

**Coalification of Expired Oatmeal: Hydrothermal Carbonization for Solid Biofuel  
Production**

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## ABSTRACT

Hydrothermal carbonization (HTC) of food waste is limited by heterogeneous, compositionally undefined feedstocks, as carbohydrates, proteins, and lipids behave differently during HTC, making precise composition essential for predicting product quality and optimizing process conditions. This study addresses this gap by using expired oatmeal (EO), a well-characterized substrate containing 68.66 wt% carbohydrates, 12.99 wt% protein, and 7.25 wt% oil (as received basis), to examine HTC performance and the physicochemical features of the resulting hydrocoals. Experiments were conducted under systematically varied conditions (200–250 °C, solid-to-water ratios of 12.5–50 g EO per 150 mL, and residence times of 1.5–12 h). This is among the first studies to use an expired commercial food product with a known macronutrient profile as a model HTC feedstock, enabling isolation of composition-driven effects on hydrocoal properties. All hydrocoals exhibited substantially enhanced fuel characteristics relative to raw EO (HHV: 18.1 MJ/kg), with higher heating values of 29.6–32.3 MJ/kg, ash contents reduced from 1.62 wt% to 0.14–0.48 wt%, higher fixed carbon, reduced volatile matter, and atomic H/C and O/C ratios of 0.92–1.08 and 0.12–0.21, respectively placing the products in or near the bituminous coal region of the Van Krevelen diagram. The hydrocoals exhibited high heating values and low ash contents support their suitability as drop-in solid biofuels; the composition-defined approach provides a stronger basis for designing scalable industrial HTC systems for waste-to-energy conversion.

**Key words:** Hydrothermal carbonization, synthetic coal, food waste, Py-GC-MS

## **1. Introduction**

Global energy demand has been steadily increasing each year, driven by rapid urbanization and the continuous growth of the world's population. This rising energy demand has intensified concerns about the depletion of fossil fuels and the environmental impacts associated with their use. In this context, renewable and alternative energy sources have become essential for achieving a sustainable and secure energy future. Among various renewable feedstocks, waste-derived materials-particularly food waste-have recently attracted significant attention due to their high organic content and global abundance <sup>1</sup>. Food waste is generated in large quantities from households, food industries, and agricultural activities, and it poses severe environmental challenges when not properly managed. Recognizing the urgency of this issue, global initiatives such as the United Nations' Sustainable Development Goal 12.3 aim to halve food waste and reduce food losses along the supply chain by 2030 <sup>2</sup>. Converting such wastes into value-added products through thermochemical or biochemical processes provides a dual benefit: effective waste management and sustainable energy generation. The HTC is a thermochemical process used to valorize food wastes (FWs) and other biomasses by treating them in hot-compressed water at mild conditions (i.e., relatively low temperatures and autogenous pressure) <sup>3</sup>. The process converts organic matter into carbon-rich solid products (typically a dark brown or black powder), accompanied by a liquid phase containing organic and inorganic compounds, and a minor gaseous phase <sup>4</sup>. The solid product, commonly referred to as hydrocoal or hydrochar, exhibits favorable fuel characteristics and offers a sustainable route for waste valorization through synthetic coalification.

Numerous studies have investigated the HTC of various types of FW under different operating conditions. Akarsu et al. reported hydrocoal mass yields of 47.0–69.8 wt% from HTC of fruit and vegetable waste at 175–250 °C, while Periyavaram et al. demonstrated that increasing temperature from 180 to 240 °C reduced yields but raised HHV from ~21 to ~29 MJ/kg using leachate as process water. Mannarino et al. similarly observed improvements in HHV, fuel ratio, and energy density with increasing temperature for fruit and vegetable-based FW at 200–230 °C<sup>5–7</sup>. Collectively, these studies confirm that operating conditions, particularly temperature and residence time, govern hydrocoal yield and fuel properties. However, food waste composition varies widely depending on regional and dietary factors. Since food waste can be rich in carbohydrates, fats, or proteins, its macromolecular composition is also critical for predicting hydrocoal quality and ensuring industrial applicability<sup>8</sup>.

To better understand the role of individual components in HTC, some studies have investigated model compounds or feedstocks with controlled compositions. For instance, Yang et al. examined the HTC of kitchen waste using pure model substances, namely potato starch, soybean protein, and oleic acid, as representative compounds for carbohydrates, proteins, and lipids, respectively, and proposed a multi-component kinetic model based on the identified reaction pathways<sup>9</sup>. While such model compound studies provide valuable mechanistic insights, they do not capture the complexity of a real food waste matrix, where macronutrient interactions under hydrothermal conditions may produce synergistic or antagonistic effects on hydrocoal properties that cannot be predicted from individual component behavior alone.

