


# Catalytic pyrolysis of torrefied olive stone for production of potential petrochemical alternatives

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**Abstract:** Bench-scale fluidized bed fast pyrolysis of as-received and torrefied residual olive stone (OS) was carried out at 500 °C in the presence or absence of a solid acid catalytic bed. Light to mild torrefaction conditions were investigated, with temperatures of 200, 225, and 250 °C, set in a bench-scale fluidized bed torrefier. Light torrefaction temperatures (200 and 225 °C) did not yield appreciable differences in the thermogravimetric pyrolysis studies, despite notable changes in mass and energy yield resulting from the influence of temperature difference. The mass and energy yields decreased from 91.1 to 74.0% and from 92.0 to 80.9%, respectively, moving from light to mild torrefaction. The higher heating value (HHV) increased linearly with an increase in torrefaction temperature, reaching a maximum of 22.1 MJ/kg at 250 °C, which was 9.7% greater than the as-received OS sample. A comparison was made between the influence of light and mild torrefaction on subsequent bench-scale pyrolysis experiments. In particular, the quality of bio-liquids for torrefaction coupled to fast pyrolysis shifted significantly towards the production of higher phenolic and aromatic derivatives that may find applications as potential drop-in alternative hydrocarbons. © 2022 The Authors. *Biofuels, Bioproducts and Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

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## Introduction

The bioenergy sector has been growing rapidly, encouraged by recent pledges to curb the environmental footprint associated with extensive fossil fuel overdependence, which has seen emissions rise to unprecedented levels and become a cause for concern.<sup>1</sup> Lignocellulosic feedstocks represent an abundant, carbon-neutral, renewable energy resource with a wide geospatial distribution and the potential to increase the bioenergy footprint.<sup>2</sup> A broad variety of techniques have been exploited to unlock the bioenergy potential of lignocellulosic materials, with fast pyrolysis emerging as an alternative direct pathway for the production of liquid fuels and/or chemicals due to its particularly large bio-liquid product yield (bio-oils).<sup>1,3</sup> Significant research work is underway on the implementation of second-generation biorefineries, which address the environmental, ethical, economic, and social issues that have plagued first-generation biorefineries, with a greater focus on the use of sustainable feedstocks.<sup>1,4</sup> Biomass fast pyrolysis is usually operated under an inert atmosphere, at a high heating rate ( $10^3$ – $10^4$  K s<sup>-1</sup>), moderate temperature (~500 °C), short hot vapor residence time (<2 s), and rapid quenching to maximize the bio-liquid yield, with char and pyrolysis gas as by-products.<sup>5</sup>

The large presence of oxygen-containing functional groups in biomass pyrolysis oil represents the major challenge for its direct utilization, these groups being primarily responsible for the storage instability and the thermal instability of bio-oils as well as for the high upgrading cost for their use as alternative drop-in hydrocarbons.<sup>6,7</sup> The significant influence of the structure and chemical composition of biomass on its degradation pathways offers a unique opportunity to influence its thermal behavior by introducing one or more pretreatments prior to pyrolysis to realize selective conversion to suitable products.<sup>8</sup> There are a variety of pretreatment steps such as leaching of inorganic material, dilute acid hydrolysis, and organosolv preprocessing, which have been explored successfully so far to improve biomass prior to fast pyrolysis, even though a cost–benefit analysis should be considered to assess whether the benefits outweigh the economic costs of additional pretreatment steps.<sup>9</sup> Among them, *torrefaction* has been gaining particular attention in recent decades as an effective pretreatment, able to improve the quality of biomass in terms of both physical and chemical properties for subsequent thermochemical conversion processes, including pyrolysis.

A significant number of torrefaction reactor configurations have been explored so far, including screw conveyors, drum reactors, vertical moving beds, fluidized beds, cyclonic, and microwave reactors.<sup>10,11</sup> Physicochemical constraints of biomass heavily influence the choice of reactor – for example

particle size, may influence heat transfer rate, feeding pattern, fluidization behavior, and particle entrainment, resulting in inconsistent residence time when utilizing fluidized or moving-bed reactor units.<sup>12,13</sup> The degree of conversion and uniformity of torrefied biomass is a critical parameter for subsequent processing, with the different types of reactors offering a broad range of torrefied solid product quality.<sup>10,12,14</sup> Two main physical parameters of biomass have been found to impact the torrefaction performance, and these are the bulk density and particle size/shape, which respectively significantly affect the mixing and the heating rate of biomass particles in bench scale torrefiers.<sup>12,15</sup>

