

Torrefaction of Solid Olive Mill Residue

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Solid olive mill residue (SOMR), a lignocellulosic material obtained from olive oil extraction, is a potential attractive source of biomass for energy generation. Although SOMR can be directly combusted, a pretreatment can reduce the oxygen and moisture contents of raw SOMR for efficient energy generation. Torrefaction is a promising thermal pretreatment method for improving fuel characteristics of raw SOMR. In this study, torrefaction characteristics of SOMR were investigated at three different torrefaction temperatures and holding times. Ultimate and proximate analysis results of torrefied SOMR were compared with dried SOMR. Results indicate that an increased torrefaction temperature and holding time can lead to a more qualified solid fuel with higher carbon content, increased higher heating value (HHV), and reduced oxygen content. Further, increased HHV and removal of volatiles are indicators of more energy-dense solid fuel obtained from SOMR. Experimental results revealed that moderately severe torrefaction conditions with holding times not exceeding 30 minutes are suitable for torrefaction of SOMR.

Keywords: Biomass; Energy; Torrefaction; Solid olive mill residue; Pretreatment

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INTRODUCTION

Torrefaction is a thermo-chemical process for upgrading cellulosic biomass into a more homogeneous fuel that can be utilized in other conversion processes for energy purposes (Quang-Vu *et al.* 2014). Torrefaction was first studied in France in the early 1930s for upgrading fuel properties of biomass (Van der Stelt *et al.* 2011). The process is also known as mild pyrolysis. Torrefaction occurs at 200 to 300 °C under an inert atmosphere with slow heating rates of less than 50 °C min⁻¹ (Deng *et al.* 2009). Although there exist torrefaction studies conducted with heating rate of 50 °C min⁻¹ (Li *et al.* 2012), slow heating rate is important for the homogeneity of products (Fang 2013). Torrefaction can be divided into two categories according to torrefaction temperature, namely light torrefaction and severe torrefaction. Light torrefaction occurs at temperatures less than 240 °C, whereas severe torrefaction occurs above 270 °C (Rousset *et al.* 2011).

Wood is the fundamental source of biomass all over the world and, like all other thermo-chemical processes, its torrefaction has been a topic of major research interest (Prins *et al.* 2006a,b; Eseltine *et al.* 2013). Besides wood, torrefaction of several biomass types such as bamboo (Rousset *et al.* 2011), wheat straw (Shang *et al.* 2013), rice straw (Huang *et al.* 2012), sewage sludge (Atienza-Martinez *et al.* 2013), and red oak (Carrasco *et al.* 2013) have been studied extensively. Torrefaction experiments with different biomass samples have shown that torrefaction provides solid hydrophobic fuel with reduced moisture content (Felfri *et al.* 2005; Sadaka and Negi 2009), increased energy density (Prins *et al.* 2006a; Yan *et al.* 2009; Rousset *et al.* 2011), and increased higher heating

value (HHV) (Bridgeman *et al.* 2008; Couhert *et al.* 2009; Deng *et al.* 2009; Yan *et al.* 2009). Previous experimental studies with agricultural (Uemura *et al.* 2011; Li *et al.* 2012), and woody (Prins *et al.* 2006a,b) biomass have shown that, in order to reach the above listed characteristics of torrefaction, the torrefaction temperature and the holding time are considered to be critical parameters. Moreover, the differing composition of each biomass sample brings about the necessity of investigating the torrefaction characteristics of each sample separately.

As mentioned earlier, SOMR is an agricultural residue obtained from olive oil extraction. It is estimated that 900 million olive trees cover over 10 million hectares worldwide (Sesli and Yeğenoğlu 2009). Dermechea *et al.* (2013) stated that Mediterranean countries produce approximately 2.5 million metric tons/year olive oil. During the olive oil extraction process 200 kg of oil and 400 kg of SOMR are produced for each ton of olive (Sadeghi *et al.* 2010).

SOMR is a lignocellulosic material that contains high amount of xylans (Sánchez *et al.* 2014), and its open disposal causes environmental harm (Dermechea *et al.* 2013). SOMR has a non-homogenous structure. The chemical composition of SOMR varies according to the olive species, culture conditions, origin of the olives, and extraction process (Dermechea *et al.* 2013). SOMR mainly consists of water, seed, pulp (Gomez-Munoz *et al.* 2012), and olive stone (Lopez *et al.* 2000; Doymaz *et al.* 2004).

