Microwave Assisted Torrefaction of Plant Biomass of Different Origin with a Focus on Solid Products Valorisation for Energy and Beyond

Anna Andersone[a], Alexandr Arshanitsa[a*],Yegor Akishin[a],Aleksandr Semenischev[b], Galina Telysheva[a]

[a]Latvian State Institute of Wood Chemistry, 27 Dzerbenes street, Riga, LV-1006, Latvia
[b]Ekokompozit Ltd., 27 Dzerbenes street, Riga, LV-1006, Latvia
arshanica@edi.lv

In the present paper, the microwave-assisted torrefaction of three types of the most widely spread lignocellulosic biomass feedstock, namely, wood, wheat straw, and peat, in the form of commercial fuel pellets, was studied using a laboratory-scale microwave torrefactor of original design. The torrefaction process, at temperatures varied in the range of 175-300 °C, was on-line monitored in terms of energy consumption and the temperature of the treated pellets. Elemental analysis, thermogravimetric analysis, Py-GC/MS and FTIR spectroscopy were used to characterize the biomass transformation and confirmed the simultaneous development of destruction and condensation processes in lignocarbohydrate complexes at microwave treatment. Torrefaction promoted the increase in the calorific value of all treated biomass. Higher heating values of the treated solid biomass compared to non-treated softwood, wheat straw, and peat increased by 24 %, 42 %, and 31 %, respectively. Biomass weight loss significantly depends on the structure and chemical composition of lignocellulosic matrixes of different origin. Wheat straw revealed itself as the most thermodegradable material. Therefore, although wheat straw had the highest calorific value, the overall output/input energy balance for the process of wheat straw torrefaction was less beneficial in comparison with that of peat and softwood. The microwave-assisted torrefaction promoted the increase in the hydrophobicity of the material and the improvement of its surface characteristics. Therefore, the possibility of torrefied biomass application as a natural sorbent for oil-derived products from the water surface was proposed.

1. Introduction

Today, torrefaction or low-temperature pyrolysis is recognized as a key route for increasing the potential of plant biomass for large-scale production of renewable solid fuel with high energy density. The potential application of torrefied biomass includes small scale residential boilers, district heating systems (Kostas et al., 2017), and large power producers using co-firing technologies (Deutmeyer et al., 2012). An average co-firing share on the EU market could be about 70 Tg/y (Thrän et al., 2016). Finding the resources for fuel production beyond wood is an urgent task today. In this respect, wheat straw and peat, belonging to the category between fossil and renewables (Green et al., 2019), could be the most prospective due to their availability in high volumes. The use of microwave (MW) irradiation to supply heat energy for thermal conversion of biomass is recognized as a prospective decision (Hoa, 2018) because it will allow to avoid external heat carriers. Instead, volumetric heating of biomass owing to the electromagnetic energy transformation into heat energy directly inside a biomass particle with low thermal conductivity will occur and therefore will not be accompanied by the formation of additional pollutants: CO, CO_2, NO_X, and volatile organic compounds. In this work, the comparative effect of MW treatment on the torrefaction process of commercial pellets from softwood, wheat straw, and peat was studied, with a focus on the yield of solid products and their potential application as a fuel and a sorbent for collection of liquid fossil spills from the surface of the water area.

2. Materials, experimental setup, and procedures

Commercial softwood pellets with a diameter of 6.0 mm, wheat straw, and peat pellets, both with a diameter of 8.0 mm, produced in Latvia, were used as objects of investigation (Table 1).

