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Fluidized Bed Torrefaction of Agro-Industrial Residues: the Case Study of Residues from Campania Region, Italy

(Abstract)

Supervisor
Prof. Michele Miccio

Ph.D. Student
Paola Brachi

Scientific Referees
Ing. Giovanna Ruoppolo (IRC-CNR)
Dott.ssa. Letizia Magaldi (Magaldi Industrie S.r.l.)

Ph.D. Course Coordinator
Prof. Paolo Ciambelli

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The purpose of this Ph.D. project was to investigate the potential of the torrefaction treatment for upgrading low-value agro-industrial residues into useable solid fuels to be employed as high-quality energy carriers.

The first phase of the project involved a screening of the agro-industrial residues available in Campania region (Italy) with good potentiality for energy applications. As a result of this analysis, tomato processing residues and olive mill residues, which have stood out as those in need of a more sustainable and environmental friendly disposal solution, were at first selected as biomass feedstocks for this Ph.D. project. However, practical difficulties encountered in the pre-treatment of the virgin olive husk (i.e., specifically in reducing the size of olives stone fragments which compose olive mill residues together with the olive pulp) led afterwards to discard such residue as a potential feedstock for the subsequent lab-scale torrefaction tests

The main chemical and physical properties (i.e., moisture content, elemental composition, calorific value, ash content, etc.) of virgin olive husk (OH) and tomato peels (TPs) were analyzed in order to evaluate their potential for energy recovery. A special focus was also devoted to the study of the thermal behavior of both residues by means of thermogravimetric analysis (TGA) coupled with mass spectrometry (MS) with the aim of studying the weight loss kinetics during the torrefaction of both the virgin olive husk and tomato peels as well as obtaining useful information about the qualitative composition of the evolved torgas.

Specifically, the kinetic analysis of thermal degradation of virgin olive husk, 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. Modeling analysis of TGA data was performed by means of two selected integral isoconversional methods, i.e., the nonlinear Vyazovkin incremental approach, which is more rigorous but time-consuming, and the linear Ozawa–Flynn–Wall (OFW) method, which is computationally simpler but based on mathematical approximations. Results showed that the values of the activation energy of the thermal decomposition reaction derived from both models were very similar. This suggests that the OFW method, which is more user-friendly than the Vyazovkin procedure, is suitable for studying the weight loss kinetics upon the torrefaction of virgin olive husk. The reliability of the OFW method was further confirmed by the successful application of the derived kinetic parameters to reproduce two experimental TGA curves not included in the kinetic computations.

The kinetics of the thermal decomposition of tomato peels (TPs) under nitrogen atmosphere was studied by non-isothermal thermogravimetric measurements in the heating rate range 2-40 °C/min. Due to the complexity of the thermal decomposition mechanism of TPs, which implies simultaneous multi-component degradation reactions, an analytical approach involving the deconvolution of the overlapping degradation steps from the overall differential thermogravimetric curves (DTG) and the subsequent application of model-free kinetic methods to the separated peaks was adopted. To this end, two different open-source Matlab functions employing a non-linear optimization algorithm to decompose a complex pattern of overlapping peaks into its component parts, were used. Different conventional 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 a suitable combination of Gaussian and Lorentzian functions. The differential Friedman's isoconversional method was selected for the kinetic analysis of the deconvoluted DTG peaks. The reliability of the evaluated kinetic parameters was checked by reproducing a dynamic experimental curve recorded at a heating rate of 60 °C/min and not included in data used for kinetic computations. Theoretical and experimental data showed a good agreement in the conversion range 20-80%, suggesting that the computed kinetic parameters could be used for modeling torrefaction processes involving the investigated tomato processing residues.

An extensive experimental program was carried out in a new laboratory-scale batch experimental apparatus, which was purpose-designed and built for this Ph.D. project. The torrefaction section of the apparatus is represented by a batch fluidized bed reactor made up of a tubular glass column (inner diameter 100 mm, length 750 mm) surrounded by a glass jacket, which was kept under vacuum to ensure thermal insulation of the reactor while keeping the advantage of its transparency. This arrangement allowed visual monitoring of both the fluidization pattern and particles movement in the bed at any time and temperature tested for torrefaction.

An ancillary investigation on the cold fluidization and segregation behavior of two different sand and tomato peels binary mixture was preliminary carried out, by varying the biomass weight fraction in the range 2-9 %, in order to identify suitable operating conditions in terms of biomass particle size and maximum biomass batch loading (i.e., the mass fraction of biomass in the bed of sand beyond which the fluidization properties deteriorate) to be used during the fluidized torrefaction tests. Specifically, two different Geldart

group B silica sands, in the 100-400 µm size range (FSS, fine silica sand) and in the 100-700 µm size range (CSS, coarse silica sand), were tested in cold flow experiments and then discriminated for their use as inert bed material to assist the biomass fluidization and also to maintain the desired hydrodynamics of the fluidized bed when biomass particles experience different degrees of devolatilization. As the coarse silica sand proved to be poorer as fluidizing material compared to the fine sand, this latter was selected to be the inert bed component for fluidized bed torrefaction tests.

The effects of the main torrefaction process variables (i.e., temperature and reaction time) on both the key performance parameters (i.e., mass and energy yields) and the main properties of the solid product were investigated for tomato processing residues. Fluidized bed experimental runs were performed at 200, 240, and 285 °C and for holding times equal to 5, 15 and 30 min. Results showed that the thermochemical transformations that tomato peels underwent, as a results of the release of volatile matter arising from the thermal decomposition of its organic constituents, led to a significant improvement of their chemical and physical properties. In particular, it was observed that higher temperatures and longer holding times (with a more marked effect of the torrefaction temperature) determine an increasing in the calorific value (by a factor of 1.2 for the biomass torrefied at 285 °C and 30 min), a reduction of the O/C (up to approximately 40 % for the biomass torrefied at 285 °C and 30 min) and an improved hydrophobicity of the torrefied biomass with respect to the parent one, while maintaining the mass yield (approximately between 75 and 94 %, daf basis) and energy yield (approximately between 90 and 96 %, daf basis) at acceptable levels. These findings suggest tomato peels as a valuable and convenient candidate for the torrefaction treatment.

A limited set of torrefaction tests were also performed in a bench-scale fixed bed reactor which was purposely set-up in order to compare the performance of this configuration with respect to the fluidized bed one, under identical operating conditions. Results showed that at the laboratory-scale, where mass and heat transfer limitations are not negligible, the fluidized bed configuration is more suitable to obtain reliable and reproducible test results, good-quality of the torrefied solids and excellent process performance in terms of mass and energy yields.