In this context, the present study investigates the HTC of expired oatmeal (EO), a commercially available food product with a precisely known macronutrient profile (68.66

wt% carbohydrates, 12.99 wt% protein, 7.25 wt% lipids), as a model food waste feedstock. To the best of our knowledge, this represents one of the first studies to employ a commercially expired food product with a defined macronutrient composition as an HTC feedstock, rather than artificial mixtures of pure compounds, enabling the systematic isolation of composition-driven effects on hydrocoal properties under realistic processing conditions. Specifically, the HTC of EO was conducted under varying operating conditions, including reaction temperatures of 200–250 °C, feedstock-to-water ratios of 12.5–50 g per 150 mL water, and residence times of 1.5–12 h, which fall within the well-established operational range for hydrothermal carbonization <sup>3</sup> and were selected to systematically examine the influence of process conditions on hydrocoal yield and properties. Throughout this study, the solid product is referred to as "hydrocoal", a term used in the HTC literature alongside hydrochar, biocoal, and synthetic coal, to specifically emphasize its coal like fuel properties intended for solid fuel applications. The physicochemical properties and structures of the hydrocoals were characterized using elemental analysis, proximate analysis, FTIR, solid-state <sup>13</sup>C NMR, SEM, XRD, TGA, TG-MS, and Py-GC-MS, and the aqueous phase composition was investigated for selected runs.

## 2. Materials and Methods

### 2.1. Materials

EO was purchased from a local market in Safranbolu, Türkiye. The properties of EO were presented in Table 1. The oil, protein content, and oil composition of EO were determined by an accredited laboratory (T.R. Ministry of Agriculture and Forestry, Bilim Private Food Control Laboratory, Istanbul, Türkiye). The carbohydrate content was calculated by difference.

