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FINAL ACCEPTED MANUSCRIPT
Torrefaction of tomato industry residues

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G.Toscano [a], A.Pizzi [a], E. Foppa Pedretti [a], G. Rossini [a], G. Ciceri [b], G. Martignon [b], D. Duca [a]

[a] Dipartimento di Scienze Agrarie, Alimentari e Ambientali, Università Politecnica delle Marche.

Via Brecce Bianche, 60131 Ancona (AN), Italy

[b] Dipartimento Ambiente e Sviluppo Sostenibile di RSE S.p.A - Ricerca sul Sistema Energetico

Corresponding author: Daniele Duca, Dipartimento di Scienze Agrarie, Alimentari ed Ambientali,

Università Politecnica delle Marche. Via Brecce Bianche – 60131 Ancona (AN) – Italy.

e-mail: d.duca@univpm.it - tel. +39 071 2204297

Abstract

The standardization is an important aspect for fuel products. Some residual biomass are highly heterogeneous making their energy use rather difficult. Torrefaction can represent an interesting process to improve the standardisation and quality of the lignocellulosic biomass. In the present research torrefaction has been applied on tomato peels, an important Italian industry residue. Different residence times and torrefaction temperatures have been employed in a bench top torrefaction reactor. Proximate, ultimate, thermogravimetric and infrared analyses of raw and torrefied material have been performed to evaluate the influence of the process. From the mildest condition studied to the most severe one, mass yield, energy yield and energy densification vary in the ranges of 94.7-69.9 %, 98.0-86.0 % and 1.04-1.23 respectively. According to mass and energy yields, ultimate analysis and thermogravimetric profiles, temperature parameter results more significant than residence time. Torrefaction makes the material increasingly hydrophobic as torrefaction temperature increases. This results in a more biologically stable and standardised material suitable to be employed as fuel for energy application. The results of this paper provide useful indications and suggest a mild torrefaction.

Keywords: torrefaction, residues, biomass, bioenergy, thermochemical process.

Abbreviations

TG - thermogravimetric curve
DTG - first derivative thermogravimetric curve

CP - crude protein
EE - ether extract
NDF - nitrogen detergent fiber
ADF - acid detergent fiber
ADL - acid detergent lignin

Notations
Tt - torrefaction temperature, °C
Rt - residence time, min
M_Y - mass yield, %
E_Y - energy yield, %
I_{ed} - energy densification index
LHV - low heating value, kJ kg^{-1}
A - ash mass content, % d.b.

1 Introduction

Biomass is an important renewable energy source as a way to reduce net CO_2 emission contributing to climate change mitigation. The use of biomass wastes for energy purposes, in particular, is considered one of the most interesting solutions by policy makers and scientific community to achieve this goal. In this case, in fact, in addition to the CO_2 reduction, the waste becomes a raw material for other processes avoiding waste disposal problems. However, energy use of the biomass wastes is often difficult due to several drawbacks: heterogeneity of material; high moisture content; poor biological stability; low energy density. To overcome these issues a pre-treatment is necessary and currently there is a high interest in the torrefaction process.

Torrefaction, a mild pyrolysis, represents a thermochemical process that consists in treating biomass at relatively low temperature (200-300°C) under an inert atmosphere such as nitrogen. Heat provides the energy needed for breaking chemical bonds of the organic molecules, mainly cellulose, hemicellulose and lignin, leading to a change of the biomass structure with the production of volatile and liquid compounds (tar) together with the solid torrefied product. This process causes in the wood, and generally in ligno-cellulosic materials, very interesting changes for a biofuel production: the energy density increase, the strong hygroscopicity decrease [1] and the ease of grinding [2] are some of the most important aspects and an example of how the torrefied material approaches the behaviour of a traditional solid fossil fuel [3, 4]. The best properties of the torrefied material determine benefits in terms of energy densification, ease of grinding and biological stabilization, with cost reduction in specific production chain steps where costs are a function of the volumes involved like, for example, transport and storage. Another advantage is the possibility to mix the torrefied product with coal for the supply of power plants [5-7]. It was also noticed by different authors an energy advantage of performing torrefaction as pretreatment of biomass to be used in gasification [8-10].

Many authors have focused their attention to the torrefaction of woody biomass [1, 6, 11-13] but only few of them made researches on agricultural and food industry residues. Since these kind of materials are more heterogeneous than the woody ones and often not suitable for a direct energy

valorisation, then torrefaction process can be a useful solution to overcome this issue. Wang et al. focused their attention on the torrefaction of rice husks employing microwaves [14]. Uemura et al. [15] described the effect of torrefaction on the basic characteristics of agricultural biomass wastes in Malaysia, such as empty fruit bunches, mesocarp fiber and kernel shell as a potential source of solid fuel. Shang et al. conducted torrefaction studies on wheat straw at batch scale reactor [16]. Chen et al. [17] carried out an experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction such as coffee residue, sawdust and rice husk.

No specific studies have been carried out on tomato industry residues, a material quantitatively important at European level and in particular at Italian level.

Within the European agri-food sector, tomato paste manufacturing industry represents one of the main food industry [18]. Every year it generates a big amount of tomato residues, in many cases considered as wastes, responsible of disposal problems and environmental pollution. As reported by the authors in a previous paper [19], the World Processing Tomato Council (WPTC) argues that, between 2008 and 2010, Members in Mediterranean Region (AMITOM) have processed about 15.5 Tg of tomato, with Italy contributing for almost 5.0 Tg, corresponding to a potential of 1.2 Tg of residual material in Europe.

Currently, tomato processing residues, especially peels, do not generate so many benefits for industries, in particular for storage and preservation issues. In fact, the accumulation of these residues, predominantly in the warm periods, promotes uncontrolled anaerobic fermentations leading to environmental problems. To avoid added costs related to disposal process, tomato manufacturing companies often give their production residues for free to other companies that generally use them for feeding livestock [20, 21] or in agriculture as soil amendment [22]. However Rossini et al. highlight a good energy content of tomato peels that could make the energy valorisation interesting [19].

