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Evaluation of wood residues from Crete as alternative fuels

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Abstract
Olive and citrus prunings, the main agricultural residues of Crete, are considered to be of premium importance for local energy production, substituting a large part of conventional fuels. The thermal behaviour of these fuels during combustion was studied by thermogravimetry, at non-isothermal heating conditions. Fly ashes were collected from tests in a lab-scale fluidized bed facility. The effect of the inorganic constituents of the fuels on slagging/fouling and agglomeration propensities, as well as environmental pollution was examined. Kinetic models were developed and reaction rates were determined.
The agroresidues studied were characterized as good quality fuels, having high volatile and low ash and sulphur contents. Their ash was rich in Ca, Si, K and P minerals. However, fly ashes were poorer in alkali compounds, implying lower deposition and corrosion problems in boilers. The environmental impact of heavy metals is negligible. The thermochemical reactivity of the two fuels in air was very similar. A power low model fitted the experimental results accurately.

Keywords: Ash, Combustion, Biomass fuel, Citrus pruning, Olive pruning.

1. Introduction
As energy demands increase, new energy technologies, which can offer improved efficiency and minimum environmental impact, are needed. Biomass combustion has the potential to play an increasing role in meeting these demands. So far, the technological research and development has been focused on woody fuels from forestry residues and short rotation coppices, which are best options for Northern Europe and the USA. Significant progress has also been gained from the utilisation of agro industrial residues, with most typical fuel example being the olive oil industry residues [1], which is abundant in southern European regions.
In Greece, where the economics are largely based on agriculture and forestry, plant biomass presently available in the form of agricultural residues has been found to be equivalent to 40-50% of the gross energy consumption [2]. The island of Crete in the eastern Mediterranean, where energy generation is obtained by conventional energy sources (diesel, gasoline and liquid gas), produces a large amount of biomass in the form of agricultural residues, such as olive and citrus by-products. As the annual increase of the energy demand is very high (8.5%), creating big problems in the power supply, embodiment of biomass combustion technologies in the Cretan energy system will play an important role and will contribute to the local development.
The knowledge of the chemical composition, the reactivity and the thermal events occurring during solid fuels combustion is very important for the effective operation of conversion units. Thermal analysis

techniques have been widely used in recent years, because they provide a rapid quantitative method for the examination of combustion processes under non-isothermal conditions and enable the estimation of the effective kinetic parameters for the various decomposition reactions [3-5].

All power generating plants produce a number of residues (bottom ash, boiler ash, fly ash etc.), the relative amount of each one depending on the nature of the feed, the power plant configuration and the emission control devices. The successful operation of combustion units depends on the ability to control and mitigate ash-related problems, which can reduce the efficiency, capacity and availability of the facilities, thereby increasing the power cost. Such problems include fouling, slugging, corrosion of equipment and pollutant emissions [6-8]. Biomass fuels are known to have reactive ashes, due to their high content in alkali metals, which may be easily converted to new compounds during combustion. An important issue, which needs to be faced by industrial plants, is the environmental impact, resulting from the release of volatile heavy metals contained in solid wastes. Uncontrolled disposal of these wastes is relevant to the health of plants, animals and humans [9].

Fluidized bed combustion technology has been successfully demonstrated at a large scale and has been found to be the most suitable for producing electricity from agroresidues, due to its inherent advantages over conventional systems of simple design, fuel flexibility, high efficiency and low pollutant emissions. The relative low and uniform temperature and the good mixing of bed material prevent many of the ash related problems, which might occur in other units [10-12].

The aim of this work was firstly to investigate the thermal behaviour of olive prunings and citrus prunings, which are main agricultural residues of Crete, under non-isothermal thermogravimetric conditions and to develop kinetic models. Secondly, to determine the slagging/fouling and bed agglomeration tendency of these, at conditions relevant to bubbling fluidized bed combustion, as well as their environmental impact caused by the release of toxic trace elements. The obtained information should be useful for future applications of these biofuels for local energy production.

2. Experimental

2.1 Materials and characterization

Olive and citrus prunings (OP and CP), the most abundant agroresidues in the island of Crete, were the fuels selected in this work. After air-drying, homogenization and riffling, the samples were milled and sieved to –250μm. Each sample was characterized in terms of proximate analysis, according to the ASTM standards (E871, D1102-84) using programmable laboratory furnaces, ultimate analysis using Leco type analyzers CHN-600 and S532-500 (ASTM D3176-93, D3177-33) and calorific value using a Leco AC- 300 type calorimeter (ASTM D2015-95).