**Table 1.** Properties of hydrocoals obtained from the hydrothermal carbonization of expired oatmeal (EO).

| Sample | Process Conditions |       |                        |         | Proximate Analysis, wt% |                 |      | Elemental Analysis (daf) <sup>a</sup> , wt% |     |      |      |                |                  |                  |                                        |                  |                     |                 |                 | pH <sup>k</sup> |
|--------|--------------------|-------|------------------------|---------|-------------------------|-----------------|------|---------------------------------------------|-----|------|------|----------------|------------------|------------------|----------------------------------------|------------------|---------------------|-----------------|-----------------|-----------------|
|        | Feed, g            | T, °C | Feed/Water Ratio(g/ml) | Time, h | VM <sup>b</sup>         | FC <sup>c</sup> | Ash  | C                                           | H   | N    | S    | O <sup>d</sup> | H/C <sup>e</sup> | O/C <sup>e</sup> | HHV <sup>f</sup> , MJ kg <sup>-1</sup> | EDR <sup>g</sup> | EY <sup>h</sup> , % | SF <sup>i</sup> | FR <sup>j</sup> |                 |
| EO     | -                  | -     | -                      | -       | 82.13                   | 16.2            | 1.62 | 46.7                                        | 7.0 | 2.85 | 0.24 | 43.1           | 1.80             | 0.69             | 18.13                                  | -                | -                   | -               | 0.2             | -               |
| HC1    | 12.5               | 200   | 12.5/150               | 3       | 58.02                   | 41.8            | 0.17 | 71.7                                        | 6.1 | 4.16 | 0.22 | 17.7           | 1.03             | 0.19             | 29.92                                  | 1.65             | 52.02               | 5.2             | 0.7             | 3.89            |
| HC2    | 12.5               | 225   | 12.5/150               | 3       | 55.74                   | 44.1            | 0.15 | 73.7                                        | 6.2 | 4.17 | 0.19 | 15.6           | 1.01             | 0.16             | 31.05                                  | 1.71             | 53.76               | 5.9             | 0.7             | 4.13            |
| HC3    | 12.5               | 250   | 12.5/150               | 3       | 49.86                   | 50.0            | 0.14 | 74.4                                        | 6.0 | 4.40 | 0.19 | 14.9           | 0.97             | 0.15             | 31.13                                  | 1.72             | 51.27               | 6.6             | 1.0             | 4.32            |
| HC4    | 25                 | 200   | 25/150                 | 1.5     | 55.74                   | 44.0            | 0.19 | 69.2                                        | 6.6 | 4.28 | 0.26 | 19.6           | 1.14             | 0.21             | 29.37                                  | 1.62             | 60.35               | 4.9             | 0.7             | 3.75            |
| HC5    | 25                 | 200   | 25/150                 | 3       | 54.00                   | 45.8            | 0.20 | 72.0                                        | 5.6 | 4.48 | 0.22 | 17.6           | 0.94             | 0.18             | 29.26                                  | 1.61             | 57.41               | 5.2             | 0.8             | 3.82            |
| HC6    | 25                 | 200   | 25/150                 | 6       | 54.18                   | 45.5            | 0.23 | 72.5                                        | 5.5 | 4.58 | 0.25 | 17.1           | 0.91             | 0.18             | 29.34                                  | 1.62             | 56.78               | 5.5             | 0.8             | 3.92            |
| HC7    | 25                 | 200   | 25/150                 | 12      | 55.29                   | 44.4            | 0.24 | 72.7                                        | 6.0 | 4.42 | 0.21 | 16.6           | 0.99             | 0.17             | 30.22                                  | 1.67             | 60.55               | 5.8             | 0.8             | 4.20            |
| HC8    | 25                 | 225   | 25/150                 | 1.5     | 55.55                   | 44.1            | 0.26 | 71.6                                        | 6.1 | 4.25 | 0.21 | 17.7           | 1.03             | 0.19             | 29.83                                  | 1.65             | 61.45               | 5.6             | 0.8             | 4.07            |
| HC9    | 25                 | 225   | 25/150                 | 3       | 54.14                   | 45.6            | 0.23 | 72.8                                        | 6.5 | 4.28 | 0.22 | 16.1           | 1.08             | 0.17             | 31.07                                  | 1.71             | 59.27               | 5.9             | 0.8             | 4.05            |
| HC1    | 25                 | 225   | 25/150                 | 6       | 52.42                   | 47.2            | 0.30 | 73.5                                        | 6.2 | 4.39 | 0.20 | 15.6           | 1.02             | 0.16             | 30.98                                  | 1.71             | 59.59               | 6.2             | 0.9             | 4.28            |
| HC1    | 25                 | 225   | 25/150                 | 12      | 52.87                   | 46.8            | 0.28 | 74.1                                        | 6.1 | 4.46 | 0.19 | 15.0           | 1.00             | 0.15             | 31.16                                  | 1.72             | 59.41               | 6.5             | 0.8             | 4.38            |
| HC1    | 25                 | 250   | 25/150                 | 1.5     | 52.16                   | 47.5            | 0.26 | 74.6                                        | 6.1 | 4.45 | 0.21 | 14.5           | 0.99             | 0.15             | 31.50                                  | 1.74             | 61.93               | 6.3             | 0.9             | 4.13            |
| HC1    | 25                 | 250   | 25/150                 | 3       | 49.36                   | 50.3            | 0.25 | 74.6                                        | 6.4 | 4.40 | 0.16 | 14.2           | 1.04             | 0.14             | 31.95                                  | 1.76             | 59.03               | 6.6             | 1.0             | 4.23            |
| HC1    | 25                 | 250   | 25/150                 | 6       | 48.74                   | 51.0            | 0.20 | 75.8                                        | 6.1 | 4.50 | 0.24 | 13.3           | 0.97             | 0.13             | 32.00                                  | 1.76             | 61.67               | 6.9             | 1.0             | 4.36            |
| HC1    | 25                 | 250   | 25/150                 | 12      | 44.69                   | 55.0            | 0.27 | 76.6                                        | 5.9 | 4.67 | 0.17 | 12.5           | 0.92             | 0.12             | 32.11                                  | 1.77             | 59.35               | 7.2             | 1.2             | 4.39            |
| HC1    | 50                 | 200   | 50/150                 | 3       | 55.56                   | 43.9            | 0.48 | 73.0                                        | 5.7 | 4.43 | 0.24 | 16.5           | 0.94             | 0.17             | 29.98                                  | 1.65             | 66.13               | 5.2             | 0.7             | 3.99            |
| HC1    | 50                 | 225   | 50/150                 | 3       | 54.97                   | 44.5            | 0.47 | 74.0                                        | 6.5 | 4.21 | 0.25 | 14.9           | 1.05             | 0.15             | 31.67                                  | 1.75             | 62.13               | 5.9             | 0.8             | 4.26            |
| HC1    | 50                 | 250   | 50/150                 | 3       | 52.21                   | 47.3            | 0.42 | 75.3                                        | 6.4 | 4.42 | 0.20 | 13.5           | 1.03             | 0.13             | 32.30                                  | 1.78             | 63.15               | 6.6             | 0.9             | 4.45            |