For this reason, the present work aimed at investigating the effects of the torrefaction treatment on physical-chemical properties of the tomato peels by means of a bench top reactor. The effects of torrefaction temperature and retention time on mass and energy yields were investigated. Moreover, a deep characterization of raw and torrefied materials has been carried out by proximate, ultimate, thermogravimetric and infrared analyses. Finally, the hydrophobic behaviour of treated and untreated materials was evaluated through moisture uptake tests.

2 MATERIALS AND METHODS

2.1 Introduction

The raw biomass, constituted by tomato peels, was obtained from an Italian tomato industry residue as described by the authors in a previous paper [19]. After separation and oven drying, peels were grinded in a cutting mill (mod. SM 2000, RETSCH) and the particles size between 0.25 and 1.00 mm was selected. The experimental work was then performed through the following steps:

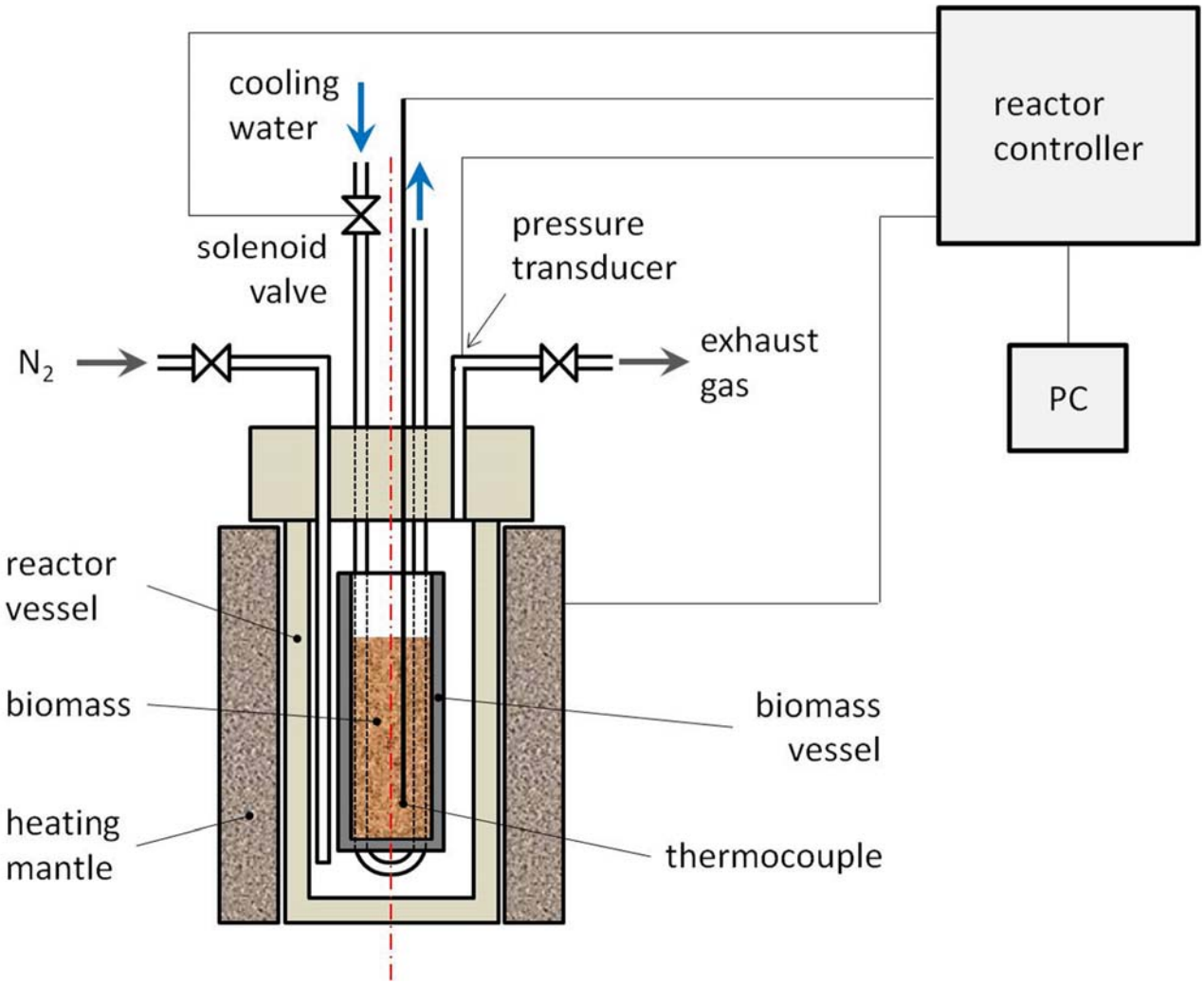
- thermogravimetric analysis of tomato peels to define torrefaction temperatures (Tt).
- torrefaction tests in a bench top reactor (Figure 1).

- physicochemical characterization of raw and torrefied materials (proximate, ultimate, thermogravimetric and infrared analyses). A single analysis of crude protein (CP), ether extract (EE), neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) has been carried out to better understand the typology of raw material studied in the paper.

- moisture uptake tests to compare hydrophobic behaviour of raw material, torrefied products and coal as fossil fuel reference.

- data processing.

Figure 1 - Scheme of the bench top torrefaction reactor employed



The work is described in detail as follows.

2.2 Thermogravimetric analysis

The thermal behaviour of the raw and torrefied biomass was studied by means of thermogravimetric analysis, which was carried out in a thermogravimetric analyzer (mod. STA PT1600, LINSEIS).

Weight loss function recorded for the whole test, with increasing temperature and time, is called thermogravimetric curve. Subsequently, the TG was processed to obtain the DTG. For all experimental runs, around 20 mg of material was heated from ambient temperature up to 700 °C. The first analysis was made for tomato peels at 5 °C min^{-1} heating rate to define the temperatures for the following torrefaction tests to be performed in the reactor. This rate has been used to allow a more homogeneous sample heating, as reported by Grønli [23], and to simulate the heating rate of the reactor. By means of DTG results the Tts for the following tests in the torrefaction reactor have been defined. At a later stage, TGs of torrefied and raw peel samples were carried out to observe the influence of torrefaction conditions on material structure. A faster heating rate (20 °C min^{-1}) was employed in order to reduce analytical time. Nitrogen was used during the analysis at a flow rate of 100 cm^3 min^{-1} to maintain an inert environment.

