# Torrefaction of tomato industry residues

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## HIGHLIGHTS

- Torrefaction of tomato peels was studied.
- Temperature results more significant than residence time.
- Up to 30% of the mass was lost with an energy densification increment of about 20%.
- Torrefaction produces high carbon content fuel-like material.
- Results suggest the application of a mild torrefaction.

## ARTICLE INFO

## 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 standardization 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 standardized material suitable to be employed as fuel for energy application. The results of this paper provide useful indications and suggest a mild torrefaction.

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## 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 behavior 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

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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 behavior 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 (Fig. 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 behavior of raw material, torrefied products and coal as fossil fuel reference.
- data processing.

The work is described in detail as follows.

### 2.2. Thermogravimetric analysis

The thermal behavior of the raw and torrefied biomass was studied by means of thermogravimetric analysis, which was carried out
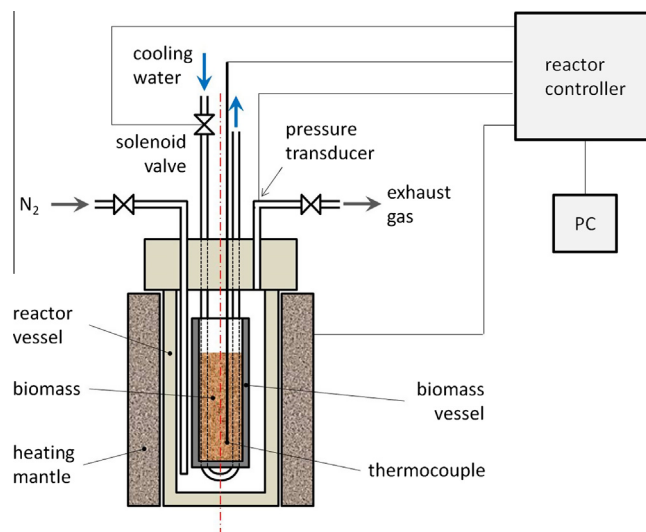


**Fig. 1.** Scheme of the bench top torrefaction reactor employed.

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 benchtop 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.

### 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.

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)

**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 |

### 2.5. 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 behavior. 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 × 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:

$$M_Y(\%) = (m_{tor}/m_{bio}) \cdot 100 \tag{1}$$

$$I_{ed} = LHV_{tor}/LHV_{bio} \tag{2}$$

$$E_Y(\%) = M_Y \cdot I_{ed} \tag{3}$$

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 Fig. 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 et al. [25]. The pyrolytic behavior 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

**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<br>Carbon mass content (C)<br>Hydrogen mass content (H)<br>Nitrogen mass content (N)<br>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.

**Table 3**
European standards and instruments employed for the analysis of ash mass content, crude protein, ether extract, neutral detergent fiber, acid detergent fiber, acid detergent lignin.

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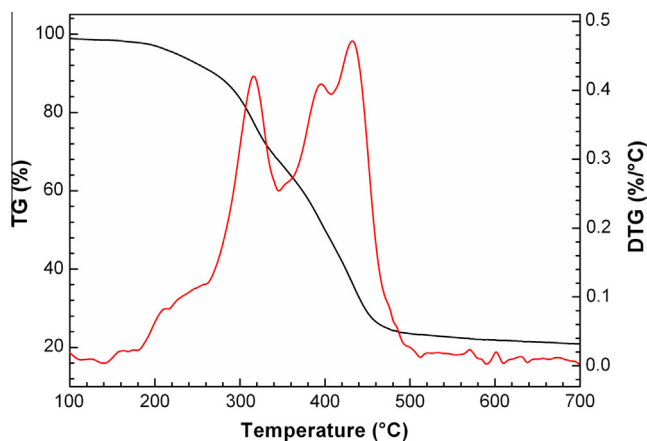


**Fig. 2.** TG and DTG for tomato peels at 5 °C min⁻¹.

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 et al. [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 min have been assessed.

In Fig. 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 toward 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 Fig. 3c and d 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 volatilization range of the tested material.