<sup>a</sup>daf: dry basis ash free, <sup>b</sup>VM: Volatile matter, <sup>c</sup>FC: Fixed carbon, <sup>d</sup>by difference, <sup>e</sup>Atomic ratios, <sup>f</sup>HHV: Higher heating value, <sup>g</sup>EDR: Energy densification ratio, <sup>h</sup>EY: Energy yield, <sup>i</sup>SF: Severity factor <sup>j</sup>FR: Fuel ratio, <sup>k</sup>pH for aqueous solution of HC.

## 2.2. HTC runs

The HTC experimental procedure used in this study follows the general approach described in our previous work <sup>10</sup>. The HTC experiments were carried out in a 500 mL Parr autoclave (Parr 4848 High Pressure Reactor, Parr Instrument Co., Moline, Illinois, USA), which has a maximum operating temperature of 500 °C and a maximum operating pressure of 35 MPa. A systematic one-factor-at-a-time (OFAT) approach was employed, in which each process variable, namely reaction temperature (200, 225, and 250 °C), solid-to-water ratio (12.5, 25, and 50 g per 150 mL), and residence time (1.5, 3, 6, and 12 h), was varied independently to assess its individual effect on hydrocoal yield and properties. For each run, predetermined amounts of EO and deionized water were introduced into the reactor to achieve the target solid-to-water ratios. The reactor was then heated to the target reaction temperature and maintained for the designated residence time. After completion of the reaction, the system was cooled to room temperature, and the products were separated into solid hydrocoal and aqueous phases via vacuum filtration. The hydrocoal samples were rinsed thoroughly with deionized water, dried at 105 °C for 4 h, and stored in airtight containers for subsequent analysis.

Hydrocoal yield was calculated gravimetrically based on the final dry mass.

$$\text{Hydrocoal Yield (wt\%)} = \frac{\text{Mass of solid recovered (g)}}{\text{Mass of EO (g)}} \times 100$$

Each HTC experiment was performed in triplicate, and the hydrocoal mass yields are reported as mean values accompanied by their standard deviations. Standard deviations are presented as error bars in Figure 1.

