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Pseudo-component thermal decomposition kinetics of tomato peels via isoconversional methods

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ABSTRACT

The kinetics of the thermal decomposition of tomato peel residues under nitrogen atmosphere was studied by non-isothermal thermogravimetric analysis in the heating rate range 2–40 °C/min. Due to the complexity of the kinetic mechanism, which implies simultaneous multi-component decomposition reactions, an analytical approach involving the deconvolution of the overlapping decomposition steps from the overall differential thermogravimetric curves (DTG) and the subsequent application of model-free kinetic methods to the separated peaks was employed. Two freely available Matlab functions, which adopt a non-linear optimization algorithm to decompose a complex overlapping-peak signal into its component parts, were used. Different statistical functions (i.e., Gaussian, Voigt, Pearson, Lorentzian, equal-width Gaussian and equal-width Lorentzian) were tested for deconvolution and the best fits were obtained by using suitable combinations of Gaussian and Lorentzian functions. For the kinetic analysis of the deconvoluted DTG peaks, the Friedman's isoconversional method was adopted, which does not involve any mathematical approximation. The reliability of the derived kinetic parameters was proved by successfully reproducing two non-isothermal conversion curves, which were recorded at a heating rate of 60 °C/min and 80 °C/min and not included in data set used for the kinetic analysis. Seven pseudo-components were identified as a result of the deconvolution procedure and satisfactorily associated with the main constituents of the investigated tomato peels.

1. Introduction

Tomato (*Lycopersicon esculentum*) is the second most important vegetable crop next to potato. Nowadays, about 150 million tons are produced and consumed each year all over the world, of which 40 million as processed products (i.e., tomato paste, peeled or unpeeled, whole or unwhole tomatoes) [1]. During tomato processing, two residual fractions, which represent 3% to 5% by weight of the whole tomato, are typically generated: i. tomato peels, which are the by-product of the peeling of tomatoes used for canning and ii. tomato pomace, which is a mixture of the tomato peels, crushed seeds and small amounts of pulp that remain after the processing for juice, soup, or ketchup [2].

In keeping with the internationally agreed waste management strategies (DIRECTIVE 2008/98/EC), research interest in the conversion of tomato processing residues into useful form of bioenergy and/or biofuels through different thermal conversion processes (i.e., torrefaction [3,4], pyrolysis [5] and hydrothermal carbonization [6]) has increased significantly in the last years.

The thermal decomposition (e.g., pyrolysis) plays a crucial role in all of the thermochemical conversion processes and mastering qualitative characteristics and quantitative kinetics of this step is essential to design and control a thermal conversion unit. However, to the best of our knowledge, there is only one work by Mangut et al. [5] in the literature addressing the kinetic analysis of the complex thermal decomposition of tomato residues (i.e., tomato seeds and/or tomato peels), which involves several and also simultaneous steps. Specifically, a multi-component model-fitting approach was employed in the above investigation to estimate kinetic parameters (i.e., activation energy, pre-exponential factor and reaction order) from non-isothermal TGA data. However, no attempts were made by the cited authors [5] to validate the computed kinetic parameters, despite the fact that it is widely recognized that model-fitting methods produce highly uncertain kinetic parameters, especially from dynamic thermogravimetric data [7,8]. In other words, non-unique solutions are usually found as a result of the fitting procedure in dynamic conditions, which is due to the so-called compensation effect [7]. As a consequence, the derived kinetic

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parameters may have no practical value in predicting the behavior of such a feedstock in order to design and control a dedicated thermal conversion plant.

With this background, the primary aim of the present investigation was to provide new insights into the thermal decomposition kinetics of tomato peels under non-isothermal conditions and to propose a set of reliable kinetic parameters for future design and optimization of thermochemical processes involving tomato peels as a feedstock. In order to overcome the aforementioned problems associated with model-fitting methods [7,9], a model-free kinetic approach based on the isoconversional method of Friedman [10] was selected to analyze data from non-isothermal thermogravimetric measurements. As the name implies, model-free techniques do not require any previous knowledge or assumption of the kinetic model and yield kinetic parameters as a function of either temperature (non-parametric kinetics) or conversion (isoconversional analysis) [11]. However, since it has been proved that model-free methods do provide incorrect kinetic results for datasets containing overlapping peaks [12], i.e., data from processes involving independent and simultaneous multiple-component reactions (as it is the case for the thermal decomposition of tomato peels), an analytical approach implying the separation of the overlapping peaks from the overall differential thermogravimetric curves (DTG curve) and the subsequent kinetic analysis of the separated decomposition steps was adopted.