During torrefaction, biomass constitutive polymers (cellulose, hemicelluloses and lignin) undergo physicochemical transformations with the resulting solid having better fuel and grindability properties as well as decreased moisture and O/C ratio.<sup>16,17</sup> The dominant reactions that occur within the torrefaction operating conditions (200–300 °C, inert environment) include deacetylation, cleavage of aryl ether linkages, and demethoxylation of lignin resulting in an overall increase in aromaticity of lignocellulosic material and a consequent improvement in the distribution of the pyrolysis product when coupled together.<sup>16,17</sup> In the study by Neupane *et al.*,<sup>16</sup> for example, the selectivity of phenolic compounds was found to increase with an increase in torrefaction severity, whereas that of furan compounds decreased under non-catalytic pyrolysis conditions, which in the presence of acidic solid catalyst transformed to aromatic hydrocarbons.

The adoption of olive stone (OS) in this study was greatly influenced by its ready availability, with Italy ranked second in terms of production, resulting in a considerable yield of residual waste of OS which has been found to have favorable physicochemical characteristics for thermochemical valorization, due to its low moisture content, uniform size, high energy density, and very low ash content.<sup>18–20</sup> Characteristically, OS, which belongs to the drupe endocarp family, is a naturally high-lignin-containing feedstock, which, due to its high aromaticity, may offer strong potential for production of phenyl-derived biofuels and chemicals.<sup>21,22</sup> During the processing of olives, OS has been said to constitute about 8–15 wt.% of the primary material leading to quite a significant residual stream, which must be properly discarded to avoid a negative environmental impact.<sup>23</sup> The pyrolytic deconstruction of such lignin-rich feedstocks typically results in greater yields of lignin-based pyrolytic products such as phenolics, which range from hydroxyl, alkyl, and alkoxy-substituted compounds, which have strong potential to serve as replacements for petroleum-derived phenols in applications such as lubricant additives, phenolic resins, polymer additives, and agrochemicals.<sup>24–26</sup>

Previous investigations by Fernández-Rodríguez *et al.*,<sup>27</sup> for example, show that the pyrolytic degradation of OS results in a phenolic-rich stream including products such as catechols, cresols, and phenols, which are very valuable in the pharmaceutical, medicinal, and polymer production industries. Despite the limited direct application of alkylphenols such as 2-methylphenol, 4-methylphenol, the bulk material has found use as intermediates for a wide range of valuable applications in pharmaceuticals, surfactants, agrochemicals, and phenolic resin production industries.<sup>28</sup> Since the over-functionalized nature of alkoxy-phenols limits their applications in industry, selective dealkoxylation towards less functionalized and more valuable alkylphenols has become increasingly important to the biorefinery economic outlook, with a special interest focused on high value products such as cresols, 4-propylphenol and 4-ethylphenol, which are essential building blocks utilized in the manufacture of synthetic resins, surfactants, and many other fine chemicals.<sup>29,30</sup>

The present study explores coupled torrefaction-pyrolysis route as a means to increase the potential to produce valuable bio-oils that can be integrated easily within the existing demands.<sup>31</sup> In particular, the torrefaction pretreatment was employed prior to catalytic fast pyrolysis in order to improve the stability of the recovered bio-oils and to improve selectivity of the preferred fractions of stable oxygenates and/or hydrocarbons. The torrefaction treatment of OS was carried out in a laboratory-scale fluidized bed reactor operated in batch mode at temperatures between 200–250 °C, whereas subsequent fast pyrolysis experiments in a bench-scale fluidized bed reactor operated under continuous flow at 500 °C and in the presence of a catalytic bed. Findings show that the intensification of the relative lignin content after torrefaction increased the selectivity towards phenolic derivatives with the ZSM-5 (Zeolite Socony Mobil-5) catalyst increasing the yields in alkyl-phenols such as phenol, 2-methyl-phenol, *p*-cresol and hydroxytoluene, which, as highlighted earlier, could play a role in substituting some of the traditional petroleum-derived phenols in various industries.<sup>32</sup>

## Materials and experimental methods

### Materials and pretreatment

The OS samples used in the present study were provided by an Italian olive oil producer, within the Campania region in southwestern Italy. It was supplied as a granular material with bulk fragments greater than 5 mm. The samples as received were sieved to remove material such as chaff, fines, and external ash of less than 1 mm, prior to size reduction or

torrefaction. Both the as-received and torrefied OS samples were ground using a batch rotor mill (IKA MF 10 Basic mill) equipped with a 1 mm mesh sieve, prior to the pyrolysis step.

