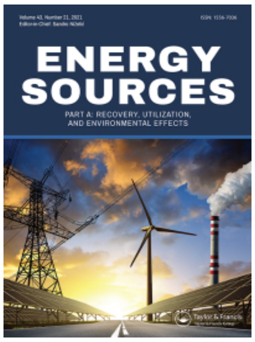

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

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Species Arar (*Phoenicea juniperus* L.) as a biomass source – A case study

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ABSTRACT

Arar (*Juniperus phoenicea* L.) is a small monoecious or dioecious evergreen species presenting as a shrub or tree around the Mediterranean. This widespread plant is also causing problems in Croatia, along its Adriatic coastal area and in particular on the island of Pag. It affects the establishment and growth of other species that share its habitat and has also reduced the grazing areas of local sheep breeding and beekeeping communities. Arar is also a frequent cause of wildfires in the region. Its spread is indeed far-reaching, from its impact on plants and livestock to its adverse effects on the local population and its tourism, which is one of the main components of the island's economy. This research aimed to evaluate biomass and biochar samples of arar, using standard methods to verify their potential energy value. Results of the study showed a favorable content of coke (16.28%) and volatiles (77.26%) in the samples. The C, H, S, N, and O ratios of the samples were 50.14%, 6.57%, 0.31%, 0.84% and 42.13%, respectively. The higher calorific value was 20.45 MJ·kg^{-1} for biomass and 29.01 MJ·kg^{-1} for biochar. Accordingly, this species can be used as a solid biofuel for direct combustion or similar processes and for other value-added applications.

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Introduction

In times of climate change, biomass in all forms (solid, liquid, and gas) is undoubtedly an important alternative fuel source. Additional advantage of biomass is that it can be developed as an on-site activity following a local biological production that will provide a direct access to clean energy for its surrounding communities (Tolon and Karaosmanoglu 2021). Burning biomass to produce energy will not pollute the atmosphere with CO_2 to the same extent as fossil fuels since it has already absorbed about the same or even larger amount of CO_2 during its life cycle than other sources of energy production (Alatzas et al. 2019).

Croatian flora includes a large number of plant species, many of which have only been superficially studied or analyzed. The genus Juniperus is one of them and belongs to the family Cupressaceae. This family consists of evergreen woody trees or shrubs, and arar (*Juniperus phoenicea* L.), also known as Somina, is one of them. In terms of height, arar is present as a smaller shrub or a small tree, its height ranging between 8–12 m and is either monoecious or dioecious (Boratyński et al. 2009). Although the biomass of arar has not been well examined in terms of energy production, this species is known to contain essential oils (Ait-Ouazzou et al. 2012) and many other biologically active compounds such as polyphenols, tannins, anthocyanins, and flavonoids (Ennajar et al. 2009a). Previous studies of arar have reported that these oils and compounds could have various pharmacological effects, such as antiviral and anticarcinogenic effects, with possible use in food (aromas), traditional medicine, and

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industrial purposes (cosmetics and drug production) (Ennajar et al. 2009b). However, in some areas, like the island of Pag, this species is not considered for its potential benefits but is considered a pest due to its invasive ability to spread on the island (García, Guichoux, and Hampe 2018). Geographically arar can be found throughout the whole Mediterranean area, from the African Atlas Mountains and the Portuguese Atlantic coast into the west and to Jordan and Saudi Arabia to the east (Boratyński et al. 2009). The distribution of arar in Croatia extends along the Adriatic coast and its islands (Nikolic 2021). Almost twenty years ago, Kovačić et al. (Kovacic, Jasprica, and Ruscic 2001), registered the arar association and studied its floristic characteristics on the Pelješac peninsula and the majority of the Croatian islands, including the coastal region of Dubrovnik (Dubrovačko Primorje). The xerothermic scrub (macchia) forest community is one in which arar is common and widespread, as can be seen from the abundance of this species. The evergreen vegetation of these areas has been threatened by spread of arar, and also by the wild fires associated with land clearing activities (Kovacic, Jasprica, and Ruscic 2001). These events helped arar to progressively colonize a majority of the island of Pag (Vuleta 2006). As arar become a dominant plant on the island it destroyed other plant species and has compromised survival of sage and other endangered medicinal plants. Arar has also significantly affected local sheep and bees grazing areas (Vuleta 2006). It is referred, by local population, as a "green monster" and compared to ragweed (Vicevic 2017). It has been established that arar is occupying more than half of the grazing area on the island. For Pag and its population this can have a devastating effect. Pag's economy and revenue rely heavily on its sheep grazing activity and food production associated with it. As Pag is well known for its local delicacies like lamb and cheese any reduction or destruction of its grazing areas will have a serious and irreversible effect on its inhabitants, potentially forcing its population to leave the island if local pastoral activities are diminished (Vicevic 2017). Local bee-keepers, like sheep graziers, are also faced with same destruction of plant species due to arar's aggressive spread. As cultivation of sage and other medicinal plants is restricted, honey production is facing equally alarming prospect as the island's sheep and dairy production (Butula et al. 2009). In Croatia, arar macchia is considered as an invasive plant species community and its management should be provided by the Ministry of Agriculture. Even though, by law, the Ministry requires eradication of invasive plants like arar, no meaningful founding or action has been provided to residents of the island of Pag so far (Croatian Parliament 2018). Or, for that matter, to any other areas affected in the same manner. Initially, the local response to arar was to incinerate or poison it, but neither that nor the last attempts at mechanical removal by excavators helped (Vicevic 2017). It has to be pointed out that of all clearing methods one can have a particularly disastrous effect. Biomass burning attempts on land can cause wild, uncontrolled fires that can result in significant harm to environment and ecosystem. These attempts are among the most common anthropogenic causes of uncontrolled fires along Croatian coast and are a desperate attempt by local population to protect not only their environment but also their economy and way of life. Since burning or using toxins on it did not help to alter or eliminate abundant communities of this species, nor did other usages of it for bioactive compounds or essential oil extraction, the purpose of this investigation was to confirm if it is possible to utilize the feedstock of invasive species arar for energy generation, which could also help reduce fire risk in affected areas. Knowledge of the overall composition of biomass properties is essential for its thermochemical conversion (combustion and pyrolysis processes). Therefore, arar biomass was studied after it was removed from nature by cutting down or clearing pastures for eventual green energy production purposes.