### 3.2. Physicochemical characterization 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.

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

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
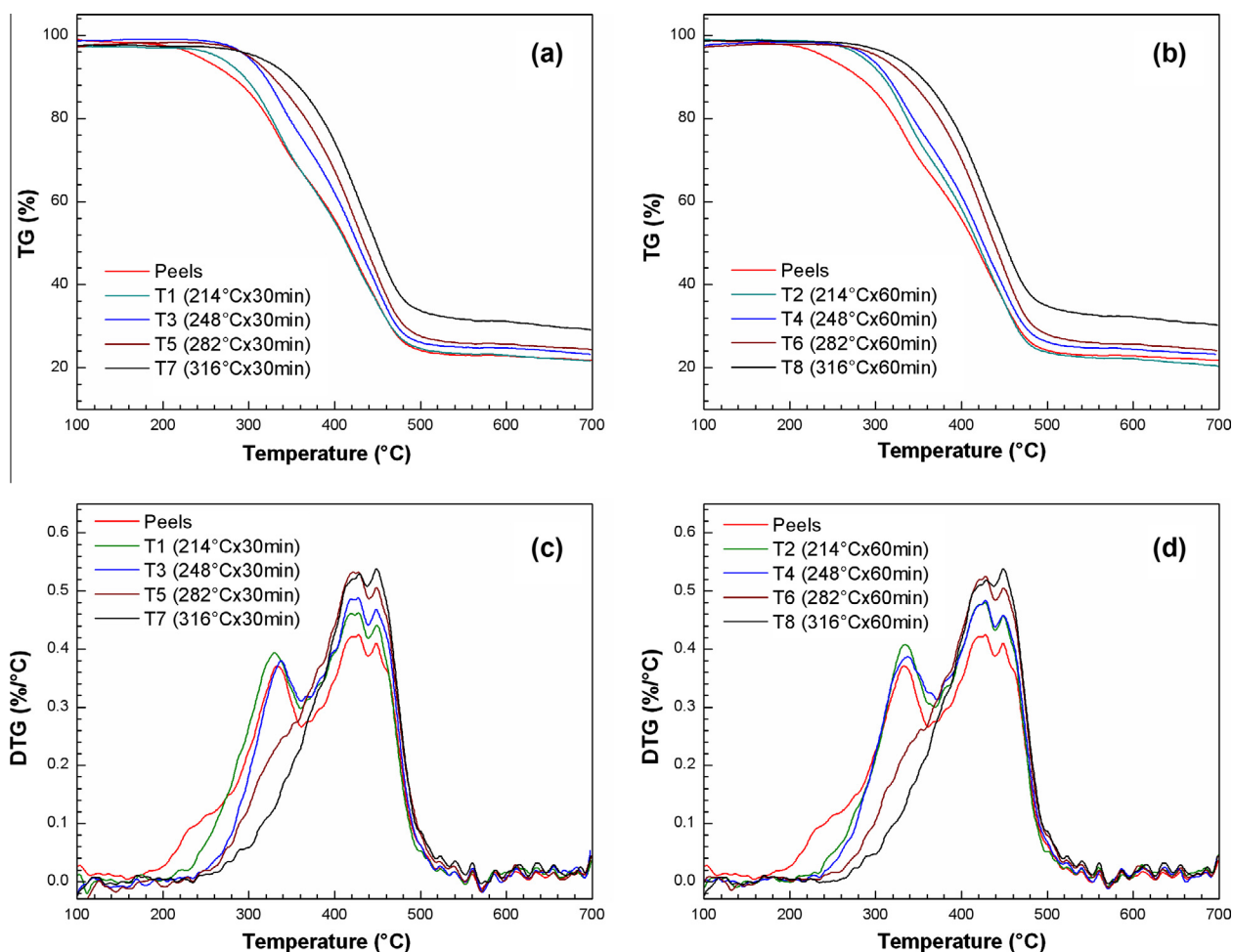
**Fig. 3.** TGs and DTGs of peels and torrefied samples at 20 °C min$^{-1}$.