SOMR is an important source of biomass that has attracted much research interest. Ergüder *et al.* (2000), and Tekin and Dalgıç (2000) investigated anaerobic treatment of solid olive mill residue and showed that methane production potential of SOMR is poor. Also pyrolysis (Jauhiainen *et al.* 2004; Özveren and Özdoğan 2013) and gasification (Vera *et al.* 2011) characteristics of SOMR have been investigated widely. Torrefaction is an important pretreatment for SOMR for purposes of producing more qualified fuel that can be stored without degradation. Also it is known that torrefaction provides more efficient gasification (Prins *et al.* 2006c) and pyrolysis (Meng *et al.* 2012).

In this work, torrefaction of SOMR was conducted at three different torrefaction temperatures and holding times. Torrefaction temperatures were selected for the identification of the effects of light and severe torrefaction on raw SOMR. The fact that the reactivity of biomass drops around 1 to 2 h was considered when choosing a holding time (Van der Stelt *et al.* 2011; Brachi *et al.* 2015). Therefore, torrefaction was performed at 210, 240, and 280 °C for 30, 60, and 120 min, respectively. The ultimate and proximate analyses of torrefaction products were conducted, and results were compared with those of raw SOMR. Additionally, thermogravimetric analysis (TGA) and the derivative thermogravimetric analysis (DTG) of raw SOMR were conducted in order to clarify the decomposition characteristics of SOMR.

EXPERIMENTAL

The SOMR used in this work was supplied by the local Aydın Olive Mill Company (a 3-phase olive mill), based in Cyprus. The moisture content of SOMR from a 3-phase olive mill was generally in the range 40 to 45% (Alba *et al.* 2001). The ultimate and the proximate analysis results of the oven-dried raw SOMR are given in Table 1. Thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) of raw SOMR were also conducted to obtain thermal decomposition characteristics of SOMR. The Mettler Toledo TGA/DSC 1 Star System (Switzerland) was used for TGA. The TGA

analysis was conducted under inert atmosphere. Nitrogen was used as inert gas, and the sample was heated by rate of 20 °C/ min. TGA and DTG analysis results of raw SOMR are shown in Fig. 1. Figure 1 shows that loss of moisture and light volatiles decreased constantly up to 200 °C. Mass reduction became more significant between 270 °C and 485 °C, where severe devolatilization occurred.