Samples used in fluidized bed were grinded to a particle size of –1180+850μm and pre-dried in the oven to a final moisture content of 1%. A Na-feldspar $NaAlSi_3O_8$ (SiO_2=67.7%, Al_2O_3=20.3%, Fe_2O_3=0.05%, CaO=0.5%, MgO=0.05%, TiO_2=0.05%, Na_2O=11.2%, K_2O=0.15%), with an average particle size of 714μm, was used as inert bed material.

2.2 Combustion tests

Char combustion tests were performed in a differential thermogravimetric analyzer TGA-6/DTG of Perkin Elmer (precision of temperature measurement ±2 ºC, microbalance sensitivity <5 μg), with which the sample weight loss and rate of weight loss as functions of time or temperature were recorded continuously, under dynamic conditions, in the range 25–850 ºC. The experiments were carried out at atmospheric pressure, under air atmosphere, with a flow rate of 60 ml/min, at a linear heating rate of 10 ºC/min. Preliminary tests with different sample masses and sizes and gas flow rates were carried out, in order to check the influence of heat and mass transfer. Small masses (20–25 mg) of each material, thinly distributed in the crucible and particle sizes of -250 μm were found proper to be used in the experiments, in order to eliminate the effects of eventual side reactions and mass and heat transfer limitations. The experiments were replicated at least twice to determine their reproducibility, which was found to be very good.

Combustion tests for production of fly ashes were carried out with an atmospheric lab-scale fluidized bed reactor. The combustor is described in a previous work [13]. For each experimental test, 0.5kg of Na-feldspar material was charged into the reactor and was preheated with air, introduced at the base of the reactor. The fluidising velocity was kept at a value two times the minimum fluidisation velocity (0.11m/s), which was determined from a Δp-versus-v_o diagram. Bed temperature was kept at 900°C. As soon as the temperature reached steady state, the pre-dried fuel was fed with an electrical vibrator to the bed, at a 2cm distance from the diffuser, from a sealed hopper, through an inclined feeding pipe, at a rate of 0.48kg/h. The product gas was discharged from the top of the reactor and before the exhaust it was transported through an insulated tube to a cyclone, to collect fly ash and elutriated particles. After 4hrs of operation at 900ºC, the reactor was allowed to cool under the flow of air. Fly ash collected in the cyclone was captured, weighed and analyzed by means of X-ray fluorescence spectrometry (XRF).

2.3 Ash analyses

Chemical analysis of major elements was conducted by using an X-ray fluorescence spectrometer (XRF) type SRS-303 of Siemens (ASTM D4326-94). Trace elements were determined by atomic absorption spectroscopy (AAS), using a Perkin Elmer, model Analyst-100, spectrometer with a graphite furnace assembly (model HGA 800) and a deuterium arc lamp background correction system. Prior to AAS analysis, all samples were dissolved by digestion with HCl, HF and HNO_3 acids in teflon beakers heated in water bath at 80ºC.

Ash behavior and deposition tendencies were predicted through the use of empirical indices for biomass type ashes. These indices, despite their shortcomings due to the complex conditions, which arise in boilers and their associated heat transfer equipment, are widely used and probably remain the most secure basis for decision making, if used in conjunction with pilot plant testing. One simple index, the alkali index, expresses the quantity of alkali oxides in the fuel per unit of fuel energy:

$$\mathrm{AI} = \frac{\mathrm{kg}\left(\mathrm{K_2O} + \mathrm{Na_2O}\right)}{\mathrm{GJ}} \tag{1}$$

When alkali index values are in the range 0.17-0.34kg/GJ fouling or slagging is probable, while when these values are greater than 0.34 fouling or slagging is virtually certain to occur [14].

Another index, the base-to-acid ratio, takes the form [6]:

$$\mathrm{R_{b/a}} = \frac{\%\left(\mathrm{Fe_2O_3} + \mathrm{CaO} + \mathrm{MgO} + \mathrm{K_2O} + \mathrm{Na_2O}\right)}{\%\left(\mathrm{SiO_2} + \mathrm{TiO_2} + \mathrm{Al_2O_3}\right)} \tag{2}$$

where the label for each compound makes reference to its weight concentration in the ash. As $R_{b/a}$ increases, the fouling tendency of a fuel ash increases.