**Table 4**
Results of CP, EE, 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 |

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

| Sample | Tt (°C) | Rt (min) | A (% d.b.) | LHV (kJ kg$^{-1}$) | C (%) | H (%) | N (%) | O (%) |
|---|---|---|---|---|---|---|---|---|
| Peels | – | – | 2.2 | 26,016 | 61.4 | 8.7 | 1.8 | 25.9 |
| T1 | 214 | 30 | 2.4 | 26,909 | 63.4 | 9.0 | 1.8 | 23.5 |
| T2 | 214 | 60 | 2.4 | 26,982 | 63.5 | 9.0 | 1.9 | 23.3 |
| T3 | 248 | 30 | 2.5 | 27,894 | 65.5 | 9.1 | 1.9 | 21.1 |
| T4 | 248 | 60 | 2.5 | 28,023 | 65.8 | 9.0 | 1.9 | 21.0 |
| T5 | 282 | 30 | 2.8 | 30,155 | 69.4 | 9.2 | 1.9 | 16.8 |
| T6 | 282 | 60 | 2.9 | 30,384 | 70.5 | 9.2 | 1.8 | 15.6 |
| T7 | 316 | 30 | 2.9 | 31,996 | 73.7 | 9.3 | 1.9 | 12.2 |
| T8 | 316 | 60 | 3.0 | 32,067 | 75.1 | 9.3 | 1.9 | 10.7 |

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. Fig. 4 shows the comparison of infrared spectra collected for peels and torrefied samples for tests carried out at Rt of 30 min.

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.

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 and 650 cm$^{-1}$ is quite complex, because different absorption bands overlap, the most of chemical information is enclosed in it.
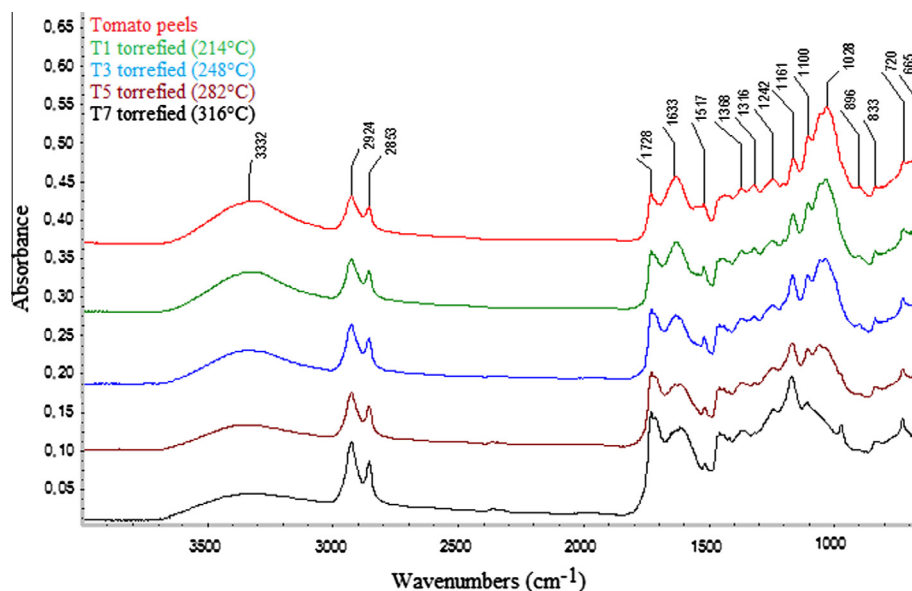
**Fig. 4.** ATR-FTIR spectra of raw and torrefied tomato peels. All spectra are separated to ease comparison.

