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Thermal behaviour and kinetic study of the olive oil production chain residues and their mixtures during co-combustion

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HIGHLIGHTS

- Co-combustion behaviour of PR with 2PH and 3PH was studied.
- Effects of blending ratio and heating rate on the combustion process were analysed.
- A synergistic effect was observed in PR-2PH and PR-3PH blends.
- Reactivity of the blends increase with increasing PR.
- The minimum apparent activation energy was obtained for 25PR752PH mixture.

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ABSTRACT

The kinetic behaviour of olive tree pruning (PR), two- (2PH) and three-phase (3PH) olive pomace and their blends was investigated under combustion condition using thermogravimetric analysis. PR was blended with 2PH and 3PH at different ratios (25:75, 50:50 and 75:25) and tested in the temperature range from ambient to 1000 °C in order to evaluate the co-combustion behaviour. Results showed that the thermal degradation of all samples can be divided into three regions (drying, devolatilisation, char oxidation) with different combustion properties, depending on the percentage of PR. Significant interaction was detected between the fuels, and reactivity of 2PH and 3PH was improved upon blending with PR. The iso-conversional methods, Ozawa–Flynn–Wall and Vyazovkin, were employed for the kinetic analysis of the oxidation process. The results revealed that the activation energy of PR was higher than the one of 2PH and 3PH, and the minimum value was obtained for 25PR752PH sample.

1. Introduction

Agricultural and agro-industrial residues have several economic and environmental benefits when employed for energy production, such as reduction in the energy dependency on imported fossil fuels and reduction of waste disposal. However, their utilization as fuel is low as expected in those regions having large quantities of agricultural residues. In particular, in the Mediterranean areas, agricultural activities are very important, and great amounts of residues from the olive oil industry are produced, including olive pomace and olive tree pruning (Barbanera et al., 2016). One hectare of olive trees produces about 1.31 ton/ha per year of olive tree pruning (Negro et al., 2015), most of which are actually burnt or left on the ground (García-Maraver et al., 2014). Global annual production of olive pomace is estimated to about 400 million tons of dry matter (Barbanera et al., 2016). The characteristics of the produced olive pomace differ according to the technology applied for the extraction of olive oil. Actually two types of centrifugation processes are applied by the majority of olive mills: two- and three-phase. These production systems are similar in the steps involved; whereas three-phase system generates olive pomace (solid fraction) and olive mill wastewater (liquid fraction) separately, in the two-phase system a solid/liquid mixture residue is produced (Christoforou and Fokaides, 2016). One of the main factors which make the energy use of olive residues difficult is the local availability, since they are widespread over a relatively large area (Barbanera et al., 2016). Therefore, an interesting option could be to blend the residues reducing the costs associated to the treatments needed for their proper removal (Garcia-Maraver et al., 2015a).

Thermochemical conversion of biomass is considered as one of the most promising routes for biomass utilization. However, the utilization of biomass in combustion applications can have some

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limitations due to low thermal efficiency, instability of heat load and slagging (Fang et al., 2013). Knowledge of the thermal behaviour and the combustion kinetics of biomass is important for the effective design and operation of furnaces at industrial scale (Garcia-Maraver et al. (2015b)). This is the reason that led to carry out several experimental investigations based on thermogravimetric analysis (TGA) under oxidative atmosphere (Fang et al., 2013). TGA is one of the main techniques used for the study of thermal behaviour of fuels and kinetics of the thermal decomposition reactions. In particular, kinetic parameters, such as activation energy, frequency factor and reaction order (kinetic triplet), can be determined from the thermogravimetric (TG) and differential thermogravimetric (DTG) curves obtained from the TGA experiments. Non-isothermal TGA was chosen as analytical technique, due to its higher sensitivity to experimental noise when compared to isothermal methods (Gai et al., 2013). Also non-isothermal approach has further advantages related to fewer experimental data and the opportunity to determine the kinetics over the entire temperature range in a continuous way (Guida et al., 2016).

The majority of published papers evaluating the thermal degradation of solid wastes from olive oil industry has been focused on the investigation and understanding of the decomposition mechanisms and kinetics of the pyrolysis process (Blázquez et al., 2014; Özveren and Özdogan, 2013). In particular, only Garcia-Maraver et al. (2015b) conducted a kinetic study of three kind of residual biomass from olive trees (wood, leaves, and pruning) by model-based and model-free methods. Results showed that the activation energy was highly dependent on the mass conversion for all the samples and the most feasible reaction order was one.

