

Energy valorisation of citrus peel waste by torrefaction treatment

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Abstract. The article deals with the issue of processing and utilization of citrus peel, which often ends unused with other biodegradable waste. The research is concerned with the energy potential of this raw material and its torrefaction conversion. The tested materials were orange peel (*Citrus sinensis* Osbeck cv 'Valencia', *Citrus sinensis* Osbeck cv 'Murcia') and grapefruit peel (*Citrus paradise* 'Ruby red'). Samples of dried materials underwent torrefaction treatment at 225 °C, 250 °C and 275 °C for 30 minutes. Samples before and after torrefaction were analysed for proximate and elemental composition and for calorific value. Consequently, stoichiometric combustion analyses were done. The torrefaction was performed in a LECO TGA 701 thermogravimetric analyzer under nitrogen atmosphere. The results of proximate and elemental analysis showed positive influence of torrefaction on the samples. The highest net calorific value for orange peel is 24.97 MJ kg⁻¹ at the temperature of 275 °C. The greatest differences in net calorific values are between 225 °C and 250 °C where the increase is almost 3 MJ kg⁻¹. Subsequently, the increase between the 250 °C and 275 °C torrefaction temperatures is 1 MJ kg⁻¹. Weight loss at respective torrefaction temperatures showed similar time-dependent curves for all samples. Stoichiometric combustion analysis shows slight differences between original samples, but great differences after torrefaction processing. Stoichiometric combustion parameters also change proportionately with increasing temperature of torrefication. The resulting combustion balance figures show significantly lower need for mass of fuel in the case of the torrefied material for a given heat output thanks to the net calorific value being nearly doubled.

Key words: calorific value, heating value, elemental analysis, stoichiometry, heat output.

INTRODUCTION

Food processing industries, including fruit processing, generate significant amounts of waste, which have to be managed properly by recycling, incineration or landfilling (Aguilar et al., 2008). Citrus fruits crops are grown widely, producing over 120 million tons of oranges, lemons, grapefruits and mandarins worldwide (Ferreira-Leitao et al., 2010). They are harvested in many countries with tropical or subtropical climate, the principal producers being Brazil, China, Japan, Mexico, Pakistan, USA and countries of the Mediterranean region (Hernández-Montoya et al., 2009). In 2010 in Mexico alone, the orange production reached roughly 4 million tons, from which 40% (about 1.6 million tons of the total produced), are wet solid residues, corresponding approximately to 800,000 tons of dry residue (Lopez-Velazquez et al., 2013). Annually

in Italy, the juice and concentrated juice industries process 1.5 million tons of citrus fruit and 1 million tons of peel waste, 80% of which is produced in Sicily (Volpe et al., 2015). Citrus wastes, which are generated in juice production, are seen as a problematic but unavoidable waste (Lopez-Velazquez et al., 2013). Approximately, 50–60% of the processed fruit becomes citrus peel waste, which is composed of the peel, seeds and membrane residues left after juice extraction (Wilkins et al., 2007b). Until relatively recently, these waste products led to significant disposal problems, since there was no satisfactory means of disposal other than dumping on landfills. This led in some regions to the generation of large tracts of land contaminated with significant quantities of putrefying waste (Ángel Siles López et al., 2010). In general, the citrus fruit residues represent an abundant, inexpensive and readily available source of renewable biomass and their utilization is attracting increased interest worldwide. Orange peel is composed of cellulose, hemicellulose, lignin, pectin (galacturonic acid), chlorophyll pigments and other low-molecular weight compounds (e.g. limonene) (Pathak et al., 2017). Grapefruit peel contains several mono and disaccharides, the main ones being glucose, sucrose and fructose, as well as polysaccharides cellulose, hemicellulose and pectin (Ting & Deszyck, 1961; Wilkins et al., 2007a). Several authors recently studied pyrolysis and gasification of citrus peel wastes and their potential use as bio-fuel for electrical and thermal energy production (Aguiar et al., 2008; Miranda et al., 2009).