Table 1: Characteristics of initial non-treated biomass pellets used as a feedstock for torrefaction

Parameters	Biomass		
	Softwood	Wheat straw	Peat
Moisture (%)	7.1	10.2	8.9
Ash content on dry matter (DM) (%)	0.3	5.0	3.4
Element composition on DM (%):			
C	50.3	46.4	52.8
H	5.5	5.8	5.2
N	0.17	0.59	1.17
O	43.8	42.2	37.4
HHV on DM (MJ/kg)	19.8	18.4	20.9

A microwave laboratory device of original construction equipped with a magnetron (MW power 850 W at 2.45 GHz), a coaxial waveguide, a rotating reactor (V=1.3 L) placed in a tubular resonator (V=40 L), a condenser tool for the collection of the liquid fraction, an ejector for removing of gaseous products from the reactor, a thermocouple controller, and a power indicator SENECA S604E-6-MOD SENECA S604E-6-MOD, was applied for processing (Arshanitsa et al., 2016). The pellets (300 g) were heated in an argon atmosphere in the rotating reactor placed inside the resonator up to the maximum temperature varied in the range of 175-300 °C at constant MW power, followed by isothermal MW heating for 20 min. The yields of solid and condensable fractions were determined by weighing. Before the physico-chemical analysis, solid fractions were ground in a knife type crusher Retch 100, followed by oven-drying at 50 °C in a vacuum. The moisture, and ash content in non-treated and torrefied biomass were measured in accordance with LVS EN 1474-2:2010 and LVS EN 14775:2010, respectively. The higher heating values (HHV) of the torrefied biomass were calculated based on elemental analysis using regression equations (Toscano et al., 2009). Thermogravimetric (TG) analysis was performed in air media by the Mettler Toledo star system (10 °C/min). FTIR spectra of biomass were recorded by a Spectrum One FTIR spectrometer in the range of 4000-450 cm^{-1}. The analytical pyrolysis (Py-GC/MS) of samples (torrefied and non-torrefied) was performed using a Frontier Lab Micro Double-shot Pyroliser Py-2020 id (pyrolysis temperature 500 °C, heating rate 600 °C/min).

3. Results and discussion

The results showed a significant difference in the structure and composition of the biomass samples under study in terms of the degree of plant cell degradation, and element and ash content, which predetermine the different dielectric losses of the presented biomass samples at MW treatment. Both softwood and wheat straw are characterized by the non-destructed morphological structure of plant cell, and the native molecular and supramolecular structure of the major cell wall components including cellulose and lignin. However, peat is formed from the biomass of terrestrial plants partly decomposed under conditions of high humidity and limited air access (initial stage of coalification) (UN, 2011; Sutton et al., 2005). Considering the elemental composition of the peat sample, its degree of decomposition (humification) can be characterized as low (H1-H3) (Fuchsman, 1980). Therefore, the cellular structure of the plant biomass introduced in the peat composition remained partly unchangeable. It was shown that, at the same regimes of treatment, the average MW assisted heating rate increased in the order: peat<wood<wheat straw (Figure 1a). The electric energy consumption was changed in the opposite order, making the process of peat torrefaction the most energy-expensive (Figure 1b).

This can be explained by the decreased polarity (the least oxygen content) of the peat substrate that has a negative effect on the transformation of microwave energy into heat by means of the dipole rotation mechanism. Besides, physical characteristics of peat such as specific heat capacity and heat conductivity responsible for heat transfer inside the material could negatively influence the average rate of biomass heating by MW. The highest MW-assisted rate was measured for wheat straw indicating the trend of faster heating with increasing torrefaction temperature. Obviously, the inorganic ash elements presented in wheat straw in the highest concentration could act as an absorber of microwave energy and then transfer the heat energy inside the biomass by the convection/conduction mechanism.