A bed agglomeration index has been developed, relating ash composition to agglomerations in fluidized bed reactors [15]:

$$\mathrm{BAI} = \frac{\%\mathrm{Fe_2O_3}}{\%(\mathrm{K_2O} + \mathrm{Na_2O})} \tag{3}$$

Bed agglomeration occurs when BAI values become lower than 0.15.

3. Kinetic model

The combustion of the chars was described by a power law model. Chars may be composed of parts with different reactivities and the reactivity of a unit surface area may vary as the sample is burning out. To include the char heterogeneity into the model, it was assumed that a char sample could be a mixture of components with different reactivities:

$$\mathrm{m(t)} = \sum\nolimits_{\mathrm{j=1}}^{\mathrm{n}} \mathrm{c_j}[1 - \mathrm{a_j(t)}] + \mathrm{m_\infty} \qquad [\mathrm{m(0)=1}] \tag{4}$$

where m is the sample mass normalized by the initial sample mass, n is the number of components, c_j is the fraction of combustibles in component j, $E_j(t)$ is the reacted fraction of component j in time t and m_∞ is the normalized amount of the solid residues (minerals) at the end of the experiment.

A separate equation was used for each component to describe the dependence of the reaction rate on the temperature and fractional burn-off:

$$\frac{da_j}{dt} = A_j \exp(-E_j / RT) g(P_{O_2}) f(a_j) \tag{5}$$

where A_j is the pre-exponential factor of component j, E_j is the activation energy of component j, g expresses the effect of ambient gas composition and f describes the change of surface reactivity as a function of the fractional burn-off.

As the function $g(P_{O2})$ represented the partial pressure of oxygen in air, its value was included into the pre-exponential factor, while the $f(a_j)$ function was described by

$$f(a_j)=(1-a_j)^{n_j} \tag{6}$$

where n_j is the reaction order.

More details about the kinetic models can be found in a previous study [16].

The component behaviour of these chars was well reflected by the shape of their experimental -dm/dt functions.

4. Results and dscussion

4.1 Fuel analysis

The proximate and ultimate analysis and the calorific value of the agroresidues studied are included in Table 1. As it can be seen, these woody materials are characterized by a low ash content and a high combustibles content, indicating a good quality for these fuels. Also, sulfur content is very low, revealing that SO_x emissions during combustion are not of concern. The calorific value is considerably higher than that of most low rank coals.

Table 1. Proximate and ultimate analyses and calorific value of the fuels (% dry weight)

Sample	Volatile matter	Fixed carbon	Ash	C	H	N	O	S	GCV[a] (MJ/kg)	NCV[b] (MJ/kg)
OP	79.6	17.2	3.2	48.2	5.3	0.7	44.2	0.03	19.1	17.2
CP	76.1	18.0	5.9	46.0	5.9	1.0	41.2	0.03	18.5	16.5

[a] *Gross calorific value*
[b] *Net calorific value*

4.2 Combustion behaviour

The burning profile of the two biomass fuels is illustrated in Figure 1. The combustion rate of the fuels was similar and the bulk of the process occurred in the 330–480ºC region, for both. The samples showed one single peak in this temperature region, representing a homogeneous char structure. The reaction threshold occurred at 458ºC for olive prunings and at 435ºC for citrus prunings.

4.3 Kinetics

For the samples under study a single reaction model was proven to be successful. The agreement between model predictions and experimental measurement was good, with a deviation value 4% (Figure 2). The calculated kinetic parameters reported in Table 2 are in accordance with those given in the literature. Activation energy values, ranging from 153 to 157 kJ/mol, suggest that the combustion process was chemically controlled [17,18]. A comparison of reaction rates, inflection temperatures and kinetic data in Table 2 shows that the reactivities of the two fuels in air are very similar and this information is important, particularly for co-firing applications of these fuels.