Pyrolysis is one of the most widely employed methods to convert biomass and organic residues into diverse products (Ranzi et al., 2008). Its application could diversify the energy supply in many situations, leading to a more secure and sustainable global energy supply chain (Lopez-Velazquez et al., 2013). Therefore, research on the pyrolysis process of various wastes is beneficial to better understanding of the pyrolytic processes and improving the products and their application as biofuels or raw materials for chemical industry (Mulligan et al., 2010). It has been studied largely on ligno-cellulosic plant biomass and wastes as a suitable sustainable way for production of conventional and new chemicals and fuels (Bridgwater & Peacocke, 2000; Kučerová et al., 2016). When biomass is employed for bioenergy, in some situations, pre-treatments of biomass are essential procedures for achieving higher efficiencies of fuel production or consumption. For example, after dewatering and drying, the calorific value of biomass is increased and the combustion efficiency of biomass is enhanced (Chen & Wu, 2009). Torrefaction is a type of pyrolytic treatment. In this process, raw biomass is heated in the temperature range of 200–300 °C under an inert or nitrogen atmosphere. Through torrefaction the properties of biomass can be improved to a certain extent (Chen & Kuo, 2011). The thermal treatment not only destructs the fibrous structure and tenacity of biomass, as well as increasing the calorific value, lowering oxygen to carbon ratio and moisture content. Generally, 80–95% of the energy and 70–90% of the dry mass of the biomass is retained in the torrefied product (Bates & Ghoniem, 2012). Also, after torrefaction the biomass has more hydrophobic characteristics and is more stable. This makes storage of torrefied biomass easier compared to non-torrefied biomass which will decompose in rate depending on storing conditions (Van der Stelt et al., 2011). Biomass properties can significantly influence both heat transfer and reaction rates during thermochemical treatment, the optimal operating conditions are highly variable (Zapata et al., 2009).

The aim of this paper was to evaluate fuel properties of the waste material from oranges and grapefruits before and after torrefaction. The contents of major elements as well as gross and net calorific value were determined. Stoichiometric parameters such as the theoretical amount of air for complete combustion and the amount of dry flue gas were determined and, also, the mass flow of the fuel depending on the desired heat output of the combustion device was determined.

MATERIALS AND METHODS

Sample preparation

Wastes from oranges and grapefruits were obtained from a company producing juices from fresh fruit and vegetable. There were two orange peel samples, orange peel 1 (*Citrus sinensis* Osbeck cv 'Valencia') and orange peel 2 (*Citrus sinensis* Osbeck cv but'Murcia'). The third sample was grapefruit peel (*Citrus paradise* 'Ruby red').

Prior to analysis, homogenous samples were prepared from the collected materials. Firstly, the materials were dried at room temperature for 7 days and after this period they were comminuted with RETSCH SM100 shear mill under the particle size of 1 mm.

Preparation of torrefied samples

Transformation of all samples by torrefaction process was performed in LECO TGA 701 thermogravimetric analyser under inert nitrogen atmosphere. For each of the samples, three measurements were made at three temperatures (225 °C, 250 °C and 275 °C) for 30 minutes. In each run, the samples were first dried at 105 °C to constant weight and then the furnace was filled with nitrogen and heated to target temperature with rate of 40 °C min⁻¹. During conversion of all samples, mass losses were monitored as time-dependent. Each sample was tested in triplicates for all conditions. The test sample size was 3 g each time. Analytical sample for each set of conditions was obtained after combining the three test samples and milling them to fine powder.

Moisture, ash, elemental composition and calorific value determinations

Investigated samples, namely orange peel 1 (OP 1), orange peel 2 (OP 2) and grape skins (GP), were analysed for moisture and ash contents, elemental composition, gross and net calorific value. Each parameter was tested at least in triplicate. Moisture and ash content were analysed in the LECO TGA 701 thermogravimetric analyser (TGA).

Determination of the elemental composition for the content of carbon (C), hydrogen (H) and nitrogen (N) was performed on a LECO CHN628+S analyzer by combustion method where the elements are measured in aliquote quantity of the flue gas. The carbon and hydrogen detection method is dispersed infrared absorption; nitrogen is detected using thermal conductivity cell. Oxygen was calculated as difference of the sum of ash and other elements from 100% on dry basis.