It was shown that the MW treatment of wood, straw and peat pellets is accompanied by partial biomass thermal degradation.
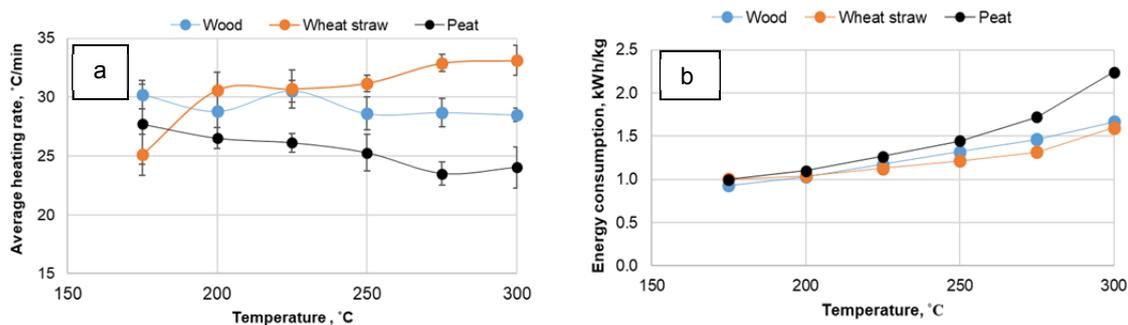
Figure 1: Average rate of MW assisted heating of biomass (a) and specific electric energy consumption (b) depending on the torrefaction temperature
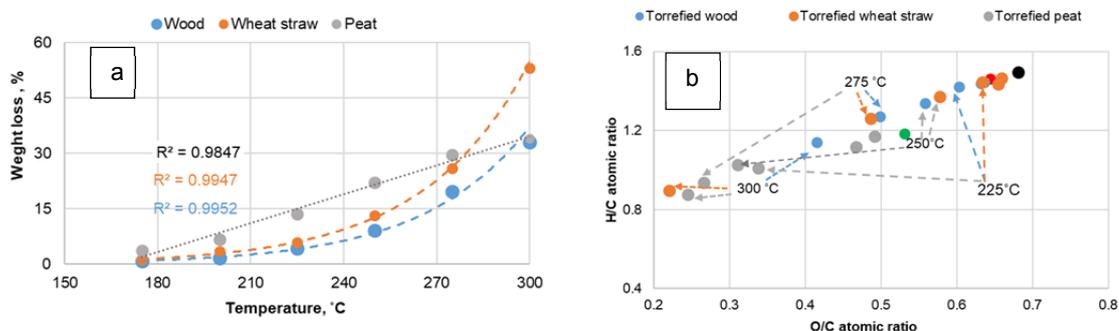

Figure 2: Weight loss on the dry matter (DM) of biomass depending on torrefaction temperature (a), and a Van Krevelen diagram for the initial biomass and the obtained torrefied solid fraction (b), where the non-treated wood, wheat straw and peat points on the Van Krevelen diagram are marked in black, red, and green, respectively

The dependence of weight loss on the torrefaction temperature strongly differed for wood, wheat straw, and peat. At given torrefaction regimes, the total weight loss of wood and wheat straw as a result of both dynamic and isothermal heating increased exponentially with torrefaction temperature (Figure 2 a). The process of drying was the dominant for the biomass, MW-treated at 175-225 °C. A negligible transformation of the biomass structure occurred in this temperature range. For peat, the measurable weight loss as a result of the thermal destruction of biomass was observed in the lower temperature range of 175-220 °C that linearly increased with increasing torrefaction temperature. The maximum weight loss on DM equal to 53 % was measured for wheat straw torrefied at 300 °C, indicating the highest thermolability of the lignocarbohydrate matrix of this biomass (Figure 2 a).

The Van Krevelen diagram indicates that at MW-assisted torrefaction, for all samples under study, carbonization takes place, steadily increasing with the increase in the treatment temperature. At the torrefaction temperature up to 275 °C, a similar carbonization degree (similar H/C and O/C ratio) of wood and wheat straw biomass was observed; as a result, similar HHV values (on the dry ash-free basis) of torrefied wood and wheat straw were established (Figure 2 b).
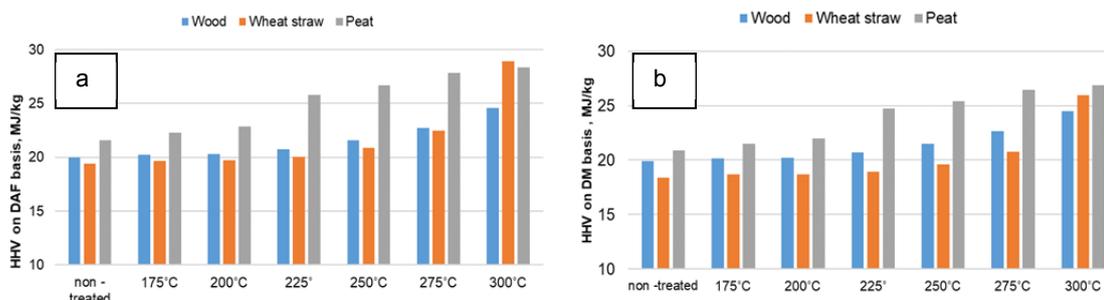