The compositional analysis of raw OS showed the following macro-component fractional content: hemicellulose ~18.8%, cellulose ~28.4%, and lignin ~40.11%. The properties of both raw and torrefied OS (TOS) were determined by means of proximate analysis (TGA 701 LECO thermogravimetric analyzer), ultimate analysis (CHN 628 LECO analyzer; SC 144 DR LECO analyzer), and isoperibolic oxygen bomb calorimeter (Parr 6200 calorimeter). All the analyses were performed in triplicate at least. Analytical data are reported as average values in Table 1.

The zeolite ZSM-5 catalyst, with a ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 38, was supplied by ACS Material, Pasadena CA, USA, and consisted of cylindrical pellets.

### Torrefaction

Torrefaction was carried out at 200, 225, and 250 °C in a laboratory-scale fluidized bed reactor consisting of a stainless steel column with an inner diameter of 41 mm and a height of 400 mm. The converter was operated batchwise (fixed time of 10 min) by feeding the granular OS in a bed of silica sand 300–400 μm particle size.<sup>33</sup> The composition of the permanent gases that evolved during torrefaction of OS was analyzed in real

**Table 1. Properties of as-received and torrefied OS feedstock.**

Sample	OS	TOS-200 °C	TOS-225 °C	TOS-250 °C
Ultimate analysis (%wt, daf)				
C	50.15	51.01	51.66	53.54
H	6.09	6.22	6.07	5.81
O <sup>a</sup>	43.76	42.77	42.27	40.65
N	—	—	—	—
Proximate analysis (%wt, db)				
VM	80.06	77.72	76.73	73.24
FC	19.65	21.78	23.00	25.56
Ash	0.29	0.51	0.27	1.20
Moisture (%wt, ar)	12.4	1.81	1.33	1.11
HHV (MJ/kg, db)	20.23	20.42	21.37	22.1
H/C ratio (Mol/Mol, daf)	1.45	1.45	1.40	1.29
O/C ratio (Mol/Mol, daf)	0.66	0.63	0.61	0.57
H/Ceff	0.14	0.19	0.17	0.15

OS: olive stone; TOS: torrefied olive stone; daf: dry ashe free basis; db: dry basis; C: carbon; H: hydrogen; O: oxygen; N: nitrogen; VM: volatile matter; FC: fixed carbon; HHV: high heating value; H/C ratio: molar hydrogen to carbon ratio; O/C ratio: molar oxygen to carbon ratio; H/Ceff: effective hydrogen to carbon ratio; a: calculated by difference

time by using a portable emission analyzer (MRU Vario Luxx Gas Analyzer, Thieme (VI)) for H<sub>2</sub>, CO, NO, SO<sub>2</sub>, and CO<sub>2</sub>, which was useful also to monitor the progress of torrefaction. In a typical experimental run, about 50 g of OS, with a moisture content of about 12%<sub>wb</sub>, was slowly fed by gravity from the top of the reactor (it took slightly less than 1 minute to load all the material), in counter-current to the purge/fluidization nitrogen stream rising from the bottom at a flow rate of 1460 NL/h. Fast recovery and quenching of torrefied OS was performed by connecting a stainless steel vacuum chamber to the fluidized bed reactor upon lapse of the 10 minute set time. Repeated tests (approximately four torrefaction runs for each pyrolysis test) were performed to recover enough torrefied material for the subsequent pyrolysis tests, which confirmed the ability of FB technology to ensure a uniform and consistent quality of the solid product and reproducibility of the experimental results.<sup>33,34</sup> Thermogravimetric analyses (TGA-DTG-DSC) were also performed on both raw and torrefied solids using a PerkinElmer STA 6000 analyzer, Milano in an inert environment with a nitrogen purge of 100 mL/min at a heating rate of 15 °C/min from room temperature to about 900 °C. The received and torrefied samples will be denoted as OS and TOS (plus the corresponding treatment temperature going forward) respectively.