Gross calorific value was determined in isoperibol calorimeter LECO AC-600. The samples were pressed into pellets and then incinerated in a calorimetric bomb filled with oxygen to 3 MPa. The reference temperature was 28 °C. All measurements were repeated at least three times to obtain reliable results. Net calorific value was determined by calculation using elemental and proximate analyses. The calorimetric procedure and calculations were done according to ČSN ISO 1928:2010. Corrections for production of nitric and sulphuric acid were not determined.

Stoichiometric calculations

Combustion characteristics were calculated for all samples before and after torrefaction treatment. Stoichiometric calculations are recalculated to normal conditions (temperature $t = 0\text{ }^{\circ}\text{C}$ and pressure $p = 101.325\text{ kPa}$). In combustion calculation, the stoichiometric amount of oxygen O_{min} ($\text{m}^3\text{ kg}^{-1}$), the stoichiometric amount of dry air L ($\text{m}^3\text{ kg}^{-1}$), the stoichiometric amount of dry flue gas ($\text{m}^3\text{ kg}^{-1}$) and the theoretical amount of emission of CO_2 ($\text{m}^3\text{ kg}^{-1}$) have been determined for unit mass of fuel.

For each sample, the necessary mass flow rate of fuel to a combustion device is determined for required heat output. The efficiency of a generic combustion device was assumed to be 90% and the heat output was varied from 10 kW to 30 kW. The mass flow rate was calculated according to the equation:

$$\dot{m}_{pv} = \frac{P_k \cdot 100}{q_n \cdot \eta} \quad (1)$$

where \dot{m}_{pv} is the mass flow rate of fuel supplied into the combustion chamber (kg s^{-1}); P_k the heat output of the combustion device (W); q_n the net calorific value of the fuel (J kg^{-1}); η the efficiency of the combustion device (90%).

RESULTS AND DISCUSSION

In the biomass, the lowest ash content was measured in OP1, 3.42% wt. on dry basis. This is comparable with 2.94% wt. in orange peel in (Miranda et al., 2009), however, in (Stella Mary et al., 2016) the ash content in orange peel was $5.50 \pm 0.70\%$ on dry basis. The highest ash content was 4.41% wt. on dry basis in GP. Compared to wood these ash contents are ten times higher (Kučerová et al., 2016). The high ash content has a negative impact not only on the calorific value, but on the combustion process (Bradna et al., 2016). During torrefaction the ash content continually increases while the oxygen and, to a lower degree, hydrogen contents decrease. Table 1. shows the results of elemental analysis of orange and grapefruit peel samples before and after torrefaction at different temperatures. Although ash represents an incombustible portion of fuel, ash from biomass is a good source of various minerals and micronutrients to soil (Havrland et al., 2013; Pathak et al., 2017). The highest ash content was reached after torrefaction at 275 °C in OP 1 reaches 9.73%, OP 2 9.84% and Grapefruit peel 9.70%. Similar values were found by (Volpe et al., 2015), where the ash content in orange peel was 2.6 % wt. in original biomass and 8.7% wt. after slow pyrolysis at 650 °C.

When comparing the results of OP elemental analysis, Pathak et al. (2017), achieved very similar results, with the exception of higher proportion of oxygen (53.4% on dry basis). After torrefaction the oxygen content in both OP and GP samples decreased with rising treatment temperature, going to nearly 15% wt. at the temperature of 275 °C. Similar trend is true for hydrogen where the mass yield decreases with increasing torrefaction temperature to 35% at 275 °C.

As a consequence, the carbon content of OP and GP increases rapidly with increasing temperature, reaching a value of about 65% at a peak temperature of 275 °C. On the other hand, the nitrogen content of these samples remains almost constant. Similar results were determined in OP by Volpe et al. (2015), where the carbon content was 68% at 300 °C and in (Volpe et al., 2017), at temperature of 300 °C, the carbon content is 64.5%.