**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 (1732 cm$^{-1}$ [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 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
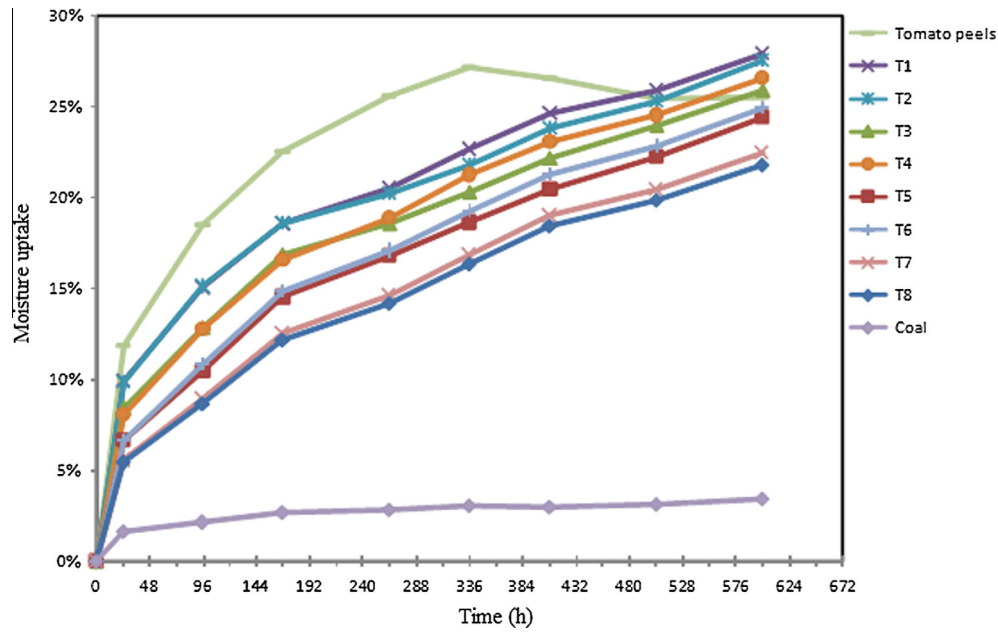
**Fig. 5.** Results of moisture uptake test carried out on raw and torrefied materials.

**Table 7**
Results for process parameters $M_Y$, $E_Y$ and $I_{ed}$.

| Test | Temp (°C) | Time (min) | $M_Y$ (%) | $E_y$ (%) | $I_{ed}$ – |
|------|-----------|------------|-----------|-----------|------------|
| 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 |

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 Fig. 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
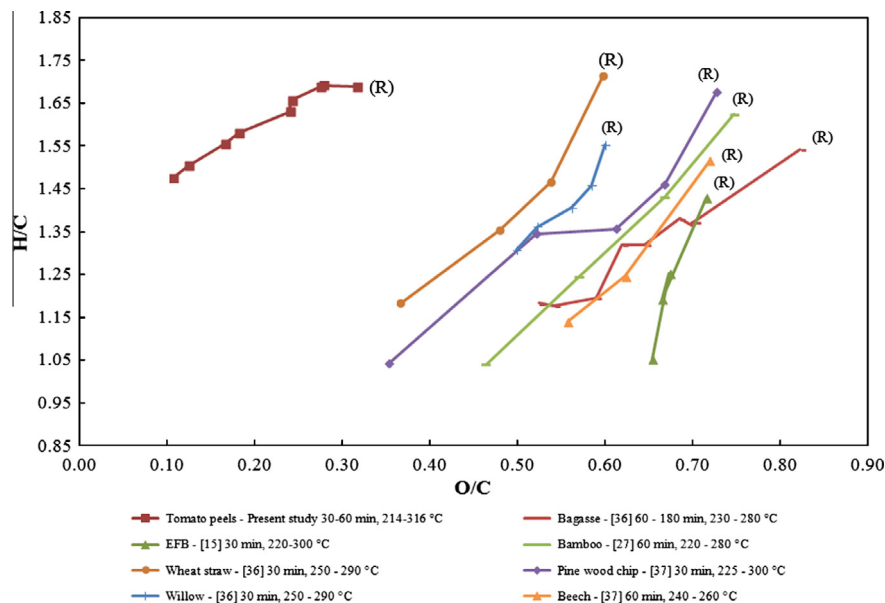


Tomato peels - Present study 30-60 min, 214-316 °C
EFB - [15] 30 min, 220-300 °C
Wheat straw - [36] 30 min, 250 - 290 °C
Willow - [36] 30 min, 250 - 290 °C
Bagasse - [36] 60 - 180 min, 230 - 280 °C
Bamboo - [27] 60 min, 220 - 280 °C
Pine wood chip - [37] 30 min, 225 - 300 °C
Beech - [37] 60 min, 240 - 260 °C

**Fig. 6.** Van Krevelen diagram (R represents raw materials).

FTIR spectra which highlight a reduction of OH groups with torrefaction, affecting the material hydrophobic behavior.