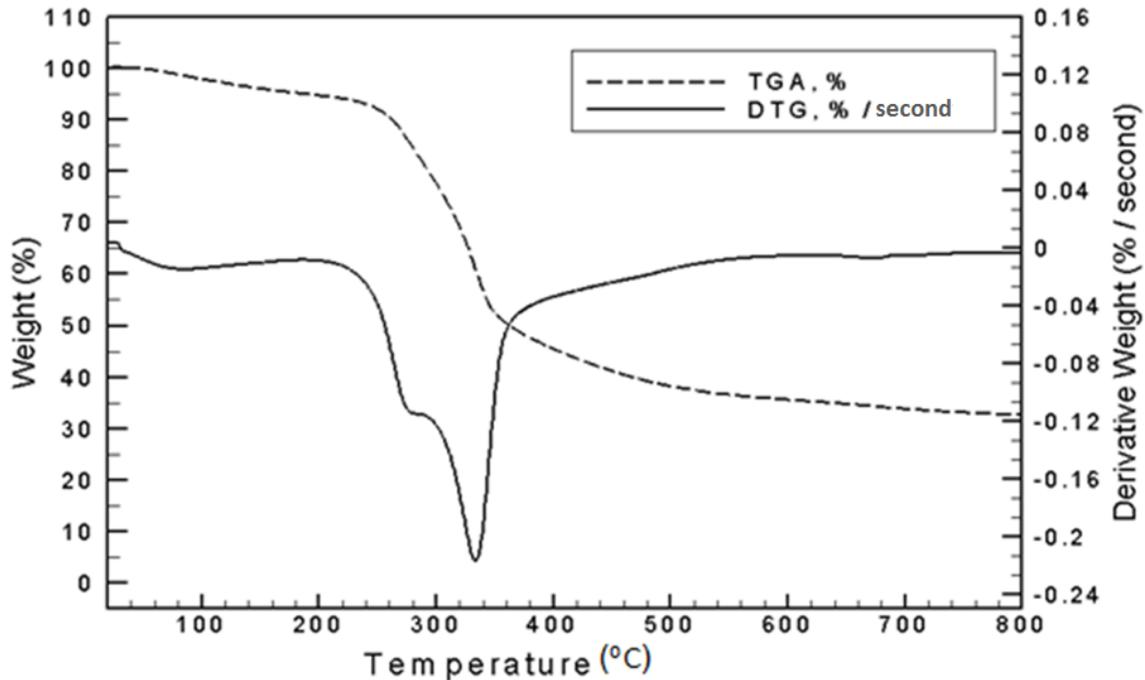


Fig. 1. TGA and DTG diagrams of dried SOMR

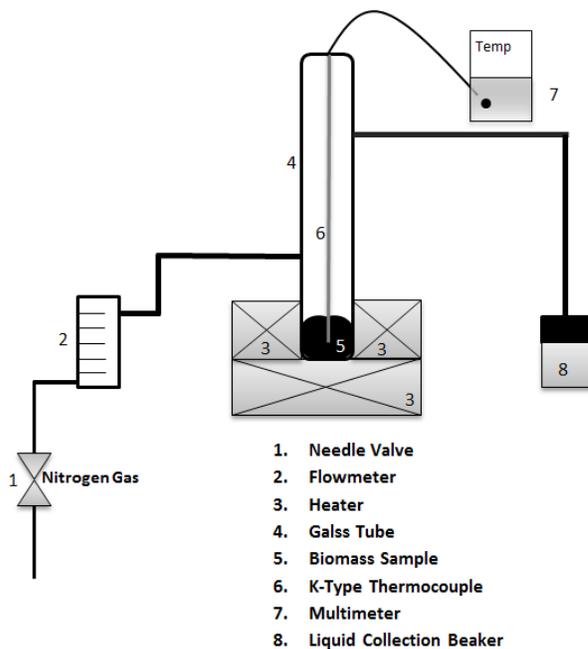


Fig. 2. Torrefaction equipment

Torrefaction experiments were conducted with dry SOMR. Raw SOMR was dried at 105 °C until the mass reached a stable point before torrefaction treatment. Torrefaction equipment used in this work consisted of a glass tube and electric heater, as detailed in Fig. 2. The glass tube, with radius of 0.02 m and height of 0.29 m, was placed into the electric heater, which has a depth of 0.065 m. The electric heater was adjusted to heat the samples to the desired torrefaction temperatures. A K-type thermocouple was also inserted into the glass tube for measuring the torrefaction temperature inside the tube. Each torrefaction experiment was conducted with 3 g of SOMR in order to have a homogenous temperature inside the glass tube.

During the torrefaction experiments SOMR was heated 15 °C/min. After reaching the desired torrefaction temperature SOMR was kept at this temperature for different holding times, which were 30, 60, or 90 min. Then, the torrefaction products were left for natural cooling in a desiccator. The heating and cooling times are not included in the holding time.

Dry SOMR was manually crushed before torrefaction processes and sieved by using 1 and 2 mm sieves. The particle size of used raw SOMR was in the range of 1 to 2 mm. The process was carried out under a nitrogen flow of 20 mL/min. In order to deplete the glass tube of any oxygen before starting the process, 50 mL/min of nitrogen was passed through for 10 min. Each torrefaction experiment was repeated twice, and results are given as the average of the two experiments where the results did not deviate more than 5%.

The elemental composition of torrefaction products and dry SOMR were obtained from ultimate analysis. Thermo Finnegan Flash EA 1112 Series Element Analyzer (Italy) was used to measure carbon (C), hydrogen (H), and nitrogen (N) in wt%. Oxygen (O) was determined from the difference for dry ash free basis (daf). Volatile matter (VM), fixed carbon (FC), and ash content composition of the torrefaction products were determined by proximate analysis in wt%. The proximate analysis was carried out in a muffle furnace. In this study, mass yield, energy yield, and HHV (MJ/kg) (Demirbaş *et al.* 1996) of the torrefaction products were calculated using the following Eqs. 1 through 3,

$$\text{Mass Yield} = \frac{\text{Mass of Torrefied SOMR}}{\text{Mass of Dried SOMR}} \quad (1)$$

$$\text{Energy Yield} = \text{Mass Yield} \times \frac{(\text{HHV})_{\text{Torrefied SOMR}}}{(\text{HHV})_{\text{Raw SOMR}}} \quad (2)$$

$$\text{HHV} = 0.335 \text{ C}(\text{wt}\%) + 1.42\text{H}(\text{wt}\%) - 0.154 \text{ O}(\text{wt}\%) - 0.145 \text{ N}(\text{wt}\%) \quad (3)$$

where energy yield and HHV of torrefaction products were calculated in dry ash free basis.