This paper represents the first successful application of a model free kinetic approach to the thermal decomposition of tomato peels. Therefore, it demonstrates novelty in extending the application of model-free isoconversional methods, most commonly used for the kinetic analysis of thermally simulated process involving polymers [13] or other complex organic compounds [14], also in the field of biomass thermochemical conversion processes, with particular reference to a scarcely investigated agro-industrial residual biomass (i.e., tomato peels).

2. Materials and methods

2.1. Feedstock sampling and characterization

Tomato peels (TPs) used in this work were collected from a tomato processing industry located in Salerno (40°47′24.5″N, 14°46′15.8″ E), Campania region (ITA), in September 2014. In order to preserve their original state and prevent microbial degradation, all samples were stored in an air-tightened plastic bag at −20 °C. Prior to use, the raw material was first conditioned to 6 wt.% moisture content by leaving it at ambient temperature for 48 h in a laboratory fume hood and then ground in a batch knife mill (Grindomix GM 300 by Retsch) for 3 min at a speed as high as 3200 rpm. The milled TPs were then sieved and the 0–400 μm size fraction was selected for the subsequent analysis.

Proximate (TGA 701 LECO thermogravimetric analyzer), ultimate (CHN 2000 LECO and SC 144 DR LECO analyzer) and calorific (Parr 6200 Calorimeter) analyses were performed in order to obtain the basic properties of tomato peels as a fuel. All these analyses were performed in duplicate at least. The average values and the related standard deviations are reported in Table 1.

The main polymeric components (i.e., hemicellulose, cellulose and lignin) of raw TPs were determined according to the procedure by Rowell et al. [15]. In accordance with Laboratory Analytical Procedures (LAP) established by National Renewable Energy Laboratory (NREL) [16], samples of air-dried TPs passing a 40 mesh screen were first submitted to Soxhlet extraction with an ethanol/toluene (1:2, v:v) solution in order to remove the extractives (i.e., fats, resin, wax, phenol, pigments, oils and other organic compounds), which could affect the subsequent analysis of polymer composition. The extraction was conducted for 24 h at the rate of about 8 siphon cycles per hour. The resulting oven-dried extractive-free sample was then submitted to a delignification process by treating it with sodium chlorite ($NaClO_2$, technical grade, 80%) and acetic acid (reagent grade) for 6 h in a water bath at 70 °C. The extractive- and lignin-free white holocellulose sample was subsequently treated with sodium hydroxide (17.5% and 8.3 wt.%) and acetic acid (10 wt.%) solutions in order to isolate the α-cellulose fraction. The soluble fraction remaining after this treatment represented hemicelluloses. The lignin content was calculated by difference. The polymeric composition, based on the above procedure, is also shown in Table 1.

Table 1
Raw tomato peel properties.

Moisture (wt.%, as received)	80.50 ± 0.01
Proximate analysis (wt.%, dry basis)	
Volatile Matter	84.34 ± 0.09
Fixed Carbon	13.40 ± 0.06
Ash	2.3 ± 0.1
Ultimate analysis (wt.%, dry basis)	
C	55.9 ± 0.5
H	8.2 ± 0.3
N	1.4 ± 0.1
S	0.05 ± 0.01
O (by diff.)	34.5 ± 0.6
Calorific value analysis (MJ/kg, dry basis)	
HHV	24.7 ± 0.6
LHV	23.8 ± 0.6
Polymeric composition (wt.%, dry basis)	
Extractive	5.2 ± 0.1
Hemicellulose	52.4 ± 0.1
A-cellulose	17.5 ± 0.1
Lignin (by difference)	24.9 ± 0.2

2.2. Experimental techniques

Non-isothermal decomposition kinetics of tomato peels were studied by means of thermogravimetric technique (TGA/DTG). The experiments were carried out in a TA Instruments analyzer Q600 SDT under linear heating conditions. The sample holder was an open-type alumina pan. Low sample masses (~10 mg) and small particle sizes (<400 μm) were selected in order to reduce the effect of intra-particle mass and heat transport limitations and thus avoid problems of "thermal lag" between the sample and the controlling (external) thermocouple during the tests. Nitrogen was used as 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. The temperature was controlled from room temperature up to about 1000 °C at seven different heating rates (2, 5, 10, 20, 40, 60 and 80 °C/min). Variations of the sample residual mass with respect to time and temperature (TG data) and its time derivative (DTG data) were collected simultaneously during each test by using Q600 Software and then analyzed according to the method described in the next section.

2.3. Theoretical background

Isoconversional methods take their origin in the following single-step kinetic equation:

$$\frac{d\alpha}{dt} = A\,exp\left(-\frac{E}{RT}\right)\cdot f(\alpha) \qquad (1)$$

where A and E are kinetic parameters, namely the pre-exponential factor and the apparent activation energy, respectively, R is the gas constant, T the absolute temperature, f(α) the reaction model and α the