2.3 Torrefaction tests

Torrefaction of tomato peels was carried out in a heated bench-top reactor (mod. 4575 HT/HP, PARR). The sample (10 g) was inserted in a sample holder and placed in the center of the reactor in order to avoid the direct contact between the biomass and the hot reactor walls [24]. Each test was performed with flowing nitrogen gas to maintain an inert environment inside the reactor. Temperature was controlled during the test using a PID controller. The temperature program consists of a slow heating rate (5 °C min^{-1}) from ambient temperature up to Tt, followed by an isothermal step defined as Rt. Afterwards the sample was cooled to room temperature by a water cooling system under continuous nitrogen flowing through the reactor. The solid sample was then weighted and collected for further analyses. Different Tts and Rts have been evaluated for peels torrefaction tests. Each test was performed in triplicate. Tts for the torrefaction tests were chosen from DTG at 5 °C min^{-1} within the reactivity range of holocellulose. This range has been equally divided into four parts, and the selected Tts are reported in Table 1.

Table 1 – Tt and Rt used for reactor tests

Test	Tt [°C]	Rt [min]
T1	214	30
T2	214	60
T3	248	30
T4	248	60
T5	282	30
T6	282	60
T7	316	30
T8	316	60

2.4 Physicochemical characterization of materials

Raw and torrefied biomass have been analyzed in order to evaluate the influence of the torrefaction conditions on biomass quality. Heating value, proximate and ultimate analyses were performed for all materials in accordance with the European standards, as summarized in the Table 2.

Table 2 – European standards and instruments employed for heating value, proximate and ultimate analyses

PARAMETER	STANDARD	INSTRUMENT
Ash mass content (A)	EN 14775	Muffle furnace (mod. ZA, PREDERI VITTORIO&FIGLI)
Elemental analysis: Carbon mass content (C); Hydrogen mass content (H); Nitrogen mass content (N); Oxygen mass content (O)	EN 15104	Elemental Analyzer (mod. 2400 Series II CHNS/O System, PERKINELMER)
Low Heating Value (LHV)	EN 14918	Isoperibolic Calorimeter (mod.C2000 basic, IKA)

NOTE: Each sample has been prepared according to EN 14780 and dried according to EN 14774-2

The analysis of CP, EE, NDF, ADF, ADL on raw tomato peels was performed according to the technical standards as reported in Table 3. NDF represents hemicellulose, cellulose and lignin as a whole. ADF represents cellulose and lignin as a whole. ADL represents acid-insoluble lignin.

Table 3 - Technical standards and instruments employed for the analysis of crude protein, ether extract, neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL)

Parameter	Method	Instrument
Ash	EN 14775	Muffle furnace (mod. ZA, PREDERI VITTORIO&FIGLI)
Crude protein	ISO 5983-1	Laboratory equipment and Kjeldahl procedure
Ether extract	ISO 6492:1999	Laboratory equipment (Soxhlet)
NDF	ISO 16472	Fibertec system (van Soest method)
ADF	EN ISO 13906	Fibertec system (van Soest method)
ADL	EN ISO 13906	Fibertec system (van Soest method)

2.5 ATR-FTIR spectroscopy

Infrared spectra were recorded using a Fourier transform infrared spectrometer (Nicolet iS 10, THERMO SCIENTIFIC) equipped with Attenuated Total Reflectance (ATR) sampling accessory (Smart iTR, THERMO SCIENTIFIC). Each milled sample was pressed against a ZnSe crystal using a spring-loaded press and all the spectra were obtained over the wavenumber range from 4000 to 650 cm^{-1} with 100 scans at 4 cm^{-1} resolution. Before every analysis background spectra were collected in the same sample conditions without material on crystal.

2.6 Moisture uptake test

The aim of the analysis is to evaluate the torrefaction effect on the biomass hygroscopic behaviour. For this purpose raw peels, torrefied peels and coal, as conventional fossil fuel, were tested at the

same conditions of temperature and relative humidity (30°C and 100 % RH) in the same climate chamber and compared at different time intervals. Each sample was previously sieved to a particle size of < 500 µm (Test Sieve, 200 mm x 25 mm, 500 µm mesh, Retsch) and dried at 105 °C until a constant weight was reached. Amounts of about 3 g were tested and the weight increases were measured by analytical balance (mod. BCA 200, ORMA - sensibility ± 0,0001 g) at defined time intervals: 1, 4, 7, 11, 14, 17, 21, 25 days.

2.7 Data processing

Process parameters were calculated to evaluate how temperature and time of the torrefaction treatment influence biomass quality and composition according to the following equations:

$$M_Y\,(\%) = (m_{tor}/m_{bio}) \cdot 100 \qquad \text{(eq.1)}$$

$$I_{ed} = LHV_{tor}/LHV_{bio} \qquad \text{(eq.2)}$$

$$E_Y\,(\%) = M_Y \cdot I_{ed} \qquad \text{(eq.3)}$$

where M_Y and E_Y are mass and energy yields and represent the amount of matter and energy remained after the process; I_{ed} is the energy densification index which represents the increasing of the energy contained in the material; m is the mass of the material, and LHV is the lower heating value. Subscripts *tor* and *bio* are referring to torrefied and raw biomass respectively. All quantities are expressed on dry ash-free base (daf).
Taking into account the results of elemental analysis, H/C and O/C atomic ratios have been calculated and plotted in a van Krevelen diagram.