Furthermore, the co-combustion behaviours and kinetics of olive pomace and olive tree pruning have not been reported before, especially concerning TGA. The present work is focused on co-combustion as a means to effectively dispose solid waste of olive oil industry, increasing the overall local availability. The combustion characteristics of two-phase olive pomace (2PH), three-phase olive pomace (3PH), olive tree pruning (PR) and their blends were studied by TGA at different heating rates. The interactions between 2PH/3PH and PR in the oxidative decomposition process were evaluated under different blending ratios. The kinetics parameters during the combustion process were calculated by employing the Ozawa–Flynn–Wall (OFW) and Vyazovkin methods.

2. Materials and methods

2.1. Materials and samples preparation

The samples of fresh olive pomace (2PH and 3PH) were supplied by local oil mills, while olive tree pruning was collected from an olive grove near Perugia, Italy. All the samples were submitted to several treatments before the combustion tests. Firstly, they were air-dried for 24 h and then oven-dried in a muffle furnace at 105 °C for 8 h. Finally, the samples were ground using an ultra-centrifugal mill (mod. ZM200, Retsch) and sieved in order to obtain a particle size lower than 500 μm, necessary to ensure the heat transfer rate within the kinetic regime of decomposition (Garcia-Maraver et al., 2015b).

The final samples were stored in desiccators. Blends were then prepared by physical mixing with different mass ratios of PR: 0%, 25%, 50%, 75%, and 100% (wt.%, dry basis). Each pure sample was subjected to proximate, ultimate, calorimetry, and biochemical analyses using the methods described by Buratti et al. (2015). The characterization of the olive oil production chain residues is shown in Table 1.

Table 1
Characteristics of the biomass samples.

Sample	100PR	1002PH	1003PH
Proximate analysis (wt% – dry basis)			
Ash	1.7	3.8	1.9
Volatile matter	79.9	77.6	78.0
Fixed carbon	18.4	18.6	20.1
Ultimate analysis (wt% – dry basis)			
C	46.9	53.5	53.2
H	8.3	9.2	8.9
N	0.4	1.0	0.6
O by difference	44.4	36.3	37.3
Calorific value (MJ/kg – dry basis)			
HHV	19.2	22.3	21.7
Chemical composition (wt% – dry basis)			
Cellulose	36.6	23.7	24.1
Hemicellulose	18.8	18.0	21.3
Lignin	20.3	38.0	33.4
Oil	–	10.3	4.4

2.2. TGA experiments and measurement of combustion parameters

Thermogravimetric analysis was performed with a Leco TGA 701 thermal analysis system. It is known that under certain conditions (gas flow rate, initial sample mass, type of crucible) the combustion kinetics in a TGA furnace could be a partially diffusion-controlled reaction (Jaramillo et al., 2015). Therefore in order to verify that the results were not affected by diffusion limitations, preliminary tests were carried out with different sample mass and gas flow rates. The initial sample mass of 0.2 g and an air flow rate of 3.5 L/min were found proper to avoid heat and mass transfer limitations. Each sample, placed in ceramic crucibles, was tested at four heating rates (10, 15, 20 and 25 °C/min) in the temperature range from 30 °C to 1000 °C. During each test, a blank run was carried out in order to correct for the effects of buoyancy, using an empty pan. At these conditions the residues left in the crucible after combustion are formed by loose particles, showing no sign of melting behaviour, caused by mass and heat transfer limitations (Zhang et al., 2013). TG and DTG curves were recorded continuously, as a function of time and temperature. Duplicate experiments for each run were performed in order to test the reproducibility of the results. The reported values correspond to the average values (standard deviations lower than 2%).

To further evaluate the burning properties of the fuels, the ignition temperature (T_i), the burnout temperature (T_b), the peak temperature (T_p), and the combustion index (S) were determined. The ignition temperature is defined as the temperature at which sudden increase in weight loss on the DTG curve (Idris et al., 2012). Burnout temperature is defined as the temperature where DTG curve reaches a 1% per minute combustion rate (Buratti et al., 2015). Peak temperature refers to the temperature where maximum combustion rate ($\mathrm{DTG_{max}}$) is reached. This parameter is important because its value and the corresponding rate give a measure of the fuel reactivity. The ignition of a material is promoted by lower values of T_p.

To comprehensively evaluate the combustion behaviour of each sample used in this study, the combustion index (S) was calculated, according to the following equation (Vamvuka and Sfakiotakis, 2011):

$$S = \frac{\mathrm{DTG_{max}}\mathrm{DTG_{mean}}}{T_i^2 T_b} \tag{1}$$

where $\mathrm{DTG_{mean}}$ is the average conversion rate between ignition and burnout temperatures. S is a parameter that integrates the ignition and burnout characteristics of the fuel for combustion, and a higher value represents better combustion performance.