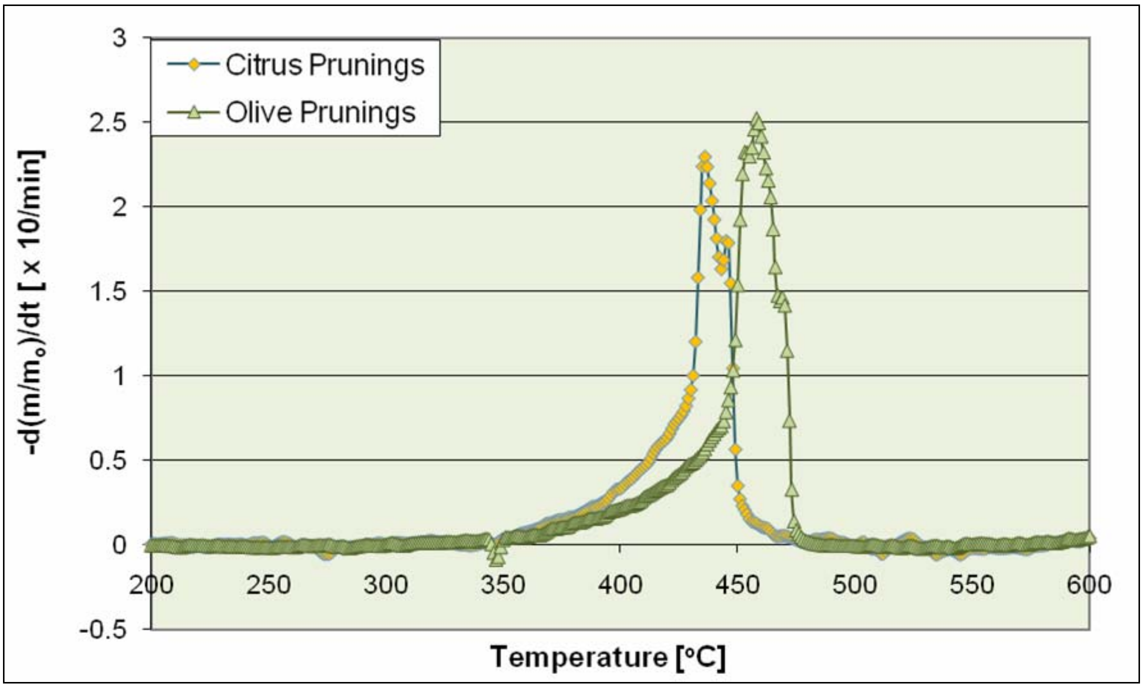

Figure 1. DTG burning profiles of biomass samples

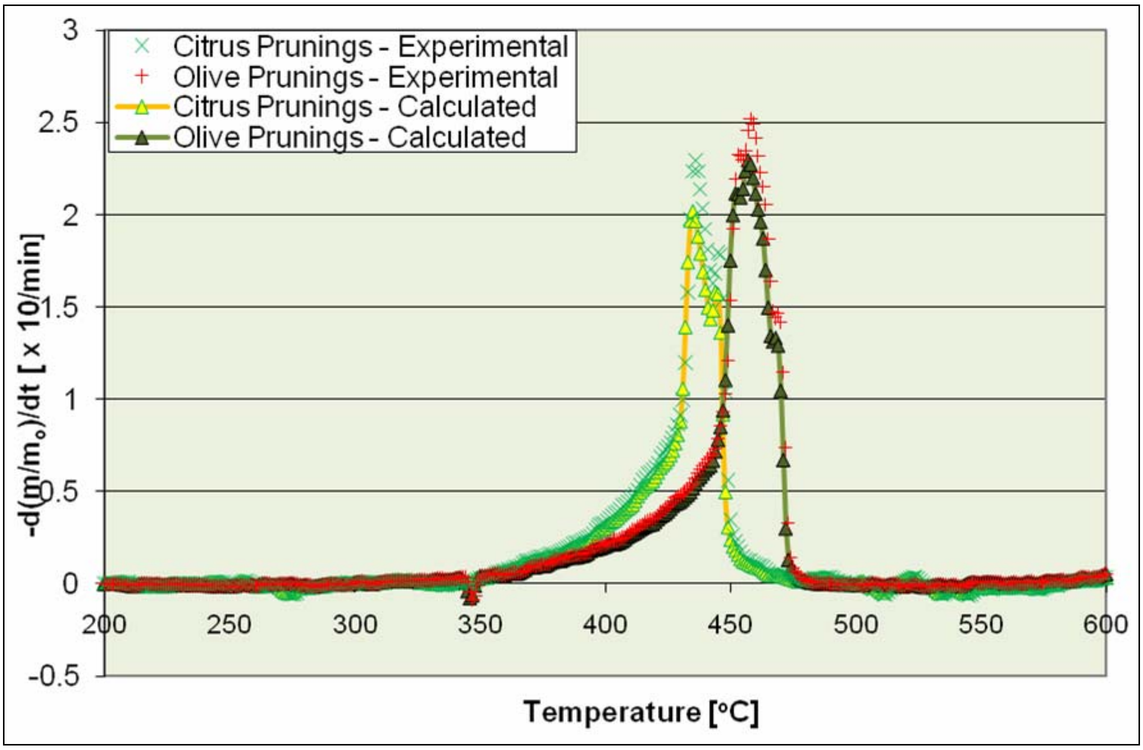

Figure 2. Experimental and calculated DTG burning profiles of biomass samples

Table 2. Kinetic parameters and characteristics of the combustion process

Sample	A (1/minMPa)	E (kJ/mol)	n	$R_{max}x10^1$ (min^{-1})	T_{max} (°C)
OP	9.5E+10	157.2	0.2	2.5	458
CP	9.5E+10	152.8	0.1	2.3	435

4.4 Ash properties

The contents of inorganic elements, expressed in the usual way for fuels as oxides, are presented in Table 3. As it can be seen, both ashes were rich in Ca, Si, K and P oxides and to a lesser extent in Mg, Na and S oxides. The ash of olive prunings showed considerably higher concentration of K_2O than the ash produced by the combustion of citrus prunings. It is noteworthy that the percentage of K oxide in the former was about 17%, while that of Ca oxide in the citrus prunings ash was 46%. In relation to these findings, the empirical slagging/fouling indices reveal that the fouling tendency of both fuels is "probable to certain", due to the high concentrations of alkali in the samples.

Table 3. Chemical analysis of ashes and slagging/fouling indices

Sample	Ash composition (%)											$R_{b/a}$	AI	BAI	Slagging/ fouling tendency
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	SO_3				
OP	8.1	1.6	0.7	2.4	32.8	2.9	16.9	-	8.5	0.1	2.1	6.1	0.3	0.04	Probable
CP	6.0	1.7	1.3	2.8	45.5	2.2	11.5	0.2	10.4	0.08	2.4	8.0	0.4	0.1	Probable-to-certain