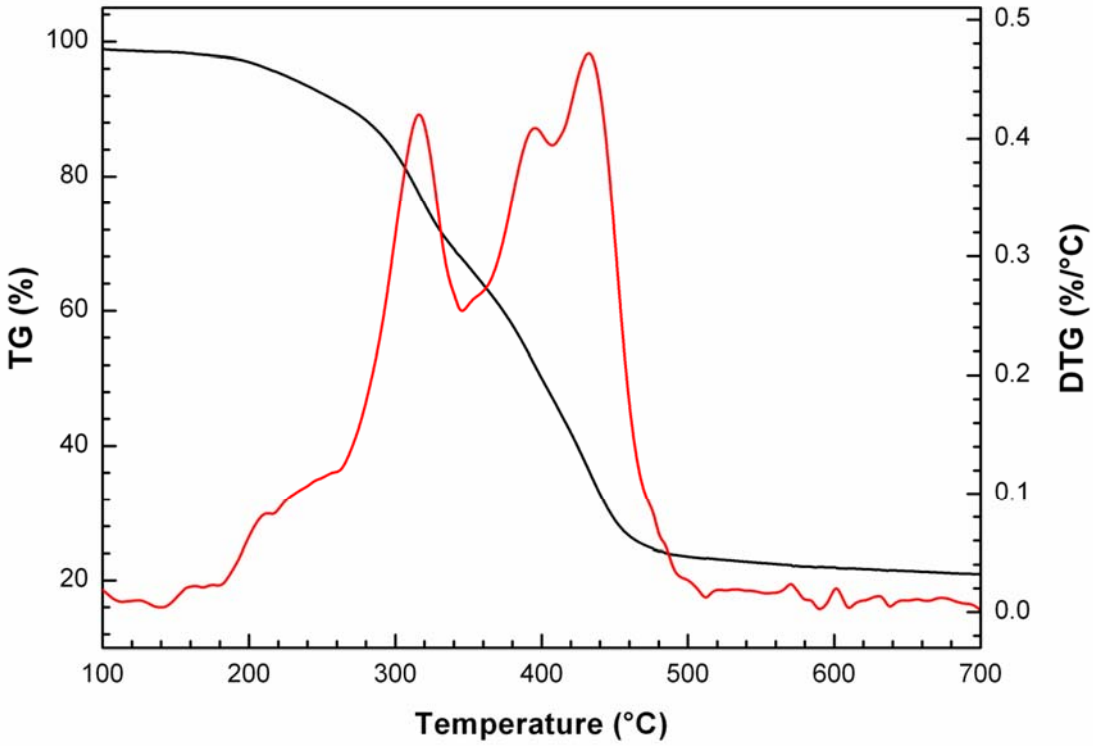
3 RESULTS AND DISCUSSION

3.1 Thermogravimetric analysis

The TG and DTG for tomato peels are plotted in Figure 2. The volatilization process begins at 180 °C and ends at 490 °C, where approximately 75 % of the initial mass is lost. After that, no significant weight losses are shown up to 700 °C.
It can be observed that the DTG of tomato peels is rather different from woody materials because presents several peaks within volatilization range as previously noticed by Mangut [25]. The pyrolytic behaviour of this biomass is quite complex, probably due to different composition of main constituents with respect to lignocellulosic biomass, i.e. lignin, and also to eventual presence of not lignocellulosic components, e.g. oil [25], proteins and waxes.
Even though the peaks are partially overlapped, the DTG can be roughly divided into two main parts: the first one represents hemicellulose [26] and cellulose degradation and is constituted by two peaks, an early shoulder followed by a more sharpened peak, with maximum points placed at 253 °C and 316 °C respectively; the second one is represented by two big peaks at 428 °C and 449 °C which are associated at lignin and not lignocellulosic constituents according to Mangut [25]. In order to evaluate the torrefaction process for tomato peels the temperature operating interval, defined within holocellulose volatilization range from volatilization starting point at 180 °C up to the maximum rate of cellulose degradation at 316 °C, was equally divided into four parts. Three

central temperatures and 316 °C have been selected for reactor tests, as reported in Table 1. For each Tt two Rt levels of 30 and 60 minutes have been assessed.

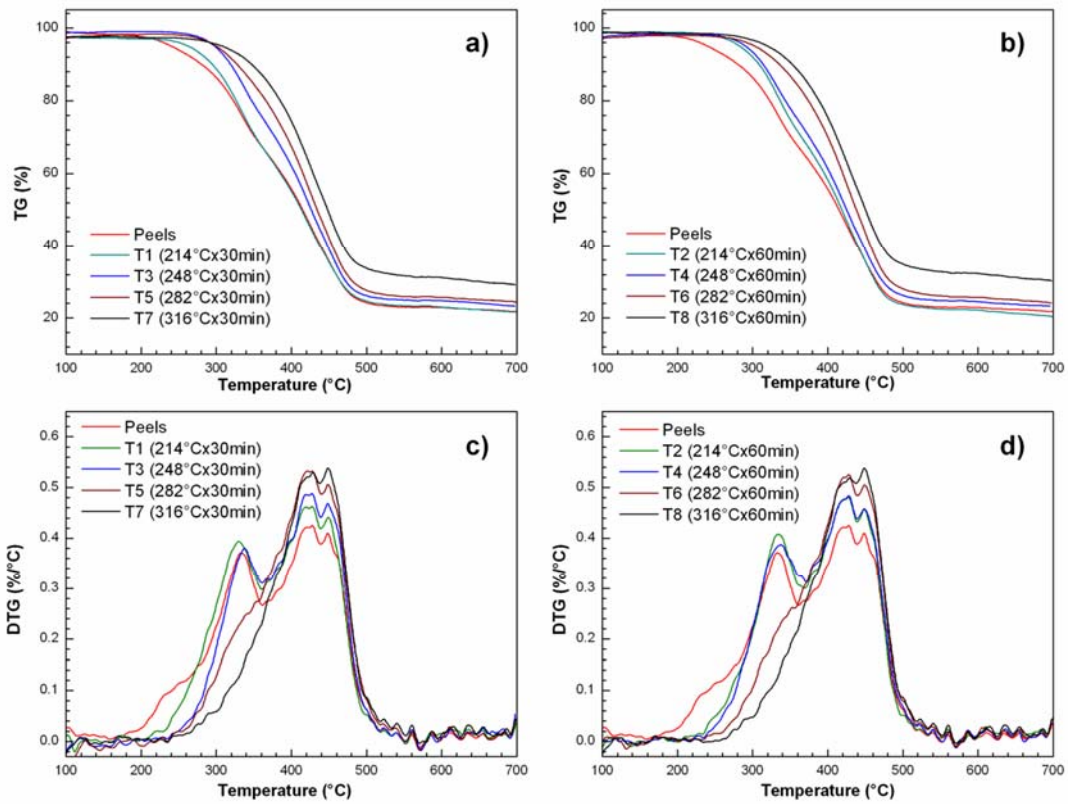
Figure 2 - TG and DTG for tomato peels at 5 °C min^{-1}