Table 1. Ultimate and Proximate Analysis Results of Dry SOMR (*daf, **db)

	C* (wt%)	H* (wt%)	N* (wt%)	O* (wt%)	Ash* (wt%)	VM** (wt%)	FC** (wt%)	HHV* (MJ/k)	Cellulose (wt%)***	Hemi- Cellulose (wt%)***	Lignin (wt%) ***
SOMR	49.68	6.78	1.93	41.69	4.20	88.84	6.96	18.8	17.37- 24.14	7.92- 11.00	0.21- 14.18

*** (Dermechea, 2013)

RESULTS AND DISCUSSION

Mass Yield

Mass yields of the torrefaction products were calculated by using Eq. 1 on a dry basis. The changes in mass yield with different torrefaction temperatures and holding times are presented in Fig. 3. Mass yield decreases with increased torrefaction temperatures and holding time. Results indicated that at torrefaction temperature of 210 °C, increasing holding time from 30 min to 60 min did not alter the mass yield. However, at a torrefaction temperature of 240 °C mass yield was significantly reduced when holding time is increased from 30 to 60 min. In contrast, at 240 °C the mass yield of torrefied SOMR was not remarkably affected when holding time was increased from 60 to 120 min. Figure 3 clearly indicates that changes in the holding time did not remarkably alter the mass yield under the more severe torrefaction conditions, *i.e.* at 280 °C. The deviation in the mass yield of the torrefaction products was no more than 5% at 280 °C for all holding times.

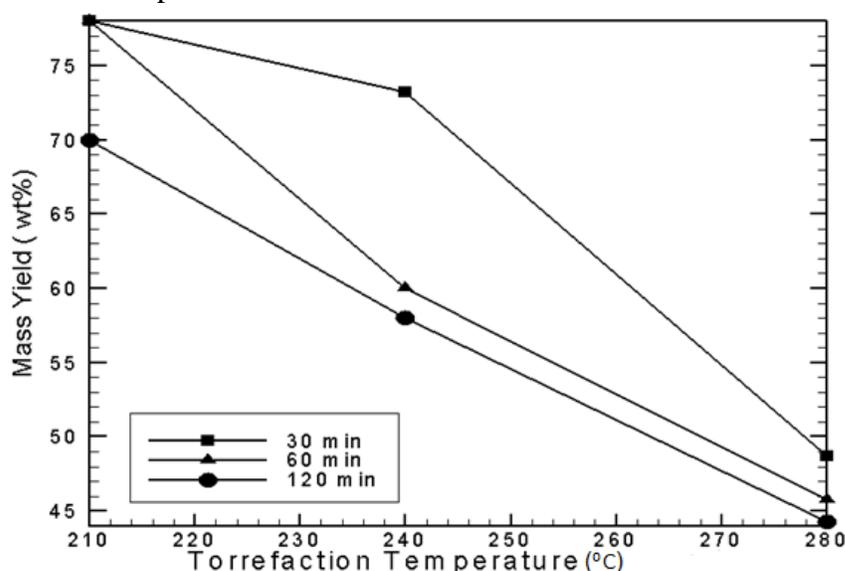


Fig. 3. The effect of torrefaction temperature and holding time on mass yield

Reduced mass yield during the torrefaction process can be mainly attributed to loss of bound moisture and thermal degradation to form volatile products such as H₂O, CO, CO₂, H, acetic acid, and other organics (Prins *et al.* 2006c). Studies on isothermal (Chen and Kuo 2011b) and non-isothermal torrefaction (Chen and Kuo 2011a) of cellulose, hemicellulose, lignin, and xylan revealed that hemicellulose degrades at torrefaction temperatures as low as 230 °C, whereas lignin does not become substantially degraded even at high torrefaction temperatures. However, these studies showed that xylan is the most reactive constituent of biomass and that it is depleted by whatever the type of performed torrefaction process.

In this study, mass loss during torrefaction of SOMR at 210 °C was mainly due to the removal of bound water, which evaporates at around 160 °C (Bhaskar and Pandey 2015). The removal of bound water is significantly observed in TGA curve as well around 162 °C. Additionally, mass loss at 210 °C is associated with removal of the light volatiles and decomposition of xylan. Increased mass loss at 240 °C was associated with the degradation of hemicellulose, and degradation of cellulose also contributed to mass loss at 280 °C (Chen and Kuo 2011a,b).

The results from the TGA and DTG analyses showed that mass of raw SOMR was remarkably reduced in range of 200 to 280 °C. TGA results revealed that 84% of SOMR remained when the temperature reached 280 °C. Chen and Kuo (2011b) showed that when cellulose and hemicellulose are torrefied isothermally, increasing holding time up to 60 minutes remarkably reduces the mass yield. In this work the lowest mass yield was obtained when SOMR was torrefied at the severe torrefaction conditions for 120 minutes, as expected. However, consistent with the work of Chen and Kuo (2011b), increasing holding time from 60 min to 120 min did not alter the mass yield more than 2% under severe torrefaction conditions.