Alternative energy sources are urgently needed. Therefore, finding efficient ways to characterize and utilize biomass and identify availability of various biomass sources should indicate most suitable processes to convert biomass into bioenergy (Ong et al. 2020). Biomass can most efficiently be converted into three primary forms: electrical, thermal, or chemical energy or fuel (Kumar et al. 2019). The biotechnological and thermochemical conversion processes are common ways to upgrade biomass. Biotechnological processes use enzymes and microorganisms to convert biomass components into a variety of valuable products, like primary and secondary metabolites (e.g., enzymes, vitamins, phenols, pigments, ethanol, antibiotics) (Solarte-Toro et al. 2021). Cellulose, hemicellulose, and lignin are the major biochemical components of lignocellulosic biomass (Sannigrahi, Ragauskas, and Tuskan 2010). While cellulose and hemicellulose rich feedstocks are better for liquid fuel synthesis, lignin rich feedstocks are better for direct combustion (Kricka et al. 2017). Thermochemical conversion mostly requires high temperatures, low-residence time (Solarte-Toro et al. 2021). Sometimes heat and catalysts are used to convert plant polymers into fuels, chemicals, or electrical energy (Brown 2011). To convert biomass into bioenergy, processes such as combustion, pyrolysis, gasification, and hydrothermal processing are used (Solarte-Toro et al. 2021). Biomass combustion can produce heat and electricity, both of which are frequently applied in process industries (Ong et al. 2020). It is the quick reaction of oxygen and fuel to generate heat and fuel gas which mainly consists of carbon dioxide (CO_2) and water (H_2O). At the same time, incomplete combustion produces potentially hazardous compounds. It serves as the fundamental basis for the worldwide electricity generation (Brown 2011). While pyrolysis, is a thermal degradation of biomass by heat in an oxygen free environment at the temperatures between 300°C and 600°C. Generally, there are many pyrolysis processes classified into six subclasses (slow, fast, flash, vacuum, intermediate and hydro pyrolysis) (Tripathi, Sahu, and Ganesan 2016). Pyrolysis processes result in the producing of biochar (solid), bio-oil (liquid), and bio-syngas (gas) (Balat 2008). No other conversion method yields such a large variety of products (Tripathi, Sahu, and Ganesan 2016). Simultaneously, the yields depend on various parameters such as temperature, heating rate, residence time, etc. As a complex mixture of water and organic chemicals, bio-oil is produced as a pyrolysis liquid fraction (Vamvuka 2011). Compared to fossil fuels, bio-oil has numerous advantages. The most significant features are its renewability and low NO_x and SO_x emissions, while some unfavorable properties of bio-oil such as large proportion of water, high viscosity, poor ignition, and corrosiveness, require processing and improvement of bio-oil before future utilization (Tripathi, Sahu, and Ganesan 2016). The pyrolysis gas contains carbon dioxide, carbon monoxide, methane, hydrogen, and other gaseous organics as well as water vapor (Vamvuka 2011), and it has also been discovered to be effective in heat and power industries (Tripathi, Sahu, and Ganesan 2016). The third product of pyrolysis is biochar, the quantity and properties of which depend greatly on the temperature. The biochar fraction contains inorganic matter, ash in varying degrees, and unconverted residues produced during, thermal decomposition of the organic components, especially lignin (Vamvuka 2011). It is often applied as activated carbon for soil improvement (Reza et al. 2019). It has a substantial outcome as water and air pacifier, and has been used for solvent recovery among other applications (Reza et al. 2020). of the most significant benefit of the pyrolysis process adjustability to reach desired outputs. For example, slow pyrolysis is useful for high biochar production, while fast pyrolysis is a more convenient process for higher bio-oil yield. Vacuum pyrolysis, on the opposite serves to obtain more evenly distributed products (Tripathi, Sahu, and Ganesan 2016).

As mentioned, arar biomass, which has recently spread extremely rapidly along the Croatian coast and islands, and throughout the Mediterranean, has been currently treated exclusively as weeds and waste. The most common technique of removing it from nature is by burning its biomass in the existing areas where it occurs. Arar is a serious problem in the area. It endangers herbs, medicinal and other plant and animal species, and bees; affects sheep, lamb, and cheese production; and can trigger uncontrolled fires if not disposed of properly. In addition, arar and its current management (uncontrolled fires) already have significant consequences on the Mediterranean environment and local communities, since the primary sources of income for local people are the production of local goods and tourism, both currently threatened by the succession of this species. Nevertheless, arar biomass currently has no function and only causes bigger problems over time. There is no comparable research evaluating the energy efficiency of arar biomass. As a result, specific examinations were performed to study its characteristics and energy potential for thermochemical conversion. Finding a solution for its elimination and exploitation of its biomass for the creation of energy supply might be a solution that wouldn't cause additional problems for the environment or local communities. It could serve them as additional source of income. This study may help develop disposal solutions for arar and other invasive plant species and promote awareness among scientists and the public about its advantages. The right management of this species might help reduce climate change, improve ecosystem health, and provide new products with value for a sustainable society.

Materials and methods

Samples of arar biomass (Figure 1)a and b were taken from five different locations on the island of Pag (44°26′53.2 "N 15°01′58.8 "E; 44°24′50.4 "N 15°02′51.0 "E; 44°28′14.9 "N 14°57′38.2 "E; 44°29′03.8 "N 14°58′10.2 "E). Each sample contained approximately 2 kg of fresh weight biomass and was taken in the early morning hours of March 2017 during dry weather. After harvesting, only the healthy aerial sections of arar were delivered to the laboratory. The collected arar samples were first dried and ground to a size of 630 µm – 1000 µm (IKA, Germany) and after, analyzed as followed by standard methods in triplicate.

For proximate analyses standard methods (moisture EN 18134–2:2015); ash EN ISO 18122:2015; coke EN 15148:2009; fixed carbon and volatile substances EN 15148:2009) were used, and higher calorific value was obtained by IKA C200 calorimeter (IKA, Germany; EN 14918:2010). Ultimate analysis included determination of C, H, N, S and O content of the raw materials using standard methods on Vario Macro Elemental Instrument (Elementar Analysensysteme GmbH, Germany; C, H, N – EN ISO 16948:2015; S – EN ISO 16994:2015; O – calculated). Structural analyses of fiber components were carried out by Van Soest method (Van Soest, Robertson, and Lewis 1991) using an ANKOM 2000I analyzer. Cellulose content was determined by subtraction of acid detergent lignin from acid detergent fiber, hemicellulose by subtraction of acid detergent fiber from neutral detergent fiber, respectively, while lignin was reported as acid detergent lignin. Following the analyses of the raw materials, the samples (particle size 600 µm to 1000 µm) were pyrolyzed under laboratory conditions (Figure 2) at a temperature of about 500°C without oxygen.