## Pyrolysis

Purely thermal and thermocatalytic fast pyrolysis runs were performed at a constant temperature of 500 °C using raw and torrefied OS feedstock in a laboratory-bench-scale fluid FB reactor. The reactor consisted of a stainless steel fluidization column with an inner diameter of 41 mm and a height of 700 mm, which was operated at steady state. Two kinds of granular solids were tested as bed material to assist the OS pyrolysis, namely (1) silica sand in the size range of 300–400 μm, and (2) ZSM-5, which was crushed to fluidizable fractions with an average size of 1350 μm (1000 <  $d_p$  < 1700 μm sieve size) used for this experiment. The fluidized bed pyrolyzer consists of an electrically heated tubular reactor, a windbox/pre-heater, a gas distributor and the fluidization column. The exhaust of the pyrolyzer was connected to a stainless steel filter (hot filtration at 300 °C), a condensation train, and a series of gas analyzers (online ABB gas analyzers, micro-GC-Agilent 3000, Agilent technologies Santa Clara, CA, USA).

The schematic representation of the experimental apparatus used for pyrolysis bench scale tests is shown in Fig 1 below.

## Analyses and characterization

A LabVIEW operated data acquisition system was used for logging experimental data related to the operation of the

reactions. The gas flow leaving the reactor was split into three substreams. The first one was sent to a set of online ABB gas analyzers to continuously monitor the concentration of O<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>. The second substream passed through a chilled impinger train consisting of seven flasks connected in series, to facilitate the condensation of the vapors to liquid pyrolysis oils. The first flask was at room temperature, while the other six were refrigerated at a temperature of –5 °C, using a frozen supersaturated solution of water and sodium chloride. The pyrolytic liquid was characterized offline using Agilent 7890A gas chromatography (GC) equipment equipped with MS 5975C-VLMSD, after collection in the condenser section.

Chromatographic peaks were recognized using the National Institute of Standards and Technology (NIST) 11 mass spectral data library based on retention times, whereas a semi-quantitative approach was adopted to determine the relative content of each bio-oil component. Following this approach, the percentage of each compound was obtained through the internal normalization of all the resolved peak areas.<sup>35</sup> Water concentration in bio-oil was measured using a Mettler Toledo V20 Karl Fischer volumetric titrator. Proximate and ultimate analyses of residual char and elutriated fine particles were also carried out.

## Results and discussion

### Physicochemical characteristics of raw and torrefied OS

The ultimate and proximate analyses as well as other physicochemical characterizations of OS before and after torrefaction are shown in Table 1. Data show that the two investigated light torrefaction temperatures (220 and 225 °C) brought relatively small changes in the volatile matter content, molar H/C, and oxygen content, whereas appreciable changes were detected with the transition to the mild torrefaction temperature (250 °C). A comparison of light versus mild torrefied feedstock was subsequently pursued in the fast-pyrolysis studies to determine the best pretreatment operating conditions that improved the pyrolysis process. Torrefaction at 200 °C yielded the lowest degree of degradation of the organic constituents for OS, with the greatest contributions of mass loss attributed to the loss of moisture, with a decrease of 85% in moisture content recorded. On the other hand, the H/C molar ratio of OS remained substantially the same ( $\approx 1.45$ ) suggesting that the oxygen removal as water may have been the dominant reaction (as evidenced by the lower oxygen fractional content, Table 1). With an increasing torrefaction temperature, increased deacetylation and demethoxylation