The Ultimate Analysis of the Torrefaction Products

Ultimate analysis results of solid torrefaction products for various torrefaction conditions are listed in Table 2. Experimental results indicated that the hydrogen and oxygen contents of solid torrefaction products became reduced with increased torrefaction temperature and holding time, whereas the carbon content was shown to increase.

Reduced hydrogen and oxygen content is mainly associated with destroyed hydroxyl group (-OH) of the biomass feedstock during the torrefaction process (Bergman *et al.* 2005; Phanphanich and Mani 2011). Loss of the hydroxyl group (-OH) results in a solid hydrophobic fuel with decreased hydrogen and oxygen contents. Besides changes in elemental composition, it is important to detect changes in H/C and O/C atomic ratios of solid torrefaction products. Reduced H/C and O/C atomic ratios are measures of pyrolysis efficiency and degree of oxidation, respectively (Schmidt *et al.* 2001; Nguyen *et al.* 2004).

Table 2. Ultimate Analysis of Torrefied SOMR (*daf)

Holding Time (min)	Temperature(°C)	C*(wt%)	H*(wt%)	N*(wt%)	O*(wt%)	HHV*(MJ/kg)
30	210	52.39	6.67	1.74	39.20	20.74
	240	57.65	6.29	1.74	34.32	22.70
	280	68.25	5.58	1.19	24.98	26.76
60	210	54.04	6.56	1.56	37.84	20.65
	240	61.69	5.98	1.46	30.87	24.20
	280	67.62	5.35	0.83	26.20	26.09
120	210	59.32	6.33	0.83	33.52	23.58
	240	63.64	5.76	1.74	28.86	24.80
	280	70.23	5.40	1.51	22.86	27.45

Also, reduced O/C ratio is a potential indicator of both hydrophobicity and polarity, where a decrease in polar surface groups results in a reduction of affinity of the fuel with water molecules (Manya 2012). Figures 4 and 5 show the effect of the torrefaction temperature and holding time on H/C and O/C atomic ratios, respectively. Reduced H/C and O/C atomic ratios imply increases in hydrophobicity and torrefaction efficiency with increased torrefaction temperature and holding time.

The ultimate analysis results indicated that, under the severe torrefaction conditions, the effect of torrefaction temperature on the elemental composition was much more significant compared to holding time. Van-Krevelen diagram of a solid fuel demonstrates the change in H/C atomic ratio as a function of O/C ratio.

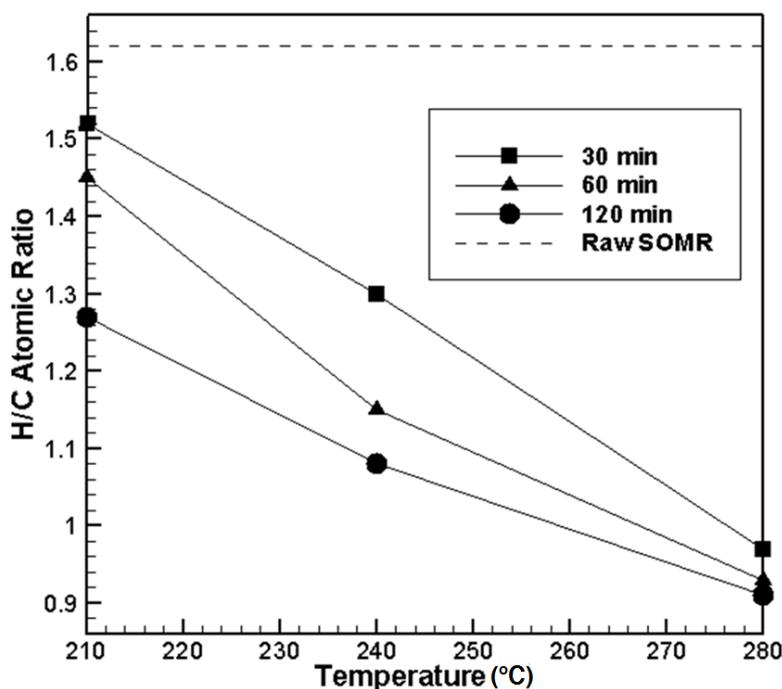


Fig. 4. The effect of torrefaction temperature and holding time on H/C atomic ratio of torrefied SOMR

