



Isoconversional kinetic analysis of olive pomace decomposition under torrefaction operating conditions



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ABSTRACT

Kinetic analysis of the olive pomace thermal degradation in the temperature range of interest for torrefaction was performed by using non-isothermal thermogravimetric measurements at different heating rates, ranging from 2 to 40 °C/min. A comparison is presented between two selected integral isoconversional methods, i.e., the nonlinear Vyazovkin incremental approach, which is more accurate but time-consuming, and the linear Ozawa–Flynn–Wall (OFW) method, which is less accurate but computationally simpler. Results show that the values of the activation energy by the OFW method are consistent with the ones provided by the Vyazovkin approach. This implies that the OFW method, more user-friendly compared to the Vyazovkin procedure, is suitable for studying the torrefaction kinetics of residual biomass, such as olive pomace. The reliability of the OFW method was further confirmed by the successful application of the derived kinetic data to reproduce (i.e., predict) experimental TG curves not included in the kinetic computations.

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1. Introduction

In the view of shortage of fossil fuels and with the increasing concerns regarding human impacts on the environmental, renewable energy sources and waste materials play an important role as a viable alternative to fossil fuels for both energy generation and production of chemicals [1]. Now on the brink of commercialization, torrefaction – a relatively new thermochemical treatment of biomass carried out at quite low temperatures (200–300 °C), atmospheric pressure and in an inert environment – is currently considered as a key process in facilitating raw biomass (i.e., grass, woody, crop or processing industry residues) market growing for energy applications, due to its potential to convert any organic material into a high-energy-density solid fuel with superior properties in view of transport, handling, storage and in many major thermochemical end-use applications (e.g., co-firing in coal-fired power stations and gasification-based production of gaseous biofuels or bio-chemicals) [2].

Olive pomace is the solid and wet by-product generated by olive-oil extraction industries. Among other possibilities of utilization (e.g. animal feed, production of fertilizer, composting, etc.), the thermal treatment is appealing because it is an intensive and effective method for converting the olive pomace into energy [3], avoiding release of pollutants and odors as well as uncontrolled fermentation [4]. Several studies [3,4] have been conducted on energy generation from the olive pomace;

however, no one includes torrefaction as pretreatment, which is able to produce an intermediate and stable material and does not suffer high moisture content, low energy density, hygroscopic behavior and limited storage life.

With this background, the primary aim of the present study was to propose a set of kinetic parameters to be used as an input to future computer-based simulations of the olive pomace torrefaction, which can be used to guide laboratory experiments as well as to generate and evaluate alternative designs [5–7] for renewable energy projects.

Non-isothermal thermogravimetric analysis (TGA) was selected as the experimental technique to obtain kinetic data due to its ability to overcome one of the major problems associated with standard isothermal experiments, i.e. the warm-up time. Actually, during the initial non-isothermal time of an isothermal TGA test the sample typically undergoes some transformations that are likely to affect the results of the subsequent kinetic analysis [8]. In addition, when a too slow heating rate is applied, the weight loss taking places during the warm-up phase is not negligible, which complicates the interpretation and deduction of kinetic data [9].

Even though traditional model fitting approaches, including single or multi-step reaction mechanisms and/or single or multiple pseudo-component models [9–13], have found to date the almost exclusive application in biomass thermochemical conversion kinetic analysis [14], a “model-free” approach based on integral isoconversional methods was adopted in this paper. This choice was motivated by the fact that the model fitting procedures, when applied to non-isothermal data, produce Arrhenius parameters strongly depending on the adopted reaction

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model. As a consequence, they are so uncertain and variable that they cannot be meaningfully used for predicting the behavior of a substance over the range of experimental temperatures [8]. Conversely, model-free techniques do not require any assumption of reaction models, thus avoiding possible errors associated with such a choice. In addition, yielding kinetic parameters as a function of either conversion (isoconversional analysis) or temperature (non-parametric kinetics) [15], these methods make it possible to study the overall kinetics throughout the whole range of experimental conversions and temperatures also for complex solid state processes, like biomass thermal decomposition, which usually involve several steps with different activation energies.

Among the large number of differential and integral isoconversional methods to date developed, two integral multiple temperature-programmed methods, i.e., the linear Ozawa–Flynn–Wall (OFW) and the nonlinear Vyazovkin incremental methods, were selected to be comparatively applied in this work for the kinetic analysis of olive pomace torrefaction from non-isothermal TGA data. It is well-known [8, 16–18] that, in a comparison between the two methods, the OFW procedure is computationally simpler, but less accurate.

In addition to proposing a set of kinetic parameters for a future conceptual process design of olive pomace torrefaction, this work aims to provide a further insight into the application of the model-free isoconversional methods, most commonly used for the kinetic analysis of thermally simulated process involving polymers [19] or other complex organic compounds [20], also in the field of biomass thermochemical conversion processes.