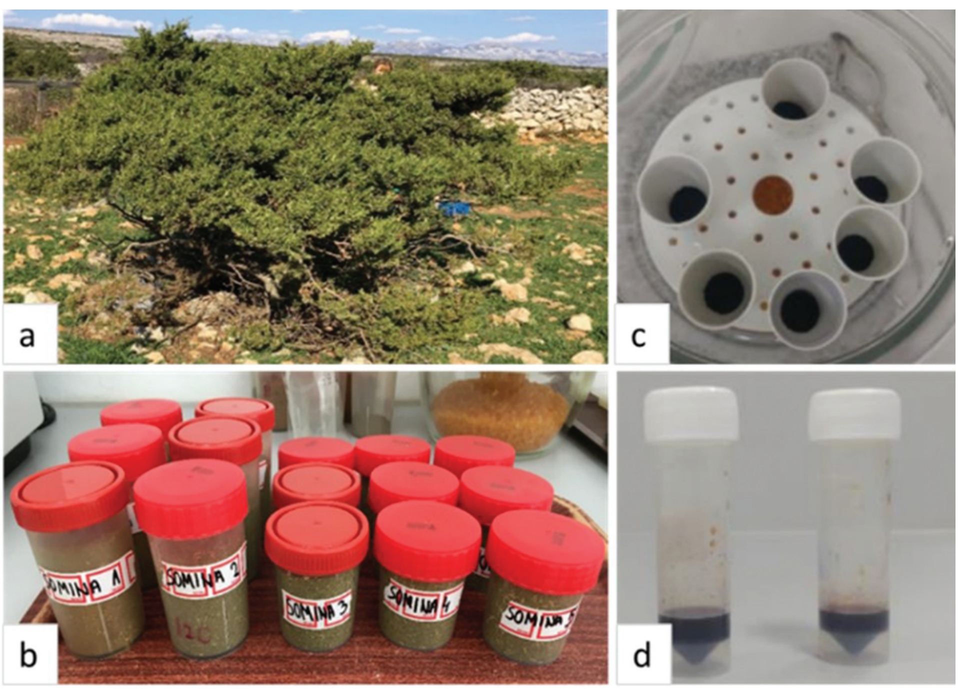

Figure 1. Biomass of arar (a – biomass at the site; b – dried and ground biomass prepared for analyses; c – biochar after pyrolysis process prepared for further analyses; d – bio-oil upon pyrolysis process).

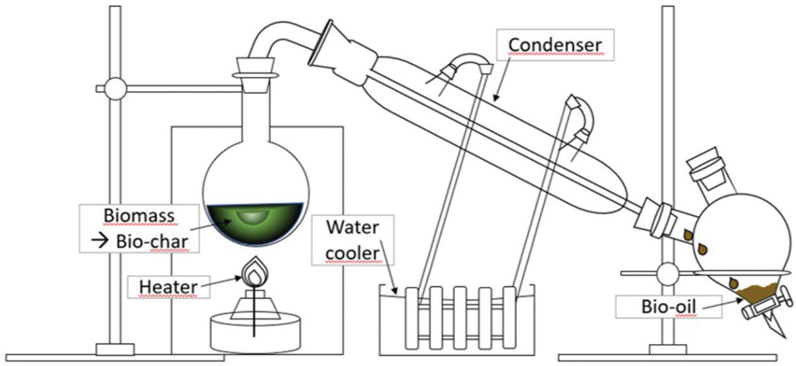

Figure 2. Experimental pyrolysis apparatus diagram.

After biomass heating, the volatiles were passed through the Liebig condenser, where the condensation process separated liquids and solids from the incondensable gases, which were discharged into the atmosphere. The amounts of biochar (Figure 1c), bio-oil (Figure 1d) and gas were calculated, and the biochar was also analyzed using the above methods for biomass samples. Based on the data reported as means ± standard deviation of triplicate measurements (where mean value is average of three repeated measurements (m) of the same sample = $m_1 + m_2 + m_3) * 3^{-1}$) ANOVA was performed. A t-test was used to examine differences between the mean values. The confidence level was set at $P < .05$.

Results and discussion

Efficient utilization of the considerable energy potential hidden in raw biomass requires not only calorific values but also proximate, ultimate, and structural analyses (Gami et al. 2011). Based on these results, it is possible to make an objective decision about whether the raw material in question, in this case arar biomass, has the potential to produce energy (heat or electricity) and how (Voca et al. 2019).

As mentioned earlier, samples of arar biomass from five different sites were subjected to proximate (Table 1), ultimate (Table 2), structural (Table 3), and pyrolysis (Table 3) analysis, while calorific values (Table 4) were also determined. From pyrolysis analysis, 36.79% biochar (BC) and 44.61% pyrolysis bio-oil (BO) were obtained (Table 3). The moisture (MC), ash (AC), coke (CK), fixed carbon (FC) and volatiles (VC) content were 40.36%, 8.35%, 16.28%, 7.93% and 77.26%, respectively (Table 1). The proximate analysis of biochar samples (Table 1) showed that the average amounts of MC, AC, CK, FC, and VM content were 6.46%, 12.17%, 66,88%, 54.71%, and 26.66%, respectively. The reason for the noticeable difference between the findings of proximate biomass and biochar analyses and the previously existing studies (Ahmed et al. 2020a, 2020b; Liu et al. 2017; Qian et al. 2020; Reza et al. 2019, 2020; Sher et al. 2020) is the type of biomass samples and their condition. Some of them were analyzed as received, while other were analyzed after drying. The lowest MC noticed is shown in Table 1, for the samples of location 1 (37.30%) and the highest for location 2 (43.46%). However, this is the MC range of raw arar biomass collected at the sites, and a MC of up to 50% is typically acceptable for thermal conversion processes. The MC is usually defined as the amount of water present in a sample that negatively affects the reactivity during pyrolysis and reduces the quality of the biofuels (Kenney et al. 2013). Only Voća et al. (Voca et al. 2019) provided data on MC as received condition, which was about 84.58%. However, since *Posidonia oceanica* is a submerged marine plant, it is expected that our samples would have had a much lower MC. The results for AC and FC differ from those in the literature. AC is slightly higher, while FC was lower than values for various woody or invasive plant species or other biomass feedstocks. For example, Ahmed et al. (Ahmed et al. 2020a), analyzed the waste biomass of different invasive species parts such as bark, twigs, pods, and branches

Table 1. Proximate analysis of investigated arar biomass and biochar samples.