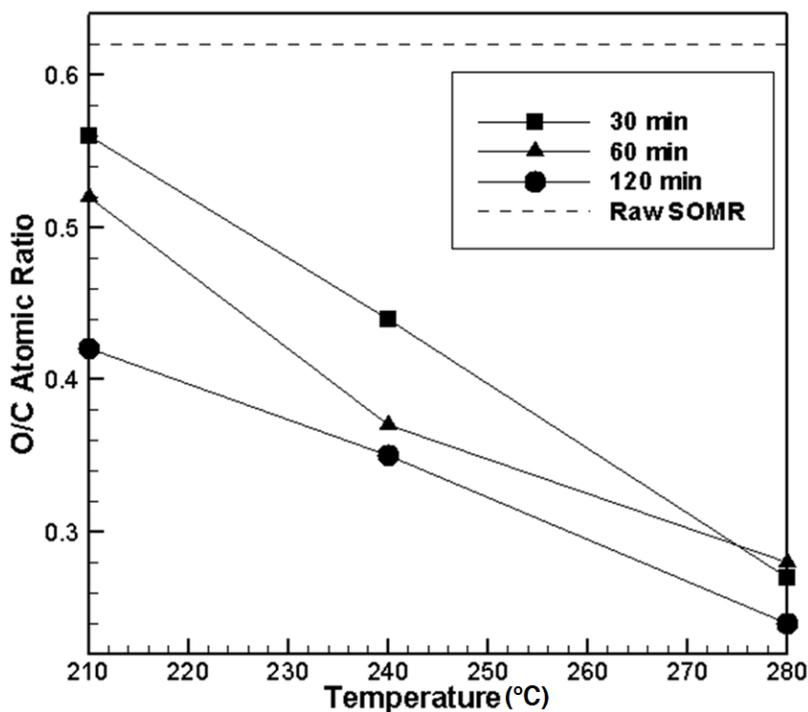


Fig. 5. The effect of torrefaction temperature and holding time on O/C atomic ratio of torrefied SOMR.

The Van-Krevelen diagram of torrefaction products is presented in Fig. 6. Besides torrefied SOMR, other torrefied biomass samples and three different coal types (Zap

Lignite, Dietz, and Utah Hindawi coal) were also included in the diagram. In this work, the Van-Krevelen diagram is used to identify similarities and differences between torrefaction characteristics of SOMR and other types of biomass. Torrefied biomass samples used for comparing torrefaction behavior of SOMR were all torrefied for 30 min. Also, the torrefaction temperatures of those biomass did not deviate by more than 10 °C from the temperatures used for torrefaction of SOMR.

Figure 6 shows that torrefied SOMR behaves similarly to other types of torrefied biomass by means of reduction in both H/C and O/C ratios (Bergman *et al.* 2005; Kim *et al.* 2012; Wu *et al.* 2012). However, the results point out that SOMR became torrefied much more efficiently compared to other types of biomass, and less oxygenated fuel was obtained. It is estimated that relatively less oxygen content of torrefied SOMR is a result of high volatile content of raw SOMR. It is well known that the oxygen bound in volatiles are removed during torrefaction (Capareda 2013).

An important difference in the torrefaction characteristics of SOMR compared to other biomass was also detected. Results revealed that torrefaction of SOMR provides a solid fuel, of which the H/C and O/C atomic ratios were very close to low rank zap lignite coal when torrefied at 280 °C for 120 min.