2. Materials and methods

2.1. Feedstock sampling and characterization

The olive pomace used in this research work was suitably sampled from the accumulated residues of a three-phase olive mill located in Frasso Telesino (41° 9' 22" N, 14° 31' 48" E) in Campania region, in November 2013. In order to preserve their original qualities and to prevent the microbial degradation before further analyses, all samples, just collected, were sealed in a plastic bag and stored at –20 °C. Prior to use, representative fractions of this agro-industrial waste were milled using a knife mill to a particle size lower than 1 mm, afterwards, if required, oven-dried at 105 °C for about 12 h and then stored in a desiccator.

Proximate (TG 701 LECO Thermogravimetric analyzer), ultimate (CHN 2000 and SC 144 DR LECO analyzer) and calorific (Parr 6200 Calorimeter) analyses were performed in order to obtain the basic properties as a fuel of this agro-industrial residue. The results are presented in Table 1.

The indicative chemical composition of the olive pomace from a three-phase centrifugation process is also shown in Table 1, based on data reported in the literature [21].

2.2. Experimental methods

Thermogravimetric analyses were carried out in a TA Instruments analyzer Q600 SDT. Nitrogen was used as the purge gas at a flow rate of 100 ml/min to ensure an inert atmosphere and to prevent secondary reactions by volatiles produced during the solid thermal decomposition. During each run, approximately 10–15 mg of oven-dried samples, with a size of 0.5–1 mm, were placed in an aluminum oxide crucible inside the furnace chamber of the microbalance. Dynamic runs at five different heating rate programs, i.e., 2, 5, 10, 20, 40 °C/min, were carried out over the temperature range from room temperature to about 1000 °C to be used for the kinetic computations.

In addition to this series of constant heating rate runs, two isothermal experiments at 250 °C and 300 °C were also performed to check the reliability of the employed kinetic approach. During the isothermal run, the dried sample was first heated up to a temperature of 105 °C,

Table 1

Proximate, ultimate, calorific and chemical analyses of olive pomace.

	Olive pomace
Moisture (wt.%, as received)	62.71
<i>Proximate analysis (wt.%, dry basis)</i>	
Volatile matter	82.06
Fixed carbon	15.76
Ash	2.18
<i>Ultimate analysis (wt.%, dry basis)</i>	
C	52.58
N	0.78
H	7.23
S	<0.01
Ash	2.18
O (by diff.)	37.23
HHV (MJ/kg, dry basis)	21.88
LHV (MJ/kg, dry basis)	20.49
<i>Chemical composition (wt.% dry basis) [21]</i>	
Hemicelluloses	15.91
Celluloses	34.90
Lignin	20.51
Fats and oils	7.82
Proteins	6.89

which was held for 10 min. Then the temperature was increased to the desired test value at a heating rate of 5 °C/min and kept constant for 7 h. Note that the aforesaid isothermal time excludes the warm-up phase, which globally lasted for about 1 h. Both thermogravimetric and differential temperature measurements were recorded simultaneously during each test.

2.3. Non-isothermal kinetic analysis

All the integral curves derived from dynamic heating rate experiments (TGA) were used in the kinetic analysis, after being converted to the plot of conversion (α) versus temperatures by Eq. (1)

$$\alpha = \frac{m(T_i) - m(T)}{m(T_i) - m(T_f)} \quad (1)$$

where $m(T)$, $m(T_i)$ and $m(T_f)$ designate the instantaneous sample weight, the initial sample weight and the final sample weight, respectively. To provide the kinetic analysis with a standard reference, the initial and the final sample weights were identified, for each run, at 150 °C and 450 °C, which correspond to the temperature range where olive pomace decomposition mainly occurs (see detailed discussion in Section 3.1). The motivation for this choice lies in the fact that, although the major objective of torrefaction is substantially the complete degradation of its hemicellulose content, it is unavoidable that such decomposition takes place without a simultaneous and partial degradation of the other biomass components, in particular the cellulose fraction [22].

As mentioned in Introduction, the model-free kinetic approach based on two integral isoconversional methods, i.e., the Ozawa–Flynn–Wall (OFW) and the Vyazovkin ones, was employed in this study in order to evaluate the effective activation energy (E_α) as a function of the conversion degree (α).

Although it is traditionally expected that a kinetic analysis produces a description of a process in terms of the so-called kinetic triplet [8], i.e., the reaction model and Arrhenius parameters ($f(\alpha)$, E and A), no further computations aimed at evaluating the pre-exponential factor and the reaction model were performed in this study. The reason is that the sole goal of the kinetic analysis carried out in this study was to predict the characteristic time needed to achieve a prefixed conversion degree under conditions typical of torrefaction that could be a valuable result for designing a torrefaction reactor. As shown by

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