Location	Moisture; MC (%)	Aah; AC (% db)	Coke; CK (% db)	Fixed carbon; FC (% db)	Volatiles; VC (% db)
Biomass samples					
1	37.30 ± 1.93c	8.65 ± 0.35b	14.62 ± 0.26b	5.97 ± 0.22c	80.71 ± 0.23a
2	43.46 ± 0.68a	9.97 ± 0.33a	18.39 ± 1.26a	8.42 ± 0.96ab	75.21 ± 1.26c
3	39.34 ± 1.28bc	7.74 ± 0.44bc	15.68 ± 0.82b	7.94 ± 1.04ab	77.33 ± 0.77b
4	40.30 ± 0.71abc	7.60 ± 0.89c	15.43 ± 0.43b	7.83 ± 0.86b	77.60 ± 0.36b
5	41.41 ± 3.21ab	7.80 ± 0.55bc	17.27 ± 0.43a	9.47 ± 0.89a	75.47 ± 0.44c
p	0.021	0.002	0.001	0.01	p < .05
Average	40.36	8.35	16.28	7.93	77.26
Biochar samples					
Location	**Moisture; MC (% db)**	**Ash; AC (% db)**	**Coke, CK (% db)**	**Fixed carbon; FC (% db)**	**Voaltiles; VC (% db)**
1	4.67 ± 0.04d	11.15 ± 0.86b	63.06 ± 0.86d	51.92 ± 0.09b	32.27 ± 0.87a
2	6.40 ± 0.05c	12.26 ± 0.30b	69.08 ± 0.38c	56.81 ± 0.15a	24.52 ± 0.36b
3	6.98 ± 0.05b	14.43 ± 0.99a	71.54 ± 0.28a	57.12 ± 0.78a	21.48 ± 0.22c
4	6.97 ± 0.07b	14.51 ± 1.51a	70.50 ± 0.35b	55.98 ± 1.36a	22.53 ± 0.42c
5	7.26 ± 0.07a	8.52 ± 0.62c	60.24 ± 0.68e	51.72 ± 0.14b	32.50 ± 0.67a
p	p < .05	p < .05	p < .05	p < .05	p < .05
Average	6.46	12.17	66.88	54.71	26.66

% – as received; % db – on dry basis; within a column different letters indicate statistically significant differences at the 5% level; p – significance level.

Table 2. Ultimate analysis of arar biomass and biochar.

Location	Carbon (% db)	Hydrogen (% db)	Sulfur (% db)	Nitrogen (% db)	Oxygen (% db)
Biomass samples					
1	50.66 ± 0.12b	6.44 ± 0.28a	0.45 ± 0.03c	0.76 ± 0.04a	41.68 ± 0.23a
2	50.14 ± 0.25ab	6.47 ± 0.27a	0.33 ± 0.01c	0.97 ± 0.03b	42.08 ± 0.05a
3	50.46 ± 0.04ab	6.67 ± 0.15a	0.29 ± 0.01ab	0.75 ± 0.02a	41.84 ± 0.17a
4	50.17 ± 0.04ab	6.93 ± 0.07a	0.23 ± 0.02a	0.88 ± 0.02ab	41.80 ± 0.11a
5	49.29 ± 0.38a	6.34 ± 0.33a	0.27 ± 0.01ab	0.84 ± 0.02ab	43.27 ± 0.69a
p	0.03	0.51	0.00	0.01	0.09
Average	50.14	6.57	0.31	0.84	42.13
Biochar samples					
Location	**Carbon (% db)**	**Hydrogen (% db)**	**Sulfur (% db)**	**Nitrogen (% db)**	**Oxygen (% db)**
1	77.53 ± 0.36c	2.80 ± 0.06a	0.14 ± 0.00a	1.69 ± 0.01c	17.84 ± 0.31ab
2	74.86 ± 0.28b	3.83 ± 0.03a	0.23 ± 0.01b	1.84 ± 0.01d	19.24 ± 0.33b
3	75.04 ± 0.12b	3.59 ± 0.01a	0.16 ± 0.01a	1.71 ± 0.02c	19.50 ± 0.16bc
4	72.56 ± 0.16a	3.56 ± 0.04a	0.17 ± 0.00a	1.16 ± 0.03b	22.56 ± 0.16c
5	78.26 ± 0.30c	3.21 ± 1.46a	0.17 ± 0.02a	1.02 ± 0.00a	15.34 ± 1.15a
p	0.00	0.27	0.01	p < .05	0.00
Average	75.65	3.8	0.17	1.49	18.9

% db-% dry basis; within a column different letters indicate statistically significant differences at the level of 5%, p – significance level.

Table 3. Structural analysis of arar samples biomass.

Location	Cellulose (% db)	Lignin (% db)	Hemicellulose (% db)	BC (%)	BO (%)	BG (%)
1	23.4	35.38	16.1	33.18	47.61	19.21
2	19.21	37.07	16.4	37.50	41.42	21.08
3	17.03	42.83	9.59	38.36	45.65	15.99
4	17.25	40.38	12.85	38.09	45.33	16.58
5	23.25	39.28	13.29	36.84	43.05	20.11
Average	**20.03**	**38.99**	**13.65**	**36.79**	**44.61**	**18.59**

% db – % on dry basis, BC – biochar, BO – bio-oil, BG – synthesized gas.

Table 4. Calorific values of investigated arar biomass and biochar.