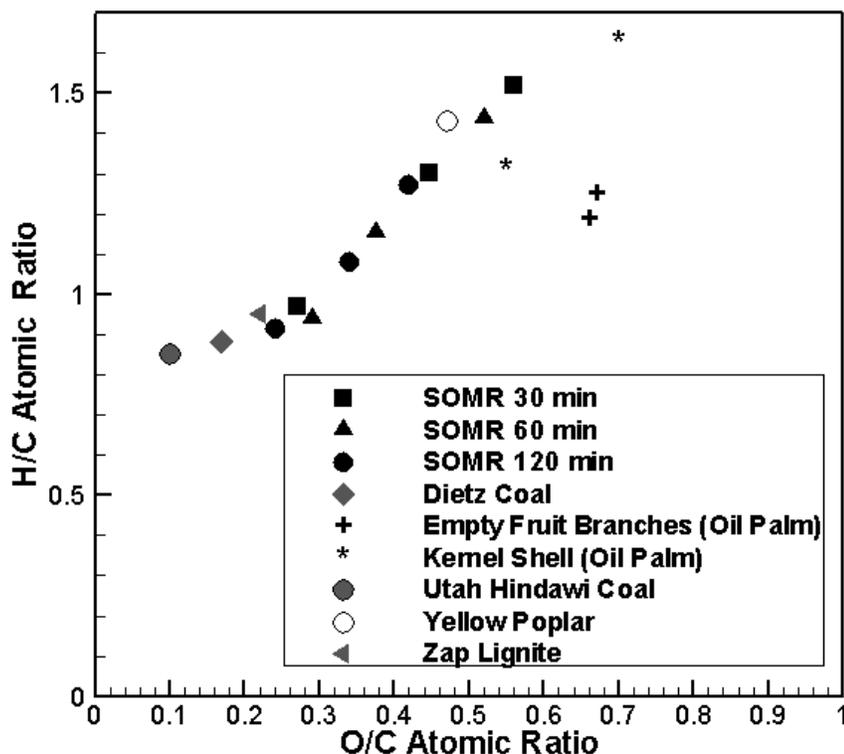


Fig. 6. Van-Krevelen diagram for dried SOMR, torrefied SOMR, and various torrefied biomass (Ma 1996; Bergman *et al.* 2005; Uemura *et al.* 2011; Kim *et al.* 2012)

The Proximate Analysis of the Torrefaction Products

The proximate analysis of torrefaction products of SOMR is given in Table 3. The experimental results show that FC and ash content increased with increasing torrefaction temperature and holding time, whereas VM content showed a different trend. High ash content inhibits the combustion of fuel because oxygen may not penetrate through the ash easily for burning (Syamsiro *et al.* 2012). The non-homogenous structure of SOMR resulted in lower ash content at the torrefaction temperatures 210 °C (for 30 and 60 min)

and 240 °C (for 30 min). However, it must be pointed out that the ash content of torrefied SOMR for all torrefaction conditions was still lower than the standards specified for barbecue charcoal (European Standards 2005). Also, reduction in volatile matter content yields a more qualified solid fuel because complete combustion of volatile matter leads to dark smoke, heat loss, and pollution hazards (Patel and Gami 2012). The proximate analysis results of torrefied SOMR reveals that both torrefaction temperature and holding time changes the FC, VM, and ash composition of products.

Table 3. Proximate Analysis of Torrefied SOMR(*db)

Holding Time (min)	Temperature(°C)	VM*(wt%)	Ash*(wt%)	FC*(wt%)
30	210	84.14	3.33	12.53
	240	68.35	3.67	27.98
	280	61.33	4.73	33.94
60	210	80.01	3.50	16.49
	240	67.11	4.66	28.23
	280	61.39	6.55	32.06
120	210	79.05	4.29	16.66
	240	61.28	5.84	32.88
	280	53.71	7.2	39.09

Higher Heating Value and Energy Yield of Torrefied SOMR

The HHV of all solid torrefaction products are given in Table 2 in dry ash free basis. Results indicated that the HHV of solid torrefaction samples increased with increasing torrefaction temperature and holding time. This phenomenon can be linked to reduced number of C-O bonds and increased number of C-C bonds during the torrefaction process (Wu *et al.* 2012).

Finally, the energy yield calculation was performed in dry ash-free basis. Energy yield can be considered as the main indicator of the amount of energy lost after torrefaction (Wannapeera *et al.* 2011). The energy yield of torrefaction products strongly depends on mass yield, which is directly linked to biomass type (Uemura *et al.* 2011; Kim *et al.* 2012). The effect of change in torrefaction temperature and holding time on energy yield obtained from the torrefaction products is shown in Fig. 7 on a dry ash-free basis. Energy yielded by torrefied SOMR ranged from 60.09% to 85.68%. The energy yield gradually decreased with increasing torrefaction temperature and dropped below 70% at 280 °C. However, an unexpected increase in energy yield was observed due to the non-homogenous chemical composition of SOMR when torrefied at 240 °C for 30 min. Similar behaviors have also been observed during the torrefaction of sawdust (Li *et al.* 2012), mesocarp fiber of oil palm waste, and kernel shell of oil palm waste (Uemura *et al.* 2011).

Optimum Torrefaction Conditions for SOMR

The properties of torrefaction products were used for specifying optimum torrefaction conditions of SOMR. The parameters evaluated for the optimization of torrefaction conditions were HHV, rate of change in carbon content, oxygen content, H/C ratio, O/C ratio, energy yield, and also proximate analysis results.