Table 1. Composition of orange peel (OP) and grapefruit peel (GP) before and after torrefaction treatment at varying temperatures and 0.5 h residence time (o.s. – original sample, d.b. – on dry basis, samples immediately after torrefaction are considered completely dry)

Sample	Water Content (% wt.)		Carbon (% wt.)	Hydrogen (% wt.)	Nitrogen (% wt.)	Oxygen (% wt.)	Gross Calorific Value (MJ kg ⁻¹)	Net Calorific Value (MJ kg ⁻¹)
	<i>W</i>	<i>A</i>						
OP 1, o.s.	69.52	1.04	14.38	1.81	0.31	12.91	5.57	3.47
OP 1, d.b.		3.42	47.19	5.94	1.01	42.37	18.26	16.97
OP 1 225 °C		6.54	57.60	5.09	1.58	29.10	21.91	20.80
OP 1 250 °C		7.78	62.99	4.69	1.88	22.57	24.66	23.64
OP 1 275 °C		9.73	67.05	4.46	2.04	16.64	25.60	24.63
OP 2, o.s.	68.51	1.26	14.72	1.86	0.37	13.26	5.65	3.57
OP 2, d.b.		4.01	46.74	5.90	1.18	42.11	17.95	16.66
OP 2 225 °C		6.63	57.47	5.12	1.77	28.92	22.15	21.04
OP 2 250 °C		8.36	63.52	4.69	2.12	21.22	24.90	23.88
OP 2 275 °C		9.84	67.38	4.52	2.25	15.93	25.95	24.97
GP, o.s.	69.99	1.32	14.26	1.80	0.36	12.25	5.48	3.38
GP, d.b.		4.41	47.51	5.99	1.20	40.82	18.27	16.96
GP 225 °C		6.67	57.96	5.10	1.76	28.43	22.19	21.07
GP 250 °C		8.67	62.97	4.76	2.01	21.51	24.40	23.37
GP 275 °C		9.70	66.75	4.57	2.18	16.72	25.64	24.64

Gross calorific value increased after the torrefaction process in proportion with increasing temperature. The net calorific value of the samples after torrefaction rose even more. The greatest difference in the net calorific value is between 225 °C and 250 °C, where the increase is almost 3 MJ kg⁻¹. Subsequently, the increase between the 250 °C and 275 °C torrefaction temperatures is only 1 MJ kg⁻¹. Similar results have been published, for example, by Volpe et al. (2015).

The mass loss curves for individual samples at different temperatures are shown in Fig. 1.

The mass loss of the samples shows a decreasing mass yield in relation to time for all the samples examined. Mass losses of the OP 1 and 2 samples show similar time-dependent curves. These curves are slightly shifted from each other due to different elemental composition, especially in the moisture of individual samples and ash content. Similar results were determined in (Volpe et al., 2015 & Volpe et al., 2017), where the treatment temperatures were in the range of 200–650 °C. For grapefruit peel samples, the weight losses are lower by approximately 10% compared with orange peel samples.