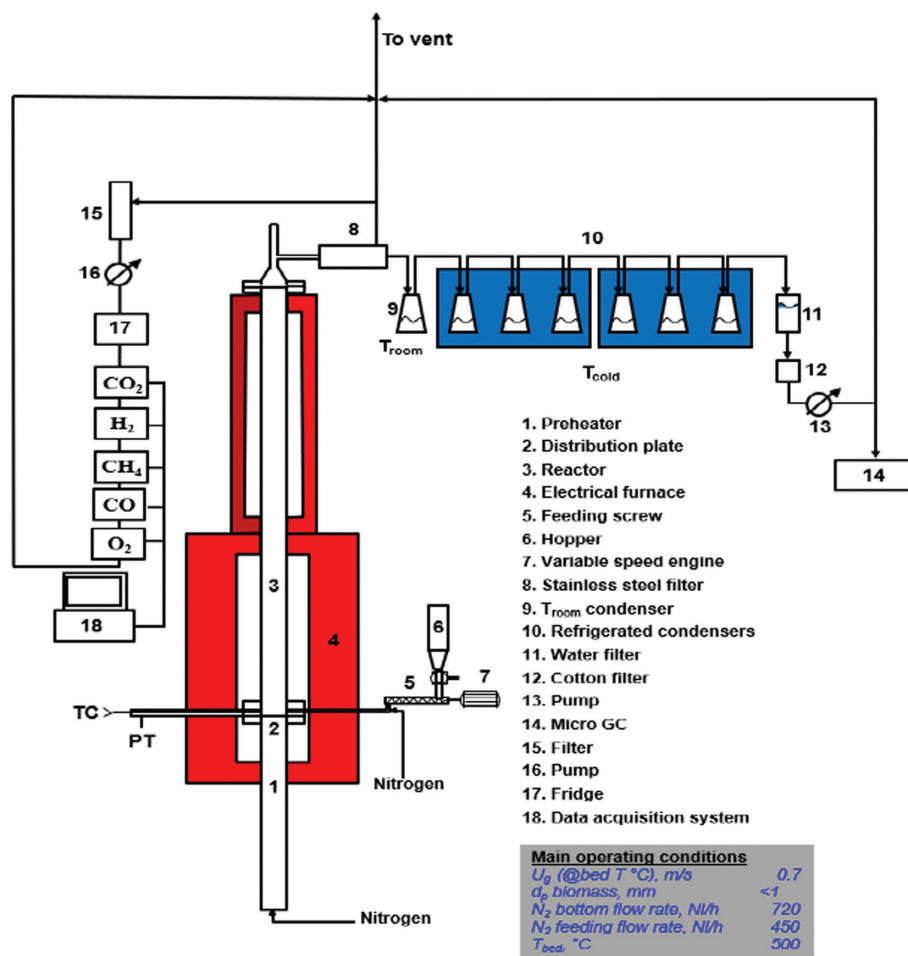


Figure 1. Experimental apparatus and main operating conditions.

reactions may be responsible for the sharper decreases in the relative content of oxygen and hydrogen, with an 11% decrease in molar H/C ratio between the lower light and mild treatment as compared to about 3% difference between the two light torrefaction temperatures employed.

The mass yield ( $Y_M$ ), energy yield ( $Y_E$ ), and the energy density index ( $I_{ED}$ ) of the torrefied OS were calculated at the different temperatures following Eqns (1) to (3):

$$\text{Mass yield } (Y_M) = \frac{\text{mass after torrefaction}}{\text{mass of raw sample fed}} \times 100\% \quad (1)$$

$$\text{Energy yield } (Y_E) = Y_M \times \frac{HHV_{\text{torrefied sample}}}{HHV_{\text{as received}}} \quad (2)$$

$$\text{Energy densification index} = \frac{HHV_{\text{torrefied sample}}}{HHV_{\text{as received}}} \quad (3)$$

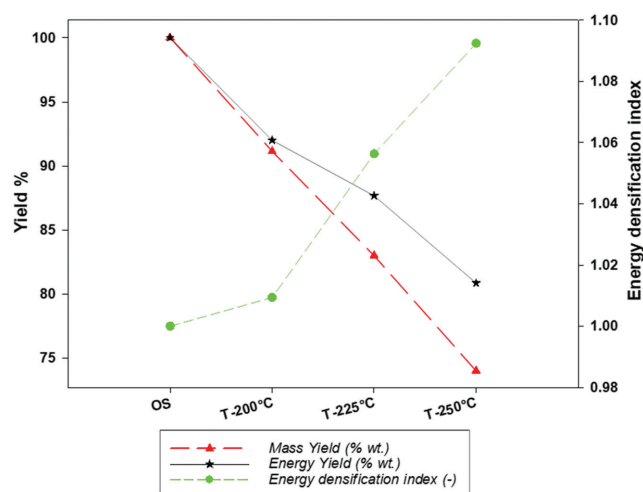


Figure 2. Mass and energy yields and energy densification index of torrefied OS at different temperatures.

A fairly linear decrease is observed with respect to  $Y_M$  with increasing torrefaction temperature; however, the total energy ( $Y_E$ ) preserved was higher than the mass yield with the gap widening with increasing temperature (Fig. 2). The results suggest that more energy per unit mass was recovered after torrefaction, which agrees with the sharp linear increase in the energy densification index with increasing torrefaction severity (Fig. 2). However, from the viewpoint of adopting torrefaction prior to pyrolysis, light torrefaction conditions suggest a better balance with higher  $Y_M$  returns, which may be able to support the volume of feedstock required to operate perspective lignocellulosic biomass-based pyrolysis refineries.