Figure 3: The HHV of non-treated and torrefied biomass samples recalculated on a dry ash-free (DAF) and DM basis

The recalculation of HHV on DM gave the significantly higher calorific values of torrefied wood samples compared to that of wheat straw. This can be explained by the higher concentration of ash in wheat straw samples that is varying in the range of 5-7.5 % vs the 0.3-0.5 % content in torrefied wood. At the torrefaction temperature of 300 °C, a drastic increase in the carbonization degree of torrefied wheat straw proceeds, coinciding with the proportional increasing of its HHV (Figure 2 b; 3 a; b). In this case, despite the highest ash content (10.2 %) the calorific value of wheat straw was higher compared to that of the low-mineralized wood sample (Figure 3 b). For torrefaction temperatures in the range of 175-275 °C, the carbonization degrees of peat samples and their calorific values were significantly higher compared to those of other biomass samples. This can be explained mainly by significantly lower H/C and O/C values for non-treated peat vs non-treated wood and wheat straw (Figure 2 b). The carbonization degrees of peat biomass and wheat straw torrefied at 300 °C were similar. However, in the case of peat, carbonization was achieved at 67 % of solid yield compared to the 47 % yield for wheat straw, indicating a much higher thermodegradability of wheat straw. It was found that, as a result of the MW-assisted torrefaction of biomass, the yield of energy (on the DAF basis) concentrated in torrefied solid fractions in relation to the energy content in the initial non-treated biomass before torrefaction decreased with increasing torrefaction temperature for all samples. However, the magnitudes of losses were significantly dependent on the structure, chemical composition, and degree of decay of lignocellulosic matrixes. For example, the yield of the energy compressed in the solid torrefied biomass obtained after the 300 °C torrefaction was 82 %, 86 %, and 65.2 % for wood, peat, and wheat straw, respectively (Figure 4 a). The balance between the output and input energy was estimated. The input portion includes the electricity consumption needed for MW-assisted torrefaction at a given temperature. The mass yield and HHV (on the dry matter) were used for output energy calculation.
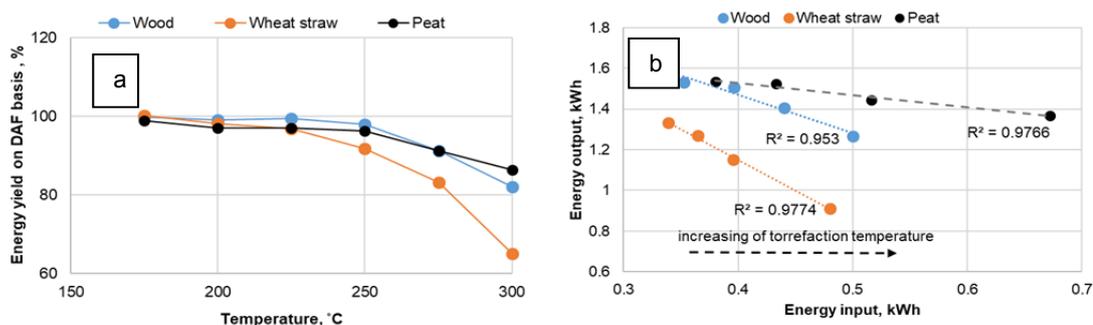

Figure 4: Energy yield for biomass samples torrefied at different temperatures (a), and input/output energy balance for biomass samples (300 g) torrefied in the temperature range 225-300 °C (b)