SAMPLES	Biomass		Biochar	
Location	HCV (MJ·kg^{-1})	LCV (MJ·kg^{-1})	HCV (MJ·kg^{-1})	LCV (MJ·kg^{-1})
1	19.97 ± 0.85	19.04 ± 0.85	29.43 ± 0,01c	27.96 ± 0.01c
2	19.95 ± 0.51	18.88 ± 0.51	28.40 ± 0,11a	26.97 ± 0.09a
3	21.16 ± 0.05	19.79 ± 0.05	28.89 ± 0,14b	27.41 ± 0.16b
4	20.87 ± 0.05	19.46 ± 0.05	28.35 ± 0,14a	26.93 ± 0.11a
5	20.29 ± 0.10	18.95 ± 0.10	29.97 ± 0,14d	28.54 ± 0.15d
p	**0.07**	**0.27**	**p < .05**	**p < .05**
Average	**20.45**	**19.22**	**29.01**	**27.56**

HCV, higher calorific values; LCV, lower calorific values; within a column different letters indicate statistically significant differences at the level of 5%, p – significance level.

of *Acacia cincinnata*. The same authors (Ahmed et al. 2020b) also analyzed sawdust from acacia wood processing. Reza et al. (Reza et al. 2019, 2020) analyzed the invasive species *Acacia holosericea* and *Pennisetum purpureum*. Sher et al. (Sher et al. 2020), studied barley, wheat, miscanthus, short rotation coppicing willow, wood waste and wood pellet. Considering that ash is a mineral residue produced as a by-product of combustion, its quantity is an indicator of the feedstock quality and generally ranges from 5% to a high of 20% (Voca et al. 2019). According to these references, the findings suggest that arar biomass has a slightly higher AC (8.35%). Reza et al. (Reza et al. 2019), determined an AC from *Acacia holosericea* biomass of 3.91%, while Sher et al. (Sher et al. 2020) determined various AC ranging from 0.79% to 10.20% from wheat, barley, miscanthus, willow, wood pellets, and various other biomass samples. Qian et al. (Qian et al. 2020) reported huge variations in the AC in the biochar samples depending on the biomass samples. AC results in biochar range from 1.49% (*Pinus sylvestris*) to 35.88% (rice husks) when compared to samples obtained by similar pyrolysis conditions at 550°C. Nevertheless, the results are quite far from desirable values. which should be as low as possible. A high content of CK and FC in samples is considered desirable because it can mean a possible higher amount of produced energy by the combustion process of a given amount of biomass (Voca et al. 2019). The calorific values of biomass increase accordingly. When the FC value goes up, the calorific value also increases, ending with increased biomass quality. Depending on the sampling location, FC values ranged from 5.97% (location 1) to the highest value of 9.47% (location 2). The values of FC in some feedstocks used in combustion range from 15% to 25% (Qian et al. 2020; Reza et al. 2019; Sher et al. 2020; Voca et al. 2019). Arar has similar values but still much lower than the reported ones in the literature. For example, the FC values obtained by Sher et al. (Sher et al. 2020) in different biomass samples ranged from 13.24% to 18.22%, while Reza et al. obtained FC values of 21.21% for the invasive species *Acacia holosericea* (Reza et al. 2019) and 16.81% for *Pennisetum purpureum* (Reza et al. 2020). In the study by Quian et al. (Qian et al. 2020), FC in the biochar samples ranged from the lowest value of 38.03% (*Ginkgo biloba*) to the highest value of 85.20% (*Pinus sylvestris*). Volatile matter, often referred to as volatiles (VC), is usually high in biomass, including light hydrocarbons, CO, CO_2, H_2, moisture, and tars (Voca et al. 2019). This property ensures that biomass ignites quickly, while the general rule is that as the VC decreases and the fuel ratio (fuel ratio = fixed carbon *·VM-1) increases. Accordingly, biochar/coal is more difficult to ignite and burns more slowly (Miller 2013). As Sadiku et al. (Sadiku, Oluyege, and Sadiku 2016) stated, the reason why the VC in fuel is higher is that a large amount of secondary air must then be supplied at high pressure at a strategic location for effective combustion. Incomplete combustion of VC results in thick smoke, heat loss, pollution hazard in the form of emissions, and incomplete combustion, which affects the operation of the boiler and leads to deposits on its surfaces. Due to their high oxygen content, the VC in biomass have a low calorific value. The amount of VC strongly depends on the pyrolysis material considered and parameters such as temperature or heating rate (Caillat and Vakkilainen 2013). Compared to the values of VC in raw biomass, it is obvious that biochar contains less VC than the starting biomass, but biochar is also much drier and therefore has a lower ignition temperature (Bach and Skreiberg 2016). Upon the comparisons, it can be stated that the values determined in this study for the VC are similar to those determined in the literature (Ahmed et al. 2020a, 2020b; Liu et al. 2017; Qian et al. 2020; Reza et al. 2019, 2020; Sher et al. 2020). From this point of view, since the arar samples contain on average 77.26% of VC, it can be said that arar could be a good raw material for energy production. The average values of proximate analysis of biochar from five different sites of arar biomass after the pyrolysis process showed AC, FC, and VM as 12.17%, 54.71%, and 26.66% (Table 1). In contrast, AC, FC, and VM for different types of biomass were reported as 5.80%, 48.80%, and 42.20%, respectively (Sher et al. 2020). Different types of biochar had values ranging from 1.49–35.88% for AC, 38.03–85.20% for FC, and 10.62%-30.28% for VM (Qian et al. 2020). Proximate analysis results for the samples from different sampling locations for arar biomass (AC, CK, FC, VM) and eventually biochar (MC, AC, CK, FC, VM) are subject to considerable variation.