### Thermogravimetric analysis

The thermal degradation behavior is illustrated in Fig. 3, with the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for light torrefaction conditions suggesting that there were marginal changes between the temperatures of 200 and 225 °C. The two curves were intertwined following a similar path profile, which suggests a high temperature dependence for torrefaction with the dominant type of reactions within an operating window homogeneous, and this was corroborated by the production of very similar residual carbon with marginal difference (less than 0.5%). The thermal decomposition range was mainly concentrated in the 200–380 °C temperature range, with the first shoulder peaks centered around 265–290 °C, while the second shoulder peaks were centered around 340–350 °C.<sup>36,37</sup> The DTG curve of the as-received sample relative to light torrefaction treatment showed that, at the lower temperature, the peak attributable to hemicellulose increased relatively before decreasing at a milder

torrefaction temperature, showing that dominant reactions transition from deacetylation and dehydroxylation towards more extensive degradation of the matrix.<sup>38</sup> With increasing torrefaction temperature this peak decreased, whereas there was an intensification and sharpening of the second peak as the relative content of cellulose increased with a decrease in other constitutive polymers. In this study, light and mild torrefaction conditions were adopted with a maximum temperature of 250 °C investigated, based on a survey that suggests that, within this temperature window, condensation and carbonization of the polymer matrix are minimized.<sup>38</sup>

### Bio-liquid chemical characterization: Main component distribution for torrefied OS with/without ZSM-5 catalysts

The bio-oil recovered was primarily composed of a phenolic derivatives oil fraction (phenols, catechols, guaiacols, and syringols), holocellulose derivatives (acids, aldehydes, ketones, and furans), and aromatic hydrocarbon in the presence of the ZSM-5 catalysts. The alkoxyated phenolics were the dominant components of non-catalytic pyrolysis, their relative content increasing with increasing torrefaction temperature. The lighter torrefaction temperature had slightly lower relative content of phenolics before an increase was noted with the milder treatment. In the presence of ZSM-5 catalyst, the alkoxyated phenolic decreased significantly with some of the components transformed to alkylated phenols with the catalyst aiding in the demethoxylation of guaiacols and syringols to yield phenols. The relative content of phenols increased by more than threefold with the use of the ZSM-5 catalyst, although there were competitive reactions for the production

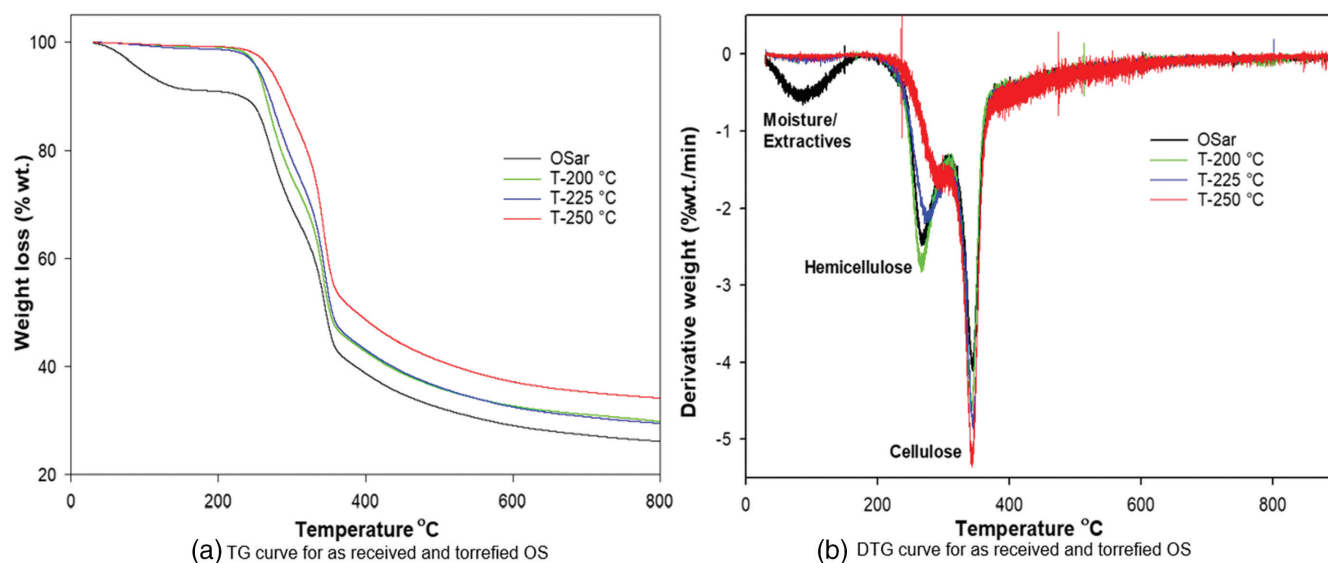


Figure 3. TG and DTG curves of as-received and torrefied material.

of aromatics with greater propensity of polymerized product stream due to the higher acidity of the catalysts (Fig. 4).