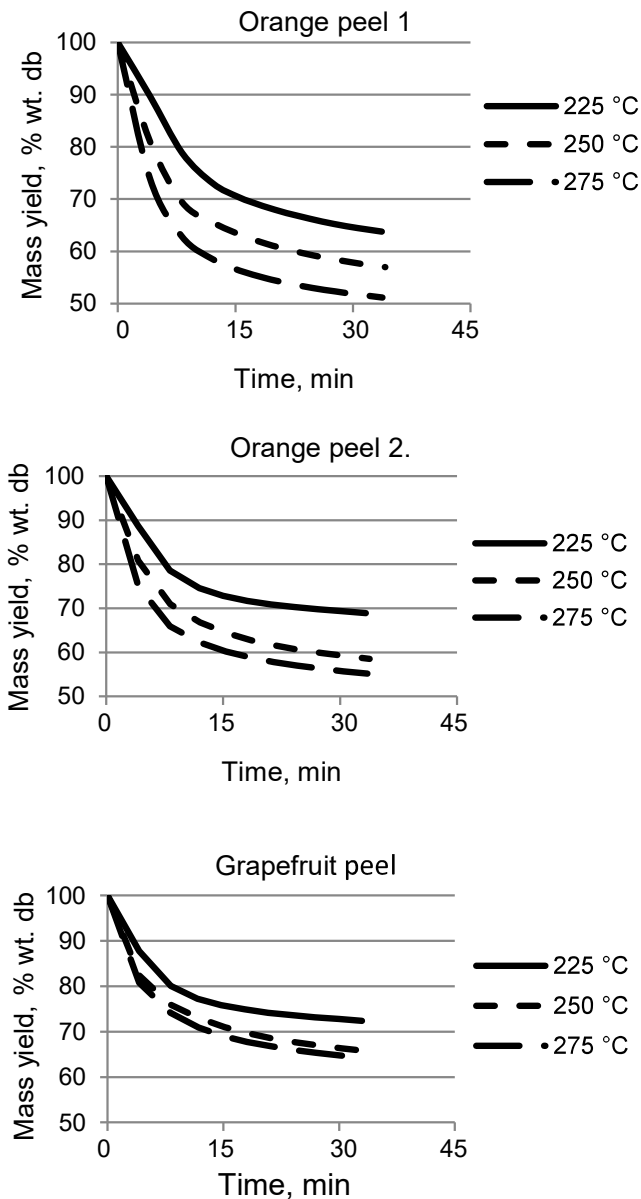


Figure 1. Mass loss curves of samples.

The results of stoichiometric analysis in Tables 2–4 show comparable values in the orange and grapefruit peels. However, in the torrefied samples the necessary volume of combustion air and subsequently created flue are increasing with each rise in torrefaction temperature. The resulting carbon dioxide emission concentrations also show that the properties of the processed samples change with temperature of torrefaction from the original biomass which has typically high concentration of CO₂ in flue gas (Malat'ák et al., 2017) and decrease to concentrations that correspond to the properties of coal (Vassilev et al., 2015). These stoichiometric parameters have a significant influence on

the total efficiency of combustion plants (Malat'ák & Bradna, 2017) and on emission concentrations. Similar results were obtained when evaluating the potential of waste biomass in (Brunerová et al., 2017).

Table 2. Stoichiometric amount of air and specific productions of flue gas components from combustion of orange peel 1

			OP 1 d.b.	OP 1 225 °C	OP 1 250 °C	OP 1 275 °C
L_{min}	Stoichiometric volume of air for complete combustion	($m^3 kg^{-1}$)	4.35	5.49	6.08	6.58
V_{sspmin}	Stoichiometric volume of dry flue gas	($m^3 kg^{-1}$)	4.28	5.37	5.93	6.40
V_{CO2}	Stoichiometric volume of CO_2	($m^3 kg^{-1}$)	0.88	1.07	1.17	1.25
V_{H2O}	Stoichiometric volume of H_2O	($m^3 kg^{-1}$)	0.83	0.79	0.76	0.76
V_{N2}	Stoichiometric volume of N_2	($m^3 kg^{-1}$)	3.40	4.30	4.76	5.57
CO_{2max}	Concentration of carbon dioxide in dry flue gas after stoichiometric combustion	(% vol.)	20.45	19.90	19.69	19.44

Table 3. Stoichiometric amount of air and specific productions of flue gas components from combustion of orange peel 2

			OP 2 d.b.	OP 2 225 °C	OP 2 250 °C	OP 2 275 °C
L_{min}	Stoichiometric volume of air for complete combustion	($m^3 kg^{-1}$)	4.31	5.49	6.18	6.65
V_{sspmin}	Stoichiometric volume of dry flue gas	($m^3 kg^{-1}$)	4.28	5.37	6.02	6.46
V_{CO2}	Stoichiometric volume of CO_2	($m^3 kg^{-1}$)	0.87	1.07	1.18	1.25
V_{H2O}	Stoichiometric volume of H_2O	($m^3 kg^{-1}$)	0.83	0.79	0.77	0.77
V_{N2}	Stoichiometric volume of N_2	($m^3 kg^{-1}$)	3.37	4.30	4.84	5.21
CO_{2max}	Concentration of carbon dioxide in dry flue gas after stoichiometric combustion	(% vol.)	20.45	19.90	19.58	19.35