The ultimate analysis (Table 2) showed carbon (C), hydrogen (H), sulfur (S), nitrogen (N), and oxygen (O) content in biomass as 50.14%, 6.57%, 0.31%, 0.84%, and 42.13%, respectively. The ultimate analysis of biochar showed 75.65% C, 3.8% H 0.17% S, 1.49% N and 18.9% O, respectively. Biomass with higher C content has a higher energy value. The average C content of the biomass samples is 50.14% and 75.65% for the bio-oil samples. Reza et al., found C values of 44.03% in *Acacia holosericea* samples (Reza et al. 2019) and 43.32% in *Pennisetum purpureum* samples (Reza et al. 2020). According to these species, arar has a higher C content than other similar materials and is therefore suitable for energy production. According to Qian et al. (Qian et al. 2020), the C content in the biochar samples of their study was lower than that in arar samples, with an average value of 69.50% for the biochar samples obtained under similar pyrolysis conditions. The higher C content of biochar (75.65%), especially compared to the C content of biomass, indicates a promising potential as a solid fuel, in addition to alternative value-added uses such as sorption processes, soil amendment, or other applications of phytonutrient additives (Ahmed et al. 2020a). Reza et al. reported H content of 5.67% in the samples of *Acacia holosericea* of (Reza et al. 2019) and 5.80% in the samples of *Pennisetum purpureum* (Reza et al. 2020), which was higher than the results obtained in this research. Quian et al. (Qian et al. 2020) reported that the H content in biochar averaged 2.72%, which was slightly lower than the average value of 3.08% in this study. Since both H and C contribute to the increase of fuel energy value, it can be confirmed that arar is a suitable feedstock for energy generation. The much better results of the biomass samples in terms of low N and S contents indicate that arar is a potential feedstock from ecological aspects compared to other literature data (Ahmed et al. 2020b; Qian et al. 2020). According to Liu et al. (Liu et al. 2017), understanding the distribution of N and S elements in the biomass pyrolysis process can help control their distribution in pyrolysis products and develop efficient techniques to limit gas pollutant emissions (NO_x, SO_x and their precursors). N and S are undesirable constituents in biomass and in bio-oil and gas products, but they are desirable elements in biochar. In biochar, they can help improve the efficiency of producing functional C compounds, and they make biochar an excellent source of nutrients for improving soil fertility. It is noticeable that ultimate analysis of N averaged about 0.84%, which is a good result compared to the literature, where most authors found N values in the biomass above 1% (Ahmed et al. 2020a, 2020b; Reza et al. 2019, 2020; Sher et al. 2020). The biochar samples contained about 1.49%, while most of the results of the different biochar samples in the literature (Qian et al. 2020) were below this value. S content was detected in most biomass samples with an average value of 0.31%. Biochar S values averaged 0.17%, while Quian et al. (Qian et al. 2020) found similar but even lower values of 0.11%. The compared values indicate that most (except S) of the ultimate analysis results for biomass and biochar samples from the literature, obtained under similar conditions, were not as good as those in this study. Compared to other literature data (Ahmed et al. 2020a, 2020b; Qian et al. 2020; Reza et al. 2019; Sher et al. 2020), there are few discrepancies between the data in either biomass or biochar analysis. However, as expected, huge differences were found between the values obtained in this study in the analysis of the biomass and biochar samples. Although it is not necessary to mention that some increase in the values (C, N) is expected, it is noticeable that the results of biochar values increase in comparison with the values for biomass samples. Aside from that, the ultimate analysis of samples of biomass and biochar did not find any statistically significant differences between the sites for the other results. The proximate (Table 1) and ultimate analyses (Table 2) results, as well as the calorific values and obtained shares of biochar and bio-oil (Table 3), were comparable to the values reported from other biomass feedstock samples (Ahmed et al. 2020a, 2020b; Liu et al. 2017; Qian et al. 2020; Reza et al. 2019; Sher et al. 2020).

Because of their propensity to spread aggressively and suppress other native species while producing large amounts of potentially useful biomass, invasive species could be an even better and cheaper source of feedstock for bioenergy production. Lignocellulosic biomass is one of the most significant naturally occurring renewable carbon reserves on the entire globe, at a very low cost (Kricka et al. 2017). It would be even lower if invasive species were counted in as feedstock. Regarding the structural composition of biomass, the most predominant component in ligno-cellulose biomass is cellulose. Hemicellulose accounts for 15% to 30% of the biomass weight, while lignin contains approximately 40% of the biomass energy potential thanks to the high share of C. Consistent with the three basic components mentioned above, biomass contains trace amounts of specialized metabolites (e.g., proteins, chlorophylls, and inorganic compounds) (Liu et al. 2017). The comparisons of structural analyses of biomass samples of arar from five different locations (Table 3) showed similar results. The highest percentage in the samples was lignin, at 38.99%, ahead of cellulose at 20.03% and hemicellulose at 13.65% .It is worth mentioning that the component with the highest share in this study is lignin, and that is a positive characteristic for arar biomass, so that could be an excellent feedstock for combustion. However, as stated by Cao et al. (Cao et al. 2019) the high content of lignin, may be the reason for the higher AC of the biomass samples.

The biofuels produced by pyrolysis are highly dependent on the temperature range, heating rate, vapor residence time, catalyst application, catalyst properties, feedstock type and its composition (Ahmed et al. 2020a; Fraczek, Mudryk, and Wrobel 2009). As for the yields after the pyrolysis process, authors (Ahmed et al. 2020b) reported elevated values of 38.73% for biochar from sawdust samples and slightly lower values of 35.44% for bio-oil. For samples of bark, twigs, pods, and branches of *Acacia cincinnata*, the average biochar yields were 45.36–58.35% at 400°C, 28.63–44.38% at 500°C and 22.68–29.42% at 600°C (Ahmed et al. 2020b), while those for bio-oil were slightly lower than in this study. In this study, the average value for biochar yield (Table 3) was 36.76% and for bio-oil yield of 44.61% (Table 3). Since the arar species, and its parts are often used for oil distillation and isolation of various compounds with another application (Ait-Ouazzou et al. 2012; Ennajar et al. 2009a, 2009b), increased quantities of bio-oil in the samples were expected. Considering the thermochemical conversion, the higher and lower calorific values are the most essential aspects of it, along with the proximate, ultimate, and structural analyses. The calorific values of biomass and biochar are shown in Table 4. The calorific value of any fuel is a general determinant to demonstrate its potential as a viable energy production option (Ahmed et al. 2020b). Biomass with higher calorific value and optimal energetic properties is more desirable for energy production. However, almost all lignocellulosic feedstocks are in the range of 15–19 MJ·kg^{-1} (Gami et al. 2011). The results of this study are comparable to other feedstocks that are considered valuable and of high quality. As for the results of the biochar produced, it was found that the average calorific value is even higher, with a value of 29.01 MJ·kg^{-1}. This is higher than obtained literature values for the *Acacia cincinnata* biomass, which ranged from 18.65 to 20.11 MJ·kg^{-1}, and for biochar from 20.71 to 27.04 MJ·kg^{-1} (Ahmed et al. 2020b) or for other investigated biomass samples of invasive species, which ranged from 18.37 to 34.47 MJ·kg-1 (Cao et al. 2019; Fraczek, Mudryk, and Wrobel 2009; Qian et al. 2020). The results of the higher calorific value of the arar biomass samples (Table 3) did not differ significantly between sites for most of the observed properties.