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.

### 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.

In Fig. 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.

It can be seen that biomass moves toward 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 behavior 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 $85 \times 10^6$ kg and according to the studies carried out by some authors [39,40] it can be estimated a production of $1.7 \times 10^6$ kg of peels as residue. Considering a mild torrefaction in the same conditions of T1 test, an amount of $1.6 \times 10^6$ 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 volatilization 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.

## References

[1] Felfli FF, Luengo CA, Suárez JA, Beatón PA. Wood briquette torrefaction. Energy Sustain Dev 2005;9:19–22.
[2] Arias B, Pevida C, Fermoso J, Plaza MG, Rubiera F, Pis JJ. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process Technol 2008;89:169–75.
[3] Van der Stelt MJC, Gerhauser H, Kiel JHA, Ptasinski KJ. Biomass upgrading by torrefaction for the production of biofuels: A review. Biomass Bioenergy 2011;35:3748–62.
[4] Chen W-H, Kuo P-C. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. Energy 2010;35:2580–6.
[5] Li J, Brzdekiewicz A, Yang W, Blasiak W. Co-firing based on biomass torrefaction in a pulverized coal boiler with aim of 100% fuel switching. Appl Energy 2012;99:344–54.
[6] Phanphanich M, Mani S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresource Technol 2011;102:1246–53.
[7] Stelte W, Clemons C, Holm JK, Sanadi AR, Ahrenfeldt J, Shang L, et al. Pelletizing properties of torrefied spruce. Biomass Bioenergy 2011;35:4690–8.
[8] Prins MJ, Ptasinski KJ, Janssen FJJG. More efficient biomass gasification via torrefaction. Energy 2006;31:3458–70.
[9] Chen W-H, Chen C-J, Hung C-I. Taguchi approach for co-gasification optimization of torrefied biomass and coal. Bioresource Technol 2013;144:615–22.
[10] Chen W-H, Chen C-J, Hung C-I, Shen C-H, Hsu H-W. A comparison of gasification phenomena among raw biomass, torrefied biomass and coal in an entrained-flow reactor. Appl Energy 2013;112:421–30.
[11] Prins MJ, Ptasinski KJ, Janssen FJJG. Torrefaction of wood: Part 1. Weight loss kinetics. J Anal Appl Pyrol 2006;77:28–34.
[12] Prins MJ, Ptasinski KJ, Janssen FJJG. Torrefaction of wood: Part 2. Analysis of products. J Anal Appl Pyrol 2006;77:35–40.
[13] Eseltine D, Thanapal SS, Annamalai K, Ranjan D. Torrefaction of woody biomass (Juniper and Mesquite) using inert and non-inert gases. Fuel 2013;113:379–88.
[14] Wang MJ, Huang YF, Chiueh PT, Kuan WH, Lo SL. Microwave-induced torrefaction of rice husk and sugarcane residues. Energy 2012;37:177–84.
[15] Uemura Y, Omar WN, Tsutsui T, Yusup SB. Torrefaction of oil palm wastes. Fuel 2011;90:2585–91.
[16] Shang L, Ahrenfeldt J, Holm JK, Barsberg S, Zhang R-Z, Luo Y-H, et al. Intrinsic kinetics and devolatilization of wheat straw during torrefaction. J Anal Appl Pyrol 2013;100:145–52.
[17] Chen W-H, Lu K-M, Tsai C-M. An experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction. Appl Energy 2012;100:318–25.
[18] Celma AR, Cuadros F, López-Rodríguez F. Convective drying characteristics of sludge from treatment plants in tomato processing industries. Food Bioprod Process 2012;90:224–34.
[19] Rossini G, Toscano G, Duca D, Corinaldesi F, Foppa Pedretti E, Riva G. Analysis of the characteristics of the tomato manufacturing residues finalized to the energy recovery. Biomass Bioenergy 2013;51:177–82.
[20] Ruiz Celma A, Cuadros F, López-Rodríguez F. Characterization of pellets from industrial tomato residues. Food Bioprod Process 2012;90:700–6.
[21] Fondevila M, Guada JA, Gasa J, Castrillo C. Tomato pomace as a protein supplement for growing lambs. Small Ruminant Res 1994;13:117–26.
[22] Zanón MJ, Font MI, Jordá C. Use of tomato crop residues into soil for control of bacterial wilt caused by *Ralstonia solanacearum*. Crop Prot 2011;30:1138–43.
[23] Grønli MG, Várhegyi G, Di Blasi C. Thermogravimetric analysis and devolatilization kinetics of wood. Ind Eng Chem Res 2002;41:4201–8.
[24] Chen W-H, Kuo P-C. Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. Energy 2011;36:803–11.
[25] Mangut V, Sabio E, Gañán J, González JF, Ramiro A, González CM, et al. Thermogravimetric study of the pyrolysis of biomass residues from tomato processing industry. Fuel Process Technol 2006;87:109–15.
[26] Jin W, Singh K, Zondlo J. Pyrolysis kinetics of physical components of wood and wood–polymers using isoconversion method. Agriculture 2013;3: 12–32.