In Figure 3 TGs and DTGs of peels and torrefied samples are compared, grouped by Rt.
It is important to note that the starting temperature of the volatilization process for torrefied samples shifts towards higher temperatures when torrefaction conditions become more severe. This is due to the part of volatile fraction removed during the torrefaction. The initial volatilization temperature increases from about 220°C for raw peels to 310°C for T7 test. For the same reason, the mass percentage of solid residue left at high temperature after volatilization increases. The mass percentage of solid residue left, calculated at 550°C, increases from 23% for raw peels to 32% for T7 test. The comparison of DTGs shown in Figure 3c and 3d allows to observe the influence of torrefaction process on biomass structure: as a whole, with increasing Tt it can be noticed a selective and progressive degradation of the more volatile compounds of the material, i.e. hemicellulose and cellulose. At 214 °C only a reduction of hemicellulose shoulder can be observed, slightly more evident for 60 min than 30 min. At 248 °C cellulose starts to decompose showing a reduced peak, which appears like a hump after 282 °C treatment. After 60 min at 316 °C, severest torrefaction conditions, the cellulose peak totally disappears. Components not degraded after the torrefaction process appear in DTGs with higher peaks than those in untreated biomass. This is due to the loss of a fraction of volatile matter during torrefaction with the consequent increment of their mass percentages. No apparent differences are shown among DTGs obtained for tests with different

Rts but same Tt. In general, the torrefaction process reduces the volatilisation range of the tested material.

Figure 3 - TGs and DTGs of peels and torrefied samples at 20 °C min^{-1}



3.2 Physicochemical characterisation of materials

The results of crude protein, ether extract, neutral detergent fiber, acid detergent fiber and acid detergent lignin on raw tomato peels, which are useful to estimate the lignocellulosic composition of the biomass, are reported in Table 4. Hemicellulose, cellulose and lignin dry mass fraction results in 4.8 %, 22.5 % and 46.9 % respectively.

Table 4 - Results of crude protein, ether extract, NDF, ADF, and ADL of tomato peels (Values are expressed as wt.%, db).

A	2.2
CP	11.9
EE	3.1
NDF	76.4
ADF	71.6
ADL	49.1

The results of characterisation analysis for tomato peels and torrefied samples are listed in Table 5.

Table 5 - Results of characterisation analysis for tomato peels and torrefied samples (where not indicated the values are expressed on dry ash-free basis)

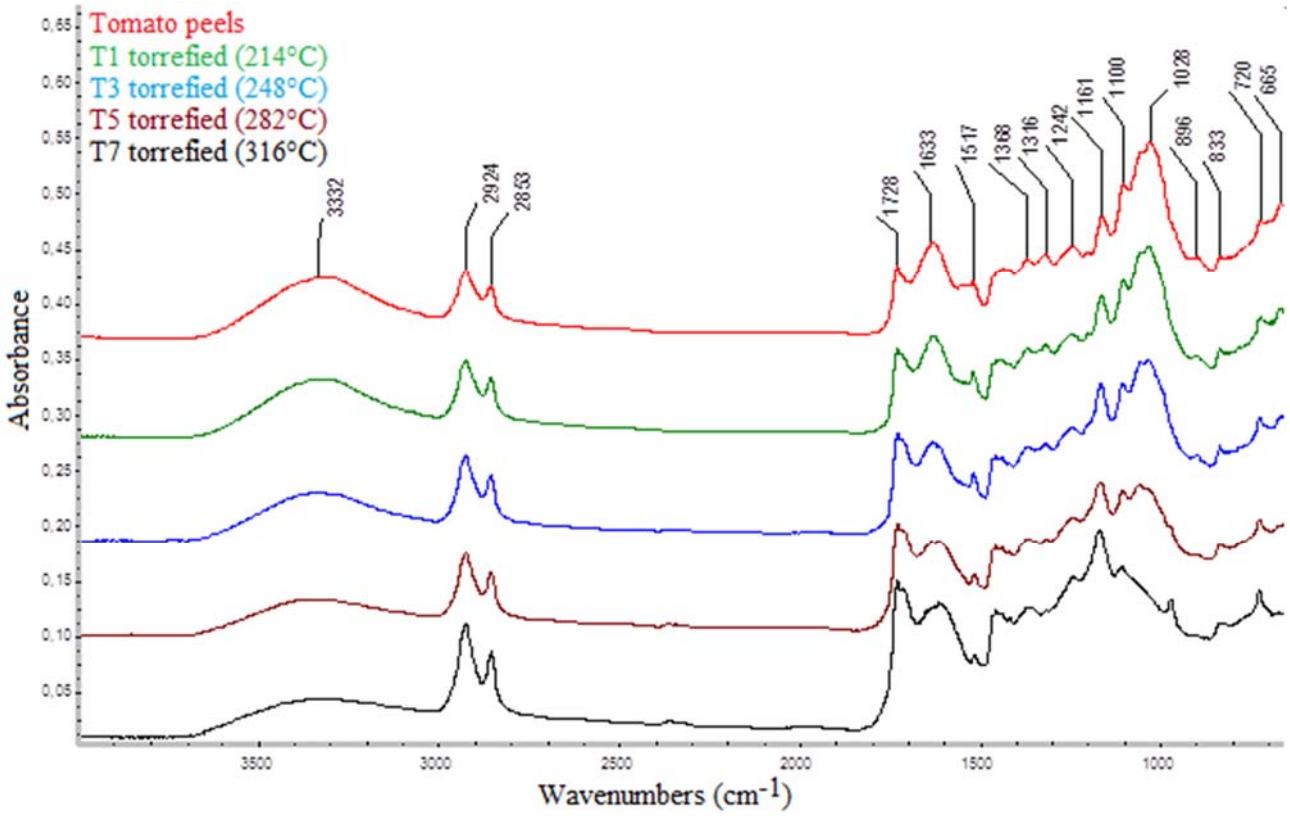
Sample	**Tt**	**Rt**	**A**	**LHV**	**C**	**H**	**N**	**O**
	(°C)	(min)	(% d.b.)	(kJ kg^{-1})	(%)	(%)	(%)	(%)
Peels	-	-	2.2	26016	61.4	8.7	1.8	25.9
T1	214	30	2.4	26909	63.4	9.0	1.8	23.5
T2	214	60	2.4	26982	63.5	9.0	1.9	23.3
T3	248	30	2.5	27894	65.5	9.1	1.9	21.1
T4	248	60	2.5	28023	65.8	9.0	1.9	21.0
T5	282	30	2.8	30155	69.4	9.2	1.9	16.8
T6	282	60	2.9	30384	70.5	9.2	1.8	15.6
T7	316	30	2.9	31996	73.7	9.3	1.9	12.2
T8	316	60	3.0	32067	75.1	9.3	1.9	10.7