Conclusions

From the studied biomass and biochar of *Juniperus phoenicea* L (arar) it can be deduced that most of the studied traits were within the published values, with little variance within the observed parameters. The biomass samples had acceptable MC, an undesirably elevated AC (8.35%), high CK (16.28%), and VC (77.26%), but lower FC (7.93%) than previous studies. The high C (50.14%) and H (6.57%) content, the low N (0.84%) and S (0.31%) content of the biomass, and the elevated C (75.65%) and N (1.49%) concentration of the bio-oil samples make it ideal for future use from an ecological point of view. Structural analysis shows an elevated content of lignin (38.99%), which is also favorable for thermochemical conversion. Both the biomass and biochar samples had high HCV (20.45 $MJkg^{-1}$ biomass, and 29.01 $MJkg^{-1}$ biochar), while pyrolyzed biomass samples resulted in high yields of biochar (36.79%) and bio-oil (44.71%).

Given the predominantly positive results of studied samples, it is obvious that pyrolysis of this type of feedstock could be an appropriate solution for the management of arar biomass, but also that this type of biomass has potential for the production of electricity or heat. This study has focused on arar, and the authors would like to suggest that further and more detailed analyses should be done to confirm the results of the study. With good management and further detailed research into its biomass and energy conversion, this species could provide an energy source that can facilitate economic growth and development of local areas. It could also help to reduce the consequences of climate change and promote long-term ecosystem health.

Data availability

Raw data were generated at the University of Zagreb Faculty of Agriculture. Derived data supporting the findings of this study are available from the corresponding author [J. Š.; jsuric@agr.hr] on request.

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References

Ahmed, A., M. S. Abu Bakar, R. Hamdani, Y. K. Park, S. S. Lam, R. S. Sukri, M. Hussain, K. Majeed, N. Phusunti, F. Jamil, et al. 2020a. Valorization of underutilized waste biomass from invasive species to produce biochar for energy and other value-added applications. *Environmental Research* 186:109596. doi:10.1016/j.envres.2020.109596.

Ahmed, A., M. S. Abu Bakar, R. S. Sukri, M. Hussain, A. Farooq, S. Moogi, and Y. K. Park. 2020b. Sawdust pyrolysis from the furniture industry in an auger pyrolysis reactor system for biochar and bio-oil production. *Energy Conversion and Management* 226:113502. doi:10.1016/j.enconman.2020.113502.

Ait-Ouazzou, A., S. Lorán, A. Arakrak, A. Laglaoui, C. Rota, A. Herrera, R. Pagan, and P. Conchello. 2012. Evaluation of the chemical composition and antimicrobial activity of Mentha pulegium, Juniperus phoenicea, and Cyperus longus essential oils from Morocco. *Food Research International* 45:313–19. doi:10.1016/j.foodres.2011.09.004.

Alatzas, S., K. Moustakas, D. Malamis, and S. Vakalis. 2019. Biomass potential from agricultural waste for energetic utilization in Greece. *Energies* 12:1095. doi:10.3390/en12061095.

Bach, Q. V., and O. Skreiberg. 2016. Upgrading biomass fuels via wet torrefaction: A review and comparison with dry torrefaction. *Renewable and Sustainable Energy Reviews* 54:665–77. doi:10.1016/j.rser.2015.10.014.

Balat, M. 2008. Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects* 30:620–35. doi:10.1080/15567030600817258.

Boratyński, A., A. Lewandowski, K. Boratyńska, J. M. Montserrat, and A. Romo. 2009. High level of genetic differentiation of Juniperus phoenicea (Cupressaceae) in the Mediterranean region: Geographic implications. *Plant Systematics and Evolution* 277:163–72. doi:10.1007/s00606-008-0122-z.

Brown, R. C. 2011. Introduction to thermochemical processing of biomass into fuels, chemicals, and power. In *Thermochemical processing of biomass*, ed. C. Stevens, 1–12. Hoboken, New Jersey: John Wiley & Sons, Ltd. doi:10.1002/9781119990840.ch1.

Butula, S., G. Adlar, I. Hrdalo, J. Hudoklin, T. Kušan, V. Kušan, B. Marković, and V. Šteko. 2009. Inventarizacija, vrednovanje i planiranje obalnih krajobraza Dalmacije: Područje jugoistočnog dijela otoka Paga. Accessed:27 June 2022. *Project COAST*, United Nations Development Programme in Croatia. https://issuu.com/undphr/docs/krajobraz_pag

Caillat, S., and E. Vakkilainen. 2013. Large-scale biomass combustion plants: An overview. In *Biomass combustion science, technology and engineering*, ed. L. Rosendahl, 189–224. Sawston, Cambridge: Woodhead Publishing Limited. doi:10.1533/9780857097439.3.189.

Cao, W., J. Li, T. Martí-Rosselló, and X. Zhang. 2019. Experimental study on the ignition characteristics of cellulose, hemicellulose, lignin and their mixtures. *Journal of the Energy Institute* 92 (5):1303–12. doi:10.1016/j.joei.2018.10.004.

Croatian Parliament. 2018. Forest act. *Official Gazette* 68:1–56.

Ennajar, M., J. Bouajila, A. Lebrihi, F. Mathieu, M. Abderraba, A. Raies, and M. Romdhane. 2009a. Chemical composition and antimicrobial and antioxidant activities of essential oils and various extracts of *Juniperus phoenicea* L. (Cupressacees). *Journal of Food Science* 74 (7):M364–M371. doi:10.1111/j.1750-3841.2009.01277.x.

Ennajar, M., J. Bouajila, A. Lebrihi, F. Mathieu, A. Savagnac, M. Abderraba, A. Raies, and M. Romdhane. 2009b. The influence of organ, season and drying method on chemical composition and antioxidant and antimicrobial activities of *Juniperus phoenicea* L. essential oils. *Journal of the Science of Food and Agriculture* 90:462–70. doi:10.1002/jsfa.3840.

Fraczek, J., K. Mudryk, and M. Wrobel. 2009. Ash-leaved maple *Acer negundo* L. – The new potential energy species. *Acta Agrophysica* 14 (2):313–22.

Gami, B., R. Limbachiya, R. Parmar, H. Bhimani, and B. Patel. 2011. An evaluation of different non-woody and woody biomass of Gujarat, India for preparation of pellets - A solid biofuel. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects* 33 (22):2078–88. doi:10.1080/15567030903503183.