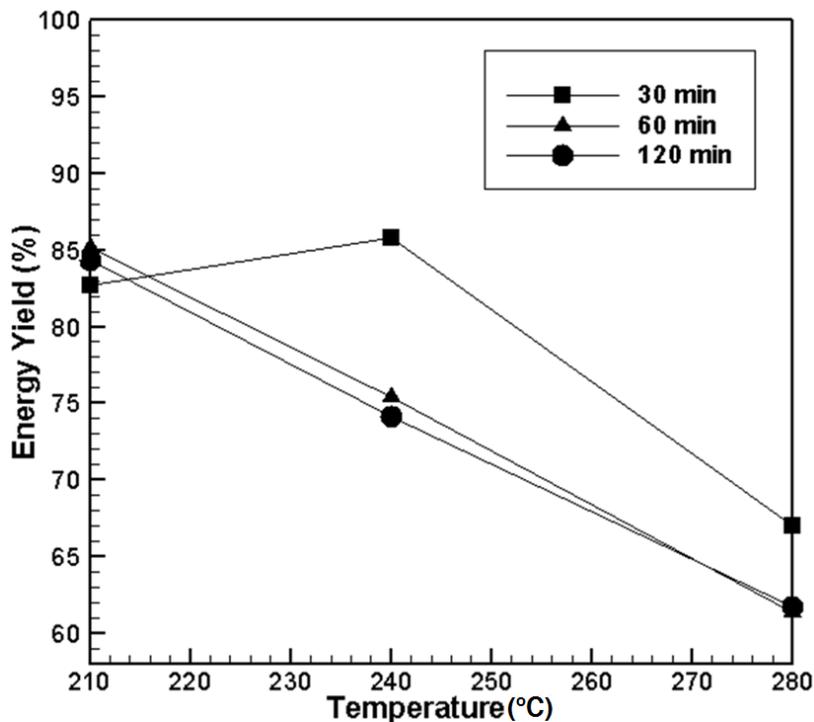


Fig. 7. The effect of torrefaction temperature and holding time in energy yield of torrefied SOMR

Experimental results indicated that the effect of temperature was much more significant than the effect of holding time, especially in terms of elemental composition after torrefaction. The greatest changes in HHV, O/C ratio, H/C ratio, carbon content, and oxygen content of torrefaction products were obtained at 280 °C, where all contributed to the upgrading of the quality of SOMR as fuel. However, results showed that at 280 °C, HHV, carbon content, and oxygen content were very similar for all torrefaction products at holding times of 30, 60, and 120 min. Similarly, a comparison of H/C ratios of torrefaction products revealed that process efficiencies were very similar at all holding times at 280 °C. The H/C ratio of products was only 5% less at 120 min compared to 30 and 60 min. The O/C ratio of products at 280 °C was approximately 10% lower at 120 minutes than that obtained at 30 and 60 min.

Proximate analysis results showed that torrefaction at 280 °C for 30 and 60 min yielded solid fuel that had very similar volatile matter, fixed carbon, and ash contents. Volatile matter, fixed carbon, and ash content of torrefied SOMR did not deviate more than 3% for both holding times. For a holding time of 120 min at 280 °C, changes in volatile matter, fixed carbon, and ash content of the products were 7.61%, 2.47%, and 5.15%, respectively, compared to 30 min.

The energy yield of the process is a measure of chemical energy stored in the solid products of the process. It was found that 40% of the chemical energy was lost when the holding time exceeded 30 min.

This study revealed that more qualified solid fuel can be produced under severe torrefaction conditions from SOMR. Also, holding times not exceeding 30 min are sufficient to obtain qualified, energy-dense, and hydrophobic solid fuel from SOMR.

CONCLUSIONS

1. Torrefaction characteristics of solid olive mill residue (SOMR) were experimentally investigated at three different torrefaction temperatures and holding times. The effects of the torrefaction temperature and the holding time on SOMR samples were precisely studied.
2. Ultimate analysis results of torrefied SOMR showed that the elemental composition of the products changes remarkably with an increase in the torrefaction temperature. However, the effect of holding time on the elemental composition of the products is less significant.
3. The proximate analysis results indicate that increasing holding time and torrefaction temperature results in reduced volatile matter content and increased ash and fixed carbon content. Results showed that both holding time and torrefaction temperature have significant effect of proximate composition of torrefaction products.
4. Torrefaction of SOMR at 280 °C for 120 min provides a solid fuel in which the H/C and the O/C atomic ratio are very close to low rank zap lignite coal.
5. A torrefaction temperature of 280 °C and a holding time of 30 min are the optimum torrefaction conditions among all considered torrefaction temperatures and holding times tested.

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