According to fiber analysis, raw tomato peels shows a low oxygen content and a high LHV with respect to conventional lignocellulosic biomass, outlining a low holocellulose content and a high lignin content. In particular, the low oxygen content in tomato peels is due to the significant presence of compounds characterized by a low oxygen content i.e. lignin, wax, lipid, protein.
As clearly shown in Table 5 the torrefaction process leads to a solid fuel with higher C and lower O than in the raw material: in fact, after 60 min at 316 °C, the C raises from 61.4 % to 75.1 % while the O is reduced from a initial value of 25.9 % to a 10.7 %. A less noticeable trend can be observed for H, which shows a slowly increasing with the increase of Tt and Rt. No significant change has been observed for N.
The partial volatilization of organic fraction obviously causes an increase of A in percentage terms. The increment of LHV is consistent with an increase in C in the treated material. Within Rts and Tts range studied, it can be noticed that by means of torrefaction, LHV increases up to around 23 % with respect to the initial energy content for the sample treated at 316 °C for 60 min.

3.3 ATR-FTIR spectroscopy

FT-IR analysis allows to understand the changes in the chemical structure of the material after torrefaction treatment. Figure 4 shows the comparison of infrared spectra collected for peels and torrefied samples for tests carried out at Rt of 30 minutes.

Figure 4 - ATR-FTIR spectra of raw and torrefied tomato peels. All spectra are separated to ease comparison



The assignment of absorption bands for raw and torrefied peels was obtained by comparison of results with literature. The outcome is reported in Table 6.

Table 6 - Assignment of FT-IR absorption bands for raw and torrefied peels

Measured Frequency (cm^{-1})	**Assignment**
3332	(s) O-H [27]
2924	(s,*A*) CH_2 (2920 cm^{-1} [28])
2853	(s,*S*) CH_2 (2850 cm^{-1} [28])
1728	• (s) C=O alchil esters of PECTIN 1740 cm^{-1} [34]) • (s) C=O carboxyl group of HEMICELLULOSE (1732cm^{-1} [31]); 1735 cm^{-1} [28])
1633	• (s, A) COO^- Polygalacturonic acid, carboxylate (PECTIN [28]) • C=C (1595 cm^{-1}, [27] LIGNIN
1517	• (s) Aromatic ring (1510 cm^{-1} [28]) LIGNIN
1316	(b) wagging CH_2 (1317 cm^{-1} [34]) HEMICELLULOSE
1242	• (s) C-O (1243 cm^{-1} [34]) PECTIN • (s, A) C-O-C gruppi acetilici (1240 cm^{-1}, [31]) HEMICELLULOSE
1161	• (s-a) glycosidic link C-O-C, ring (1160 cm^{-1}, [34]) CELLULOSE, HEMICELLULOSE
1100	• (s) C-OH, C-O-C, C-C, ring (1100 cm^{-1}, [35]) PECTIN
1080 - 940	• (s)C-O (1015 cm^{-1});(s)C-C (1000 cm^{-1} CELLULOSE [28]) • ring (1075, 1042 cm^{-1}) HEMICELLULOSE [28]) • ring (1019, 960 cm^{-1} PECTIN [28])

896	(b) C1-H β anomeric link (895 cm^{-1}, [34]) CELLULOSE, XILOGLUCANE AMOURPHOUS CELLULOSE (893 cm^{-1}, [28])
833	Ring (833 cm^{-1}, [34]) PECTIN
720	(b) CH_2 rocking of alifatic fraction
s: stretching vibration; b: bending vibration; S: symmetric; A: antisymmetric	