[27] Rousset P, Aguiar C, Labbé N, Commandré J-M. Enhancing the combustible properties of bamboo by torrefaction. Bioresource Technol 2011;102:8225–31.

[28] Kristensen J-B, Thygesen L-G, Felby C, Jorgensen H, Elder T. Cell-wall structural changes in wheat straw pretreated for bioethanol production. Biotechnol Biofuels 2008;1:5.

[29] Knoblich M, Anderson B, Latshaw D. Analyses of tomato peel and seed byproducts and their use as a source of carotenoids. J Sci Food Agr 2005;85:1166–70.

[30] Szymanska-Chargot M, Zdunek A. Use of FT-IR Spectra and PCA to the bulk characterization of cell wall residues of fruits and vegetables along a fraction process. Food Biophys 2013;8:29–42.

[31] Shang L, Ahrenfeldt J, Holm JK, Sanadi AR, Barsberg S, Thomsen T, et al. Changes of chemical and mechanical behavior of torrefied wheat straw. Biomass Bioenergy 2012;40:63–70.

[32] Navarro-González I, García-Valverde V, García-Alonso J, Periago MJ. Chemical profile, functional and antioxidant properties of tomato peel fiber. Food Res Int 2011;44:1528–35.

[33] Zheng A, Zhao Z, Chang S, Huang Z, Wang X, He F, et al. Effect of torrefaction on structure and fast pyrolysis behavior of corncobs. Bioresource Technol 2013;128:370–7.

[34] Kačuráková M, Smith AC, Gidley MJ, Wilson RH. Molecular interactions in bacterial cellulose composites studied by 1D FT-IR and dynamic 2D FT-IR spectroscopy. Carbohyd Res 2002;337:1145–53.

[35] Kačuráková M, Capek P, Sasinková V, Wellner N, Ebringerová A. FT-IR study of plant cell wall model compounds: pectic polysaccharides and hemicelluloses. Carbohyd Polym 2000;43:195–203.

[36] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 2008;87:844–56.

[37] Chew JJ, Doshi V. Recent advances in biomass pretreatment – torrefaction fundamentals and technology. Renew Sust Energy Rev 2011;15:4212–22.

[38] Basu P. Chapter 4 – torrefaction. In: Basu P, editor. Biomass Gasification, Pyrolysis and Torrefaction (Second Edition). Boston: Academic Press; 2013. p. 87–145.

[39] Sogi DS, Arora MS, Garg SK, Bawa AS. Fractionation and electrophoresis of tomato waste seed proteins. Food Chem 2002;76:449–54.

[40] Kaur D, Sogi DS, Garg SK, Bawa AS. Flotation-cum-sedimentation system for skin and seed separation from tomato pomace. J Food Eng 2005;71:341–4.

## Web references

[41] Conserve Italia. URL: <http://www.conserveitalia.it/content/view/100/193/>. [accessed 20.09.12].

[42] ECN. Phyllis URL: <http://www.ecn.nl/phyllis/>. [accessed 20.09.12].