The results of the chemical analyses of the fly ashes are illustrated in Figure 3. Ash levels were high in calcium, silicon, aluminium and iron oxides. It can be observed that the concentrations of Ca, K and P oxides were significantly reduced, as compared to the original fuels ash, while those of Al, Si and Fe oxides increased (Table 3). The lower concentration of Ca was attributed to some accumulation of calcium compounds in the bottom ash of the fluidized bed reactor, as shown in a previous work by the author [19]. On the other hand, a large portion of K minerals was either retained in the bed particles, or leaved the reactor in the vapour phase not collected by the cyclone. The enrichment of Al and Si oxides in the fly ashes was partly assigned to elutriated bed media in the cyclone. Therefore, a less alkaline ash, richer in Al phases and poorer in Ca phases, is expected to diminish deposition and corrosion problems in furnaces burning these woody residues.

The determination of trace elements of ashes by AAS is presented in Figure 4. In both samples the elements Zn and Cu were enriched, while Se and Pb ranged from 5 to 15 and 17 to 19ppb only and were omitted from the graphs. Olive prunings ash was also much richer in Ni (484ppm) than citrus prunings ash (124ppm). These differences reflect local variations of the agricultural growing conditions between the two biomass plants. As the leachability of these heavy metals was found to be very low, in a previous investigation by the author [20], their environmental impact is anticipated to be negligible.