Table 4. Stoichiometric amount of air and specific productions of flue gas components from combustion of grapefruit peel

			GP d.b.	GP 225 °C	GP 250 °C	GP 275 °C
L_{min}	Stoichiometric volume of air for complete combustion	($m^3 kg^{-1}$)	4.44	5.55	6.13	6.58
V_{sspmin}	Stoichiometric volume of dry flue gas	($m^3 kg^{-1}$)	4.36	5.42	5.97	6.39
V_{CO2}	Stoichiometric volume of CO_2	($m^3 kg^{-1}$)	0.88	1.08	1.17	1.24
V_{H2O}	Stoichiometric volume of H_2O	($m^3 kg^{-1}$)	0.84	0.79	0.77	0.77
V_{N2}	Stoichiometric volume of N_2	($m^3 kg^{-1}$)	3.48	4.35	4.80	5.15
CO_{2max}	Concentration of carbon dioxide in dry flue gas after stoichiometric combustion	(% vol.)	20.21	19.83	19.55	19.37

Table 5 shows the necessary mass flow rate of the fuel for a desired heat output. The heat output displayed from small household devices (20 kW) up to medium-sized combustion devices (300 kW). The mass flow rate of fuel decreases with the increasing torrefaction processing temperature. This decrease arises from increase in the net calorific value.

Table 5. The mass flow rate of fuel to the combustion device for given heat output

Sample	Heat output (kW)			
	20	50	100	300
OP 1, d.b.	4.71	11.79	23.58	70.74
OP 1 225 °C	3.84	9.61	19.23	57.69
OP 1 250 °C	3.38	8.46	16.92	50.76
OP 1 275 °C	3.24	8.12	16.24	48.72
OP 2, d.b.	4.80	12.00	24.00	72.02
OP 2 225 °C	3.80	9.50	19.01	57.05
OP 2 250 °C	3.35	8.37	16.75	50.25
OP 2 275 °C	3.20	8.01	16.02	48.07
GP, d.b.	4.71	11.79	23.58	70.74
GP 225 °C	3.80	9.50	19.01	57.04
GP 250 °C	3.42	8.56	17.12	51.36
GP 275 °C	3.24	8.11	16.23	48.69

CONCLUSIONS

Fuel parameters of orange and grapefruit peel before and after torrefaction treatment show considerable changes. Torrefaction is generally able to produce a superior fuel compared to original biomass, most notably by increasing the calorific value and decreasing oxygen content. In the studied materials and within the tested conditions, the highest net calorific value is reached in orange peel torrefied at 275 °C for 0.5 h. While increasing the torrefaction temperature, the increase in calorific value is greater at lower temperature ranges: 2.7 MJ kg⁻¹ between 225 °C and 250 °C versus 1.1 MJ kg⁻¹ between 250 °C and 275 °C as averages in all samples. In contrast to beneficial effects, torrefaction also has a detrimental effect in raising the ash content. Grapefruit peel, which had 4.41% wt. ash in dry state, reaches 9.7% wt. after torrefaction at 275 °C and 0.5 h residence time. Such a high ash content limits the use of torrefied fuel at least in some areas, e.g. in small home devices. The three citrus peel samples showed similar behaviour during torrefaction in weight loss and in the composition change. Therefore, it can be assumed that in practice most sources of citrus peel would be of similar value for torrefaction treatment. The results of the stoichiometric calculations show minor differences between the original materials but significant differences between them and the torrefied samples. In energy utilization of torrefied biomass this would mean significantly different combustion characteristics and possible need to adjust the combustion device. For example, the mass flow rate of fuel for a particular heat output decreases with its rising calorific value and therefore also depends on the treatment conditions. The theoretical calculations show considerable savings in the

weight of fuel in the case of torrefied materials due to the rising net calorific value. This would lead to decrease in cost associated with the transport and storage of fuel.

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