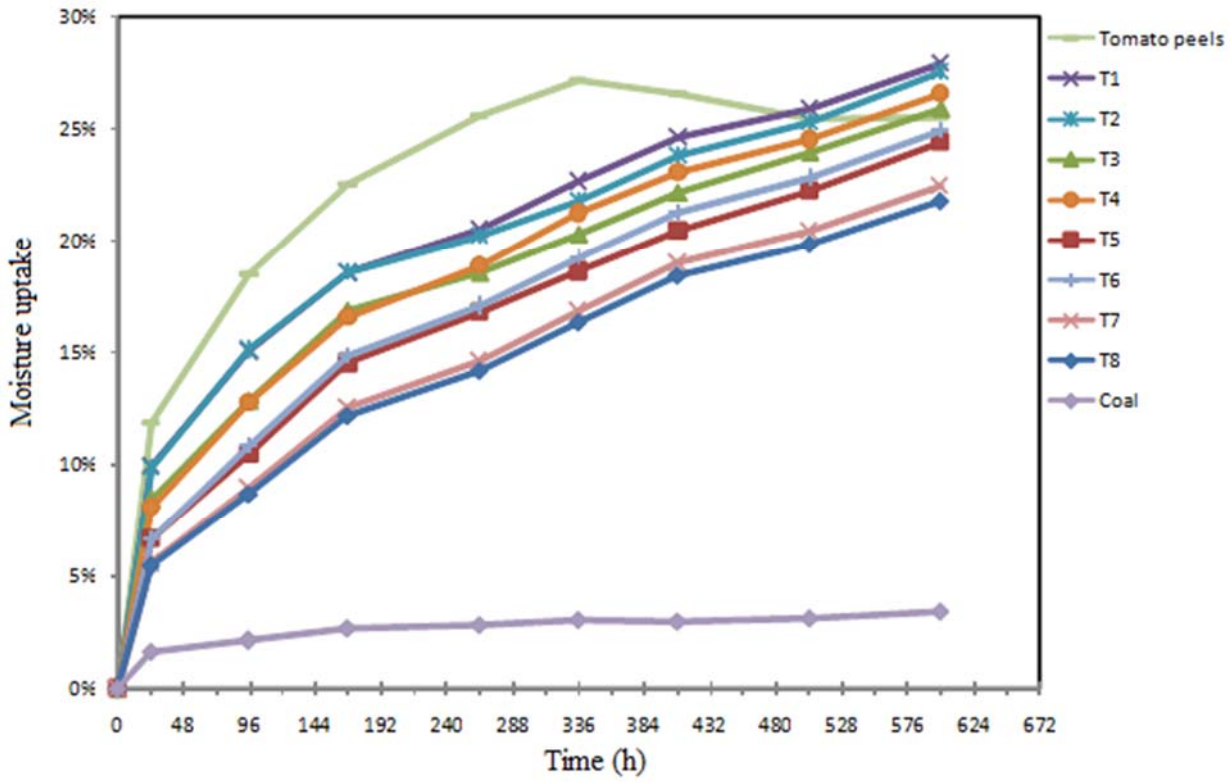
The intensity of absorption band of OH, corresponding to a broad peak at 3332 cm^{-1}, decreases with torrefaction temperatures as result of carbohydrates decomposition, similarly as Rousset et al. [27] for bamboo torrefaction.
The two narrow peaks at 2924 and 2853 cm^{-1} and the peak at 720 cm^{-1}, corresponding to CH_2-stretching [28] and rocking bending respectively, are associated with crude fat contents in tomato peels [29]. The spectra show that this fraction does not undergo degradation reaction at tested conditions, becoming thus more concentrated in torrefied material.
Although the portion of the spectra between 1800 - 650 cm^{-1} is quite complex, because different absorption bands overlap, the most of chemical information is enclosed in it.
The peak at 1728 cm^{-1} was assigned to the stretching band of the carbonyl ester of pectin, component found in tomato peels residues, which is situated around 1740-1730 cm^{-1} depending on its degree of esterification [30]. This band does not change over the temperature range studied and the formation of a new product band shifted to lower frequency (around 1713 cm^{-1}) can be seen as found by Shang et al [31]. Even though pectin signals are evident in FTIR spectra their quantity is probably very low as reported by other authors [32].
Another difference between torrefied and raw material can be found in the broad band located between 1690 and 1590 cm^{-1}, where intensity decreases and maximum peak shifts to lower wave numbers as the torrefaction temperature increase. This is a clear signal that the composition of material is changed. In this case, since several bands overlap, i.e. carboxylate ion stretching (1630-1600 cm^{-1}), lignin (1599 cm^{-1}) and amide I (1650 cm^{-1}) it is difficult to assign a specific molecular vibration to the peak. The characteristic band at 1517 cm^{-1} reveals that lignin is stable up to 248°C, after which starts to degradate. With severe torrefaction conditions, above 282°C, it can be noticed a significant reduction of cellulose characteristic bands (1316, 896 and 666 cm^{-1}) associated with degradation of this component, according to DTG results. The band at 1161 cm^{-1} is attributed to the antisymmetric stretching of glycosidic linkages C-O-C in all cellulose, hemicelluloses and pectin. Contrary to what might be thought the peak does not reduce significantly during torrefaction process. The higher intensity of the C–O–C vibration with increasing torrefaction severity could be attributed to a presence of thermostable compounds in torrefied material which have glycosidic linkage and the formation of cross-linking during cellulose torrefaction [33].
The group of peaks between around 1080-940 cm^{-1}, C-O and C-C stretching vibration of cellulose, hemicellulose and pectin [34, 35], is linked to polysaccharide content of material and shows an evident reduction as torrefaction temperature increase. In general terms the information obtained by FTIR analysis is in line with thermogravimetric analysis.

3.4 Moisture uptake

Torrefaction treatment makes the biomass more hydrophobic depending on the severity of the condition adopted, as evident in Figure 5. Both higher torrefaction temperatures and longer residence time reduce the moisture uptake of the material tested making it progressively more

similar to fossil coal. This result is in line with FTIR spectra which highlight a reduction of OH groups with torrefaction, affecting the material hydrophobic behaviour.
It is noted that only the untreated material shows a biological degradation after 336 h in tested conditions due to mold growth. This put in evidence how torrefaction treatment, even at the milder conditions tested, determines positive and significant effects in terms of biological stabilization and biomass storability.

Figure 5 - Results of moisture uptake test carried out on raw and torrefied materials



3.5 Data processing

Table 7 shows the results for process parameters. It can be seen that increasing Tt causes a reduction in both M_Y and E_Y, while I_{ed} increases.
It is worthy of note that in tomato peels torrefaction is lost more mass than energy: the reduction of mass content after 60 min at 316 °C treatment, the severest conditions, is approximately 30 % while only a 13.9 % of energy is lost.