The decrease in yield of furan compounds is due to a reduction in hemicellulose components. An increase in phenolic yield due to torrefaction can be attributed to changes in lignin structure characterized by cleavage of ether linkages and demethoxylation. Demethoxylation of guaiacyl lignin to form hydroxyphenyl units in a torrefied biomass can favor the production of phenolic compounds and reduce the guaiacols.<sup>28,39</sup> Torrefying biomass increased the relative lignin fraction, which led to an increase in lignin-derived phenolic and guaiacol compounds.

For non-catalytic pyrolysis, the light torrefaction treatment produced the highest catechol content, which could suggest that demethylation was the dominant reaction, in contrast with demethoxylation, leading to the maximum production of hydroxylated phenols (phenols plus catechols).<sup>40</sup> With increasing torrefaction temperature, the total hydroxylated phenols decreased marginally, and the demethylation intensity of the prior pretreatment was evident from the gas analysis of the torrefaction gas (not shown here for the sake of brevity), in which the methane content increased.

The phenol group here refers specifically to simple phenolic compounds, including phenol and the alkyl-substituted phenols. For non-catalytic pyrolysis, the relative content of phenols increased by about 10% at a torrefaction temperature of 250 °C, whereas there was little to separate the as-received and light torrefied material. The added benefit of torrefaction was noted by the increase content of detectable depolymerization components, which increased by a maximum of 10% for light torrefied material with respect to the raw OS. Results for bio-oil compounds as detected by gas chromatography–mass spectrometry (GC/MS) revealed

that the relative selectivity towards phenol increased to over 50% for catalytic pyrolysis with raw and mild torrefied feedstock whereas guaiacol selectivity was significantly reduced to constitute less than 10% with the use of catalyst from about 50% and over for non-catalytic pyrolysis. Non-catalytic depolymerization of biomass lignin mainly produces alkoxyated phenols, with further deoxygenation yielding alkylated phenols.<sup>39</sup> However, it has been suggested that the cleavage of the C<sub>ar</sub>-O-C bond<sup>39,41</sup> does not readily occur without a deoxygenating catalyst, which may explain the relatively low yield of phenols for non-catalytic experiments for both raw and torrefied OS (Fig. 5).

The greatest challenge when dealing with material with high lignin content has been to achieve selective cleavage of the C-O bonds in the C<sub>ar</sub>-O-Me (demethoxylation) and C-O-C linkage (ether bonds) while preserving the basic phenyl structure due to relatively similar bond dissociation energy for the competing reactions.<sup>42</sup> With increased torrefaction severity, the relative increase in the content of

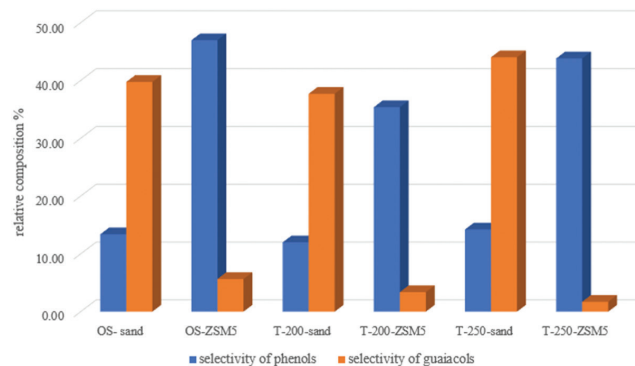


Figure 5. Selectivity of alkoxy or alkylated phenolics with/without the use of catalyst.