For any torrefaction temperature, it can be seen that, at the same energy input, the output of energy is increased in the following row: wheat straw<wood<peat (Figure 4 b). The least energy output determined for wheat straw was due to its higher thermolability and, respectively, to the consumption of additional energy for its deconstruction decreasing the energy output.
The data presented on the Van Krevelen diagram was confirmed by FTIR and Py-GC/MS data.
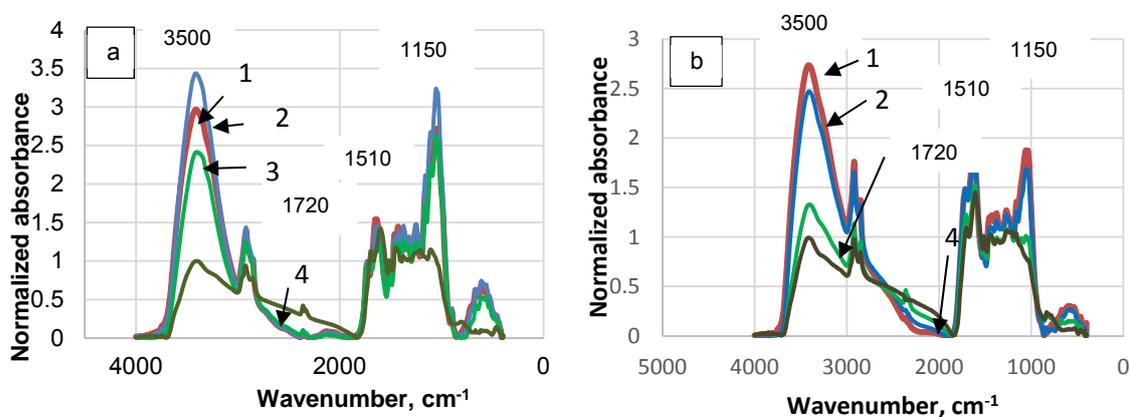

Figure 5: FTIR spectra of wheat straw (a), and peat (b) normalized at 1510 cm^{-1}: non-treated (1), and torrefied at the temperatures: 200 °C (2); 250 °C (3), 300 °C (4)

A continuous increase in the relative content of C=C bonds typical for benzenes (1510 cm^{-1}) and a continuous decrease in absorbance intensity typical for polaric OH (3400-3500 cm^{-1}) groups, C=O (1720 cm^{-1}), and ethers bonds (1100-1150 cm^{-1}) with increasing torrefaction temperature were observed for all samples under study (Figure 5 a; b). These data testify that, as a result of MW-assisted torrefaction, the biomass structural transformation is similar to that achieved at the conventional thermal treatment of biomass in the same temperature range of 175-300 °C. Two major processes have developed in this case: depolymerization/destruction of the portion of the main biomass constituents (prevailing for carbohydrates) with the release of volatiles, and intermolecular condensation (dominating for lignin). The condensation of lignin resulting from MW torrefaction leads to its transformation into a thermally stable product which is not degraded at a higher temperature during analytical pyrolysis. An increase in the relative content of carbohydrate-derived products in volatiles after torrefaction was confirmed by the analytical pyrolysis data. The steady increase of the relative content of levoglucosan in volatiles with the increase of the torrefaction temperature in the range of 200-300 °C confirms the prevailing processes of hemicelluloses destruction promoted by MW treatment.

To estimate the behaviour of torrefied biomass in conditions modelling combustion processes, a thermogravimetric analysis in an air atmosphere was performed (Figure 6 a, b).
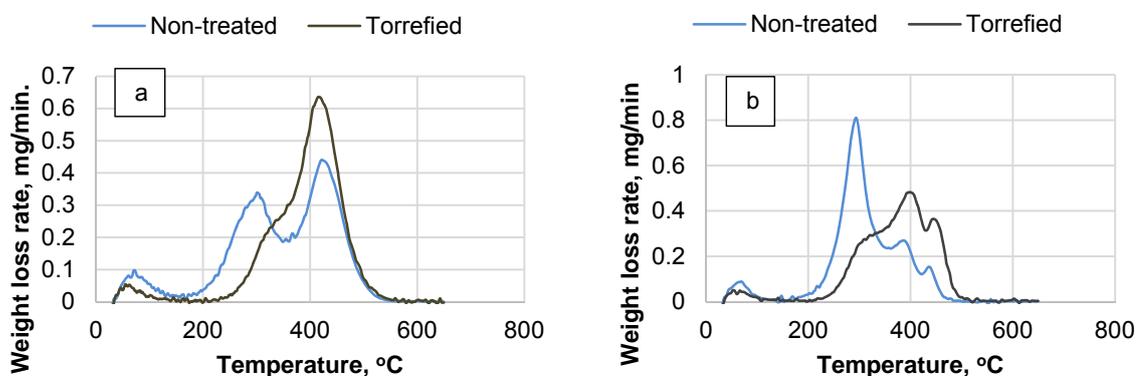