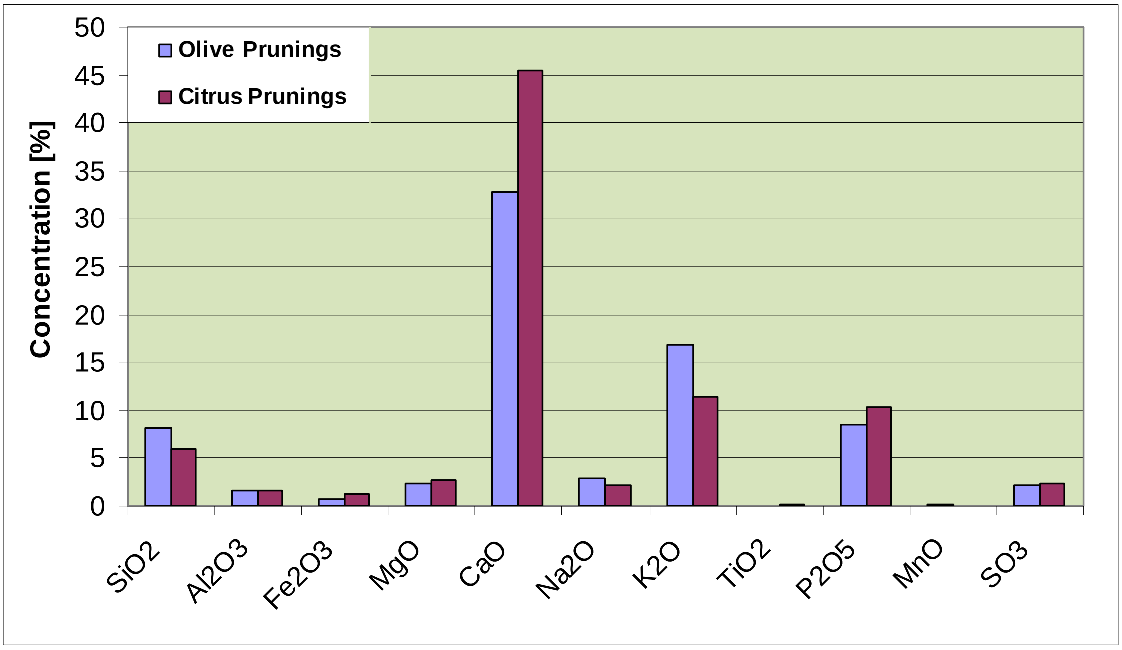

Figure 3. Main components (represented as oxides) of fly ashes of biomass samples

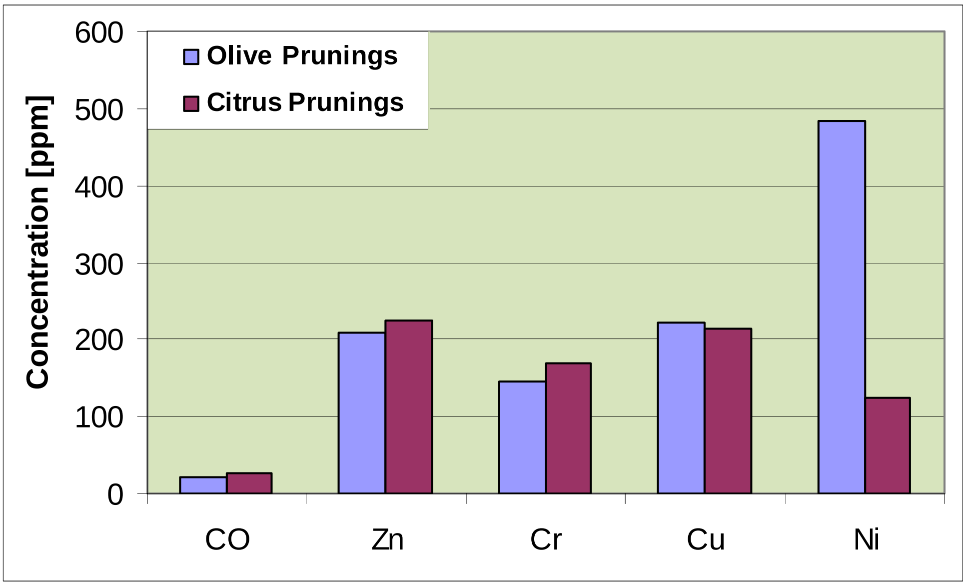

Figure 4. Trace element composition of biomass ashes

5. Conclusions

The agroresidues of this study were both characterized by high volatile and low ash and sulfur contents. Their ash was rich in Ca, Si, K and P minerals and was considered problematic concerning slagging/fouling tendency, due to the high amounts of alkali it contained. Fly ashes obtained from fluidized bed combustion of the fuels were enriched in Al and Si compounds, while they were poorer in Ca and K compounds, implying lower deposition and corrosion problems. The contents of toxic heavy metals were very low.

The thermochemical reactivity of the two fuels in air was very similar with a reaction threshold around 450°C. A power law model fitted the experimental results accurately.

The above findings are valuable for the future application of these fuels for energy production in the island of Crete, where the use of biomass-to-energy systems faces high challenges, due to the high energy demand, the environmental constraints and the large amount of agricultural residues produced. Overall, the results imply that if practical solutions, such as water leaching for ash-related problems are worked out, then these biomass fuels, or blends of them due to the same reactivity, may be suitable candidates for firing in utility boilers, contributing to the local development. They could also be used for co-firing applications in existing infrastructures for lignite, allowing for energy recovery, economic and environmental benefits.

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