García, C., E. Guichoux, and A. Hampe. 2018. A comparative analysis between SNPs and SSRs to investigate genetic variation in a juniper species (Juniperus phoenicea ssp. turbinata). *Tree Genetics and Genomes* 14 (6). doi: 10.1007/s11295-018-1301-x.

Kenney, K. L., W. A. Smith, G. L. Gresham, and T. L. Westover. 2013. Understanding biomass feedstock variability. *Biofuels* 4 (1):111–27. doi:10.4155/bfs.12.83.

Kovacic, S., N. Jasprica, and M. Ruscic. 2001. Floristic characteristics of Phoenician juniper macchia (Ass. Pistacio lentisci - Juniperetum phoeniceae trinajstić 1987) in Central and Southern Dalmatia (Croatia). *Natura Croatica* 10 (2):73–81.

Kricka, T., A. Matin, N. Bilandzija, V. Jurisic, A. Antonovic, N. Voca, and M. Grubor. 2017. Biomass valorisation of Arundo donax L., Miscanthus × giganteus and Sida hermaphrodita for biofuel production. *International Agrophysics* 31 (4):575–81. doi:10.1515/intag-2016-0085.

Kumar, G., J. Dharmaraja, S. Arvindnarayan, S. Shoban, P. Bakonyi, G. D. Saratale, N. Nemestóthy, K. Bélafi-Bakó, J. J. Yoon, and S. H. Kim. 2019. A comprehensive review on thermochemical, biological, biochemical and hybrid conversion methods of bio-derived lignocellulosic molecules into renewable fuels. *Fuel* 251:352–67. doi:10.1016/j.fuel.2019.04.049.

Liu, W. J., W. W. Li, H. Jiang, and H. Q. Yu. 2017. Fates of chemical elements in biomass during its pyrolysis. *Chemical Reviews* 117 (9):6367–98. doi:10.1021/acs.chemrev.6b00647.

Miller, K. 2013. Coal analysis. In *The coal handbook: towards cleaner production*, ed. D. Osborne, 151–89. Sawston, Cambridge: Woodhead Publishing. doi:10.1533/9780857097309.1.151.

Nikolic, T. 2021. *Makija tršlje i somine. Flora Croatica database. On-line*. Zagreb, University of Zagreb, Faculty of Science, Department of Botany. Accessed 27 June 2022. http://hirc.botanic.hr/fcd/

Ong, H. C., W. H. Chen, Y. Singh, Y. Y. Gan, C. Y. Chen, and P. L. Show. 2020. A state-of-the-art review on thermochemical conversion of biomass for biofuel production: A TG-FTIR approach. *Energy Conversion and Management* 209:112634. doi:10.1016/j.enconman.2020.112634.

Qian, C., O. Lia, Z. Zhang, X. Wanga, J. Hu, and W. Cao. 2020. Prediction of higher heating values of biochar from proximate and ultimate analysis. *Fuel* 116925. doi:10.1016/j.fuel.2019.116925.

Reza, M. S., A. Ahmed, W. Caesarendra, M. S. Abu Bakar, S. Shams, R. Saidur, N. Aslfattahi, and A. K. Azad. 2019. Acacia holosericea: An invasive species for bio-char, bio-oil, and biogas production. *Bioeng* 6 (2). doi: 10.3390/bioengineering6020033.

Reza, M. S., S. N. Islam, S. Afroze, M. S. Abu Bakar, R. S. Sukri, S. Rahman, and A. K. Azad. 2020. Evaluation of the bioenergy potential of invasive Pennisetum purpureum through pyrolysis and thermogravimetric analysis. *Energy, Ecology and Environment* 5 (2):118–33. doi:10.1007/s40974-019-00139-0.

Sadiku, N. A., A. O. Oluyege, and I. B. Sadiku. 2016. Calorific and fuel value index of bamboo. *Lignocellul* 5:34–49.

Sannigrahi, P., A. J. Ragauskas, and G. A. Tuskan. 2010. Poplar as a feedstock for biofuels: A review of compositional characteristics. *Biofuels, Bioproducts and Biorefining* 4:209–26. doi:10.1002/bbb.206.

Sher, F., S. Z. Iqbal, H. Liu, M. Imran, and C. E. Snape. 2020. Thermal and kinetic analysis of diverse biomass fuels under different reaction environment: A way forward to renewable energy sources. *Energy Conversion and Management* 203:112266. doi:10.1016/j.enconman.2019.112266.

Solarte-Toro, J. C., J. A. González-Aguirre, J. A. Poveda Giraldo, and C. A. Cardona Alzate. 2021. Thermochemical processing of woody biomass: A review focused on energy-driven applications and catalytic upgrading. *Renewable and Sustainable Energy Reviews* 136:110376. doi:10.1016/j.rser.2020.110376.

Tolon, F. E., and F. Karaosmanoglu. 2021. Supply chain network carbon footprint of forest biomass to biorefinery. *Journal of Sustainable Metallurgy* 40 (2):124–41. doi:10.1080/10549811.2020.1746349.

Tripathi, M., J. N. Sahu, and P. Ganesan. 2016. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. *Renewable and Sustainable Energy Reviews* 55:467–81. doi:10.1016/j.rser.2015.10.122.

Vamvuka, D. 2011. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—An overview. *International Journal of Energy Research* 35 (10):835–62. doi:10.1002/er.1804.

Van Soest, P. V., J. B. Robertson, and B. A. Lewis. 1991. Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. *Journal of Dairy Science* 74 (10):3583–97. doi:10.3168/jds.S0022-0302(91)78551-2.

Vicevic, S. "Zelena pošast" prijeti janjetini: "Kuga je uništavala ljude, ovo će uništiti ovce." Accessed 27 June 2022. 2017. https://dnevnik.hr/vijesti/hrvatska/zelena-posast-prijeti-paskoj-janjetini-kuga-je-unistavala-ljude-ovo-ce-unistiti-ovce—467401.html

Voca, N., M. Grubor, A. Peter, and T. Kricka. 2019. Evaluation of Posidonia oceanica waste as a biomass source for energy generation. *Bioenergy Research* 12:1104–12. doi:10.1007/s12155-019-10032-7.

Vuleta, D. 2006. Sobina pojela polovicu pašnjaka s kaduljom. Accessed 27 June 2022. https://www.jutarnji.hr/arhiva/sobina-pojela-polovicu-pasnjaka-s-kaduljom/3390527/