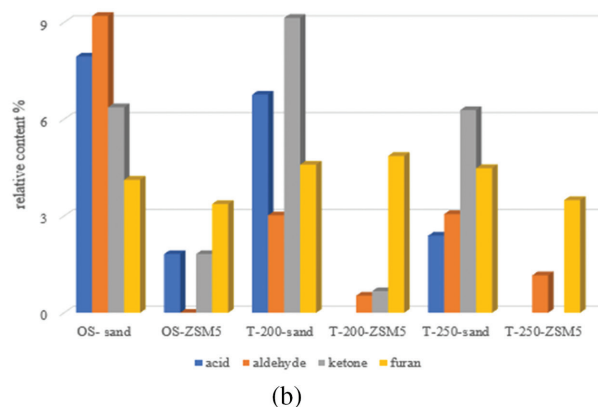
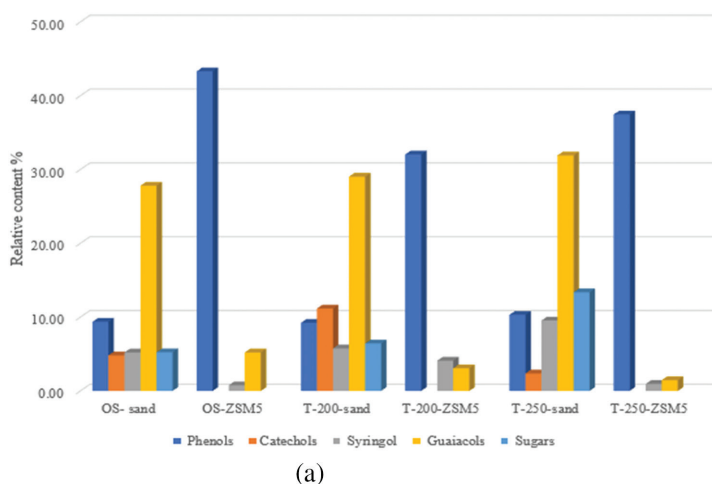


Figure 4. Relative composition based on GC/MS analysis: (a) content of lignin derivatives and sugar; (b) content of light holocellulose derivatives.

phenols points to the fact that torrefaction may have aided with partial dealkoxylation of primary lignin constituents thus increasing their yield in the subsequent pyrolysis step. The higher catechol content of the torrefied OS (T-200 °C), more than twice that of the as-received sample, suggests that an alternative deoxygenation pathway is promoted by light torrefaction where demethylation followed by dehydration occurs, closer to the hydrogenolysis pathway suggested by Saidi *et al.*<sup>41</sup> The decrease in catechol content for milder torrefied feedstock may be explained by the fact that, during torrefaction, at much lower temperature, demethylation reactions occurred, thus transforming the lignin structure so that this is not the dominant form of deoxygenation in subsequent reactions. It can be seen that, apart from our targeted phenolic derivatives, the use of ZSM-5 catalyst increased the content of aromatics creating a competitive selectivity between desired phenols and undesirable aromatics, i.e. bio-oil stream contained naphthalene derivatives, which is something that may be addressed by tuning the acidity to lower the extent of polymerization reactions.

The potential of zeolites in our case ZSM-5 to aid *in situ* hydrogen-transfer depolymerization and/or hydrodeoxygenation by utilizing the intermediate hydrocarbon pool can be postulated to aid the demethoxylation of primary lignin products towards phenols.<sup>24,30</sup> However competing condensation/polymerization reactions must be reduced to maximize selectivity, with increased torrefaction severity probably increasing the content of intermediate dealkoxylated components, which offer little to no steric hindrance to participate in the unwanted reaction mentioned above.<sup>24,43</sup> The relative content of ketones and furans increased under light torrefaction conditions, eventually decreasing at high severity, showing that the contributions of the holocellulose fraction decreased with increasing torrefaction temperature. On the other hand, the reductions in aldehyde and acid content were much sharper with increasing temperature, a feature that agrees with the fact that they are formed from the less thermally stable fractions of holocellulose, which disappear with increasing torrefaction temperature.

## Conclusions

The influence of a torrefaction pretreatment on the qualitative and quantitative features of products of either non-catalytic or catalytic pyrolysis of biomass is remarkable. There was significant reduction of methoxylated alkylphenols such as guaiacol- and syringol-type products in favour of non-methoxylated phenol-type products, such as benzenediols and alkylated-phenols, with increasing torrefaction temperature. The deployment of solid acid catalyst in the

form of ZSM-5 increased the extent of demethoxylation, resulting in greater yields of alkyl-phenols. Characterization of the catalytic pyrolysis oils showed that treatment produced some interesting monomeric alkylphenols with selectivity increasing to above 50 wt.% in the bio-liquid stream. The transformation of feedstock with high levels of lignin content, as well as torrefaction, which increases the relative lignin content, clearly shows the potential of these feedstocks to be used for the production of biobased phenols and aromatics.

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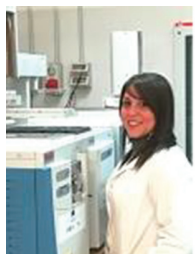
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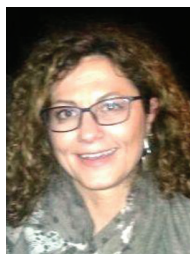
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