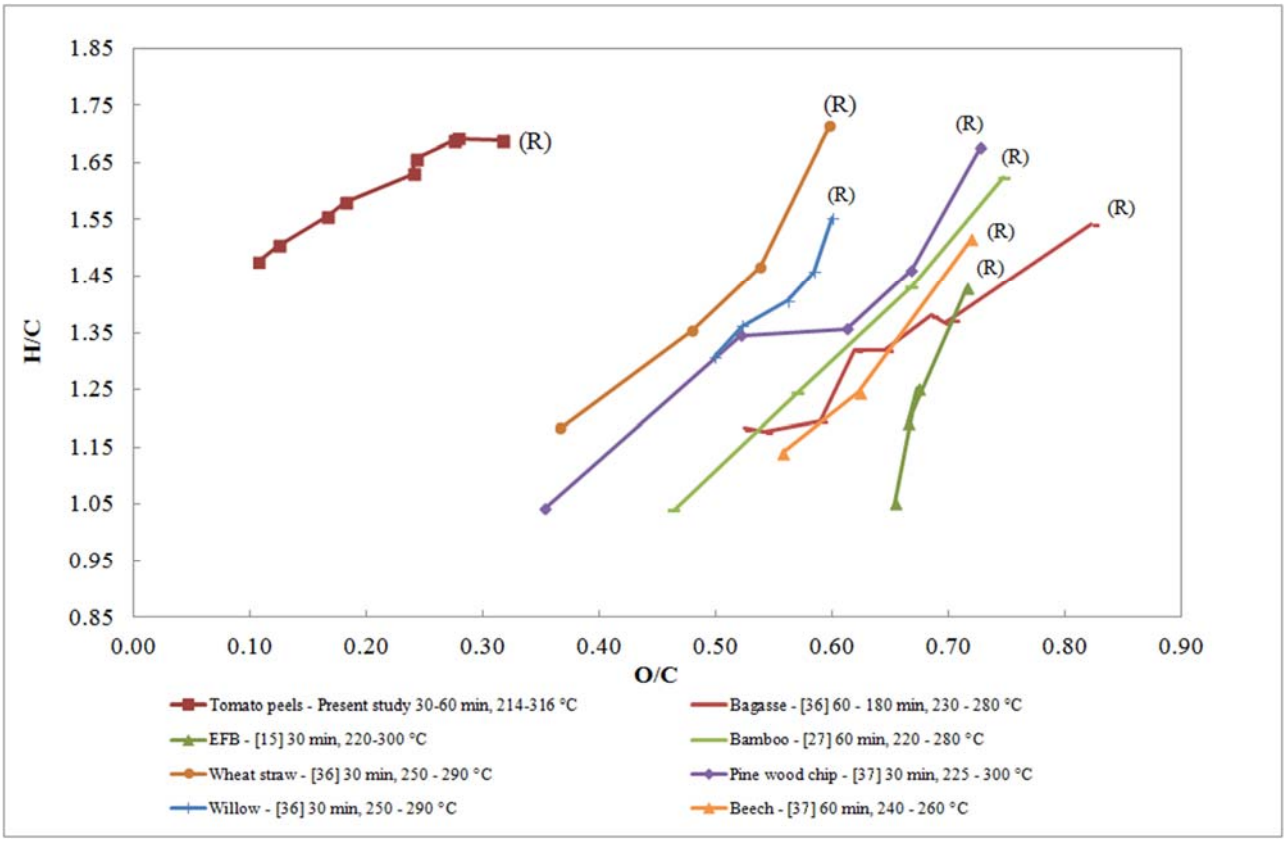
Table 7 - Results for process parameters M_Y, E_Y and I_{ed}

Test	Temp	Time	M_Y	E_y	I_{ed}
	(°C)	(min)	(%)	(%)	-
T1	214	30	94.7	98.0	1.04
T2	214	60	94.4	97.9	1.04
T3	248	30	90.6	97.1	1.07
T4	248	60	90.7	97.7	1.08
T5	282	30	81.6	94.6	1.15

T6	282	60	79.9	93.7	1.16
T7	316	30	74.2	91.3	1.22
T8	316	60	69.9	86.0	1.23

In Figure 6 the H/C and O/C atomic ratios for raw and torrefied peels are plotted in a van Krevelen diagram, in order to show the variation of the material composition after the torrefaction. In addition, other torrefied material from woody and agro residual biomass, found in literature [15, 27, 36, 37], are shown in the same Figure to make a comparison.

Figure 6 - Van Krevelen diagram (R represents raw materials)



It can be seen that biomass moves towards lower H/C and O/C values after torrefaction, since torrefied materials lose more atoms of oxygen and hydrogen than carbon atoms. According to several works [3, 4, 38] this is mainly due to chemical removal of water and carbon dioxide. The elemental composition becomes even more similar to high carbon content fuels, like coal (H/C 0.76; O/C 0.13) or peat (H/C 1.27; O/C 0.48) , as Tt and Rt increase. Tomato peels follows this behaviour too. In particular for tomato peels it can be noted how Tt significantly influences biomass conversion more than Rt, although both of these parameters increase it. It is noted that this agro industrial residue is positioned in a different area with respect to the others, mainly due to its relatively high carbon and low oxygen contents.

Taking into account the tomato processed by a representative medium sized Italian manufacturing unit of about 85 x 10^6 kg and according to the studies carried out by some authors [39, 40] it can be estimated a production of 1.7 x 10^6 kg of peels as residue. Considering a mild torrefaction in the same conditions of T1 test, an amount of 1.6 x 10^6 kg of torrefied peels can be produced.

Summarizing, for each ton of tomato fruit an energy content of 515 MJ can be obtained from torrefied peels, equal to the energy contained in about 17 kg of coal. The calculation carried out for the most severe condition tested (T8), gives a result of 448 MJ, equal to about 15 kg of coal.

4 CONCLUSIONS

The effects of torrefaction on tomato peels properties are already evident from 214°C. Besides, over 250 °C biomass modifications are even more substantial. All the analyses highlight that the process reduces volatilisation range and produces high carbon content fuel-like material making the torrefied product more suitable for further energy applications. By the torrefaction process the material undergoes chemical changes as evident with DTG, spectroscopic and ultimate analysis. Although one of the main purposes of biomass torrefaction is the increase of energy content, in the case of tomato peels is important to emphasize that a fundamental aspect is the biological stabilization of the material. In fact, as shown by the moisture uptake test, only drying the material is not sufficient to achieve that purpose. This consideration, taking also into account the high energy content of the starting material, suggests the application of a mild torrefaction. In general terms, torrefaction turns an unused agro-industrial residue with poor energy content like tomato wet residue into a more easily exploitable biofuel with energy properties similar to coal.

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