Figure 6: DTG curves (in air) of non-treated and torrefied (300 °C) peat (a), and wheat straw (b) samples

The torrefied samples differ from non-treated biomass by the significant decrease of peak areas in the temperature range of 200-300 °C attributed to the removal of the volatiles formed as a result of the thermodegradation of biomass components and by the significant increase of the areas of high temperature peaks in the temperature range of 350-550 °C, responsible primarily for char heterogenic oxidation, which is accompanied by the removal of CO_2 as a reaction product. These results testify that MW-assisted torrefaction in the conditions under study leads to the carbonization of lignocellulosic matrixes, and the combustion mechanism of torrefied wood, wheat straw and peat biomass is close to that for fossil coal, which opens up promising prospects for MW torrefied biomass application in the heat and energy production by co-firing technologies. The altering of biomass properties estimated after MW torrefaction opens up a new opportunity for torrefied products application. In particular, it concerns the increasing of hydrophobicity (due to the significant decreasing of polar compounds in biomass) (Figure 2b), and the development of a porous structure (conditioned by the removal of volatiles) (Table 2).

Table 2: Characteristics of the porous structure of non-treated biomass and that torrefied at different temperatures

Temperature of torrefaction	Wood		Wheat straw		Peat	
	Specific surface area (BET) (m^2/g)	Total pores volume (mm^3/g)	Specific surface area (BET) (m^2/g)	Total pores volume (mm^3/g)	Specific surface area (BET) (m^2/g)	Total pores volume (mm^3/g)
Non-treated	0.28	0.72	0.62	0.5	0.38	0.97
200˚C	0.43	1.74	0.59	0.72	0.29	1.28
250˚C	0.45	1.44	0.71	0.95	0.59	1.95
300˚C	0.52	1.39	1.02	3.22	0.59	3.22

The properties of MW-torrefied samples allow considering torrefied biomass as a sorbent for collection of oil derived products from the water surface with the following utilization of the spent sorbent for fuel pellet production, as it has been performed by the authors using hydrolysis lignin – waste of fuel bioethanol production (Andersone et al., 2012).

4. Conclusions

- The dielectric properties of wood, wheat straw, and peat pellets were sufficiently high for fast (33 °C/min) and uniform heating of substrates up to 300 °C despite their low heat conductivity.
- The structure and composition of biomass samples are responsible for dielectric losses, which decrease the specific electricity consumption needed for biomass pellets torrefaction in the row: peat>wood >wheat straw.
- The carbonization of biomass as a result of the combined effect of thermodegradation and condensation processes promoted by MW irradiation was proved by FTIR spectroscopy, PY-GC/MS, hermogravimetric, and elemental analysis.
- The calorific values of torrefied biomass increased up to 24, 42, 31% compared to those of non-treated biomass and corresponded to 24.5, 25.9, and 27.0 MJ/kg for wood, wheat straw, and peat, respectively.
- Wheat straw revealed itself as the most thermodegradable biomass under study, characterized, respectively, by an inferior input/output energy balance at processing.
- The decrease in the polar component content and the enhancement of the biomass porous structure achieved by its MW torrefaction at the temperature above 250 °C allows to propose them for testing as a sorbent for collection of the oil-derived products' spill from the water surface.

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