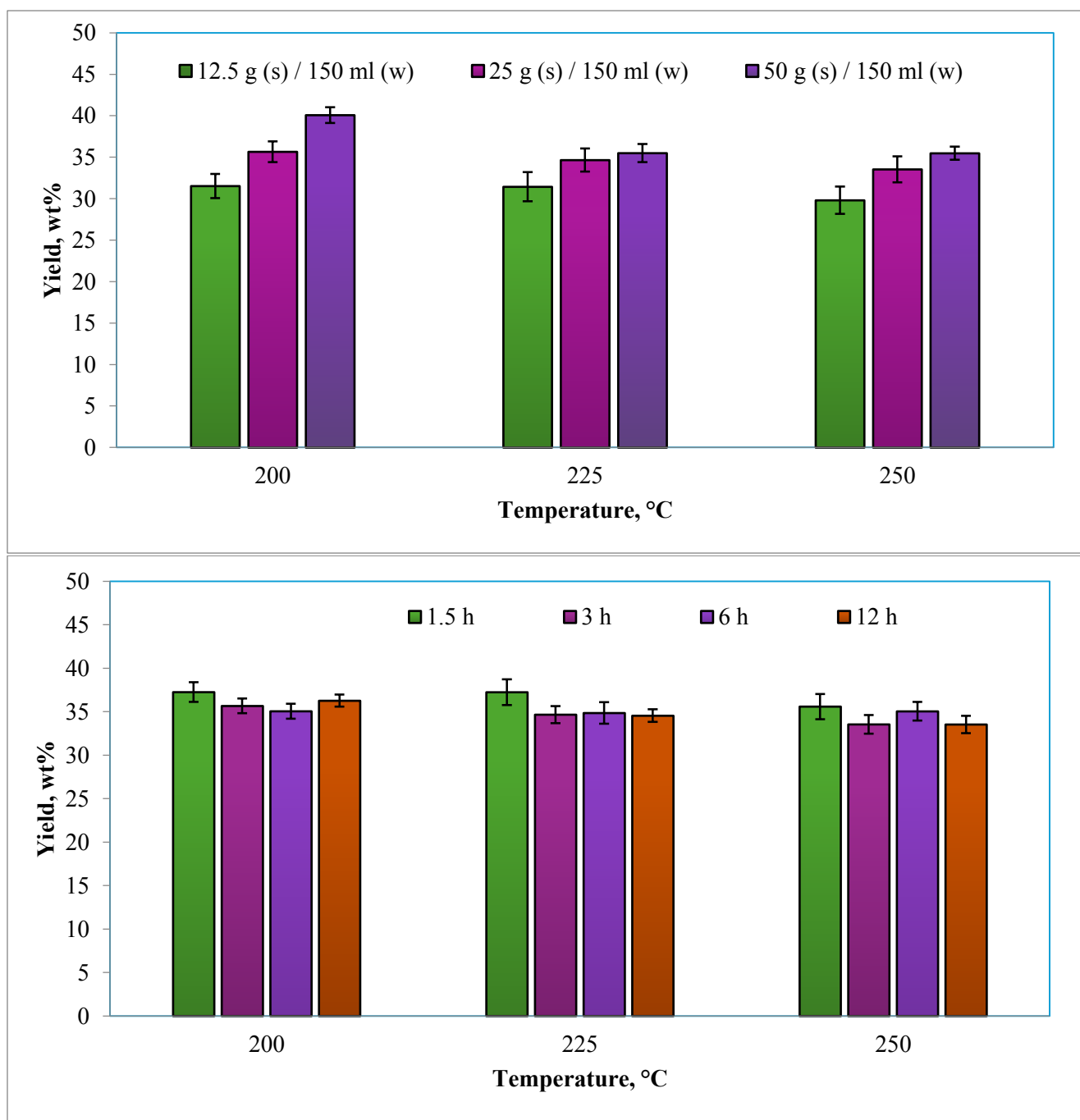


Figure 1. a) The effect of EO-to-water ratios on hydrocoal yields obtained from the HTC of EO (residence time was fixed at 3 h).  
b) The effect of temperature and residence time on hydrocoal yields obtained from the HTC of EO (EO-to-water ratio was fixed at 25 g to 150 mL).

### 2.3. Analyses

Hydrocoals were characterized using a suite of analytical techniques, including solid-state SEM (FEI Quanta FEG 450), TGA (Seiko EXSTAR 7200, 25–850 °C, 20 °C/min,

nitrogen, ~5.5 mg, 50 mL/min), FTIR-ATR (Thermo Scientific Nicolet iS50), XRD (Panalytical Empyrean, Cu K $\alpha$ ), and  $^{13}\text{C}$  NMR (JEOL ECZ 500R). Thermogravimetry/mass spectrometry (TG/MS) experiments were conducted with a Perkin-Elmer TGS-2 thermobalance (USA). The device featured a modified furnace and a temperature controller (Eurotherm, UK). It was coupled to a HiQuad quadrupole mass spectrometer (Pfeiffer Vacuum, Germany). About 1.5 mg sample was placed in a platinum sample pan. The heating rate was 20 °C min $^{-1}$  from room temperature to 950 °C under helium atmosphere at a flow rate of 140 mL min $^{-1}$ . A portion of the evolved gases and vapors were introduced into the MS through a glass-lined metal capillary transfer line heated at 300 °C. The MS ion source was operated at an electron energy of 70 eV.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) measurements were performed using a Frontier Multi-Shot Pyrolyzer (EGA/PY-3030D, Japan) connected to an Agilent 6890A/5973 GC/MS (USA). Approximately 0.4 mg of each sample was pyrolyzed at 500 °C for 30 s under helium atmosphere at a flow rate of 100 mL min $^{-1}$ . Additional Py-GC/MS experiment was performed at 250°C to selectively analyze compounds releasing in the first decomposition step.

Aqueous-phase organics were extracted with  $\text{CH}_2\text{Cl}_2$  and analyzed by GC–MS (Agilent 6890), while TOC, COD, and pH measurements were performed in an accredited laboratory. Elemental composition was obtained via CHNS analysis (LECO CHNS-932), and oxygen content was calculated by difference. Proximate and ultimate analysis procedures, as well as the equations used for estimating heating values and reaction severity, follow the methodology detailed in our previous work<sup>11</sup>.

## **2. Results and Discussion**

### *Yields and Characteristics of Hydrocoals*

Figure 1a illustrates the effect of the EO-to-water ratio on the HTC yields. At all tested temperatures, the HTC yield increased with increasing amounts of EO. This trend is consistent with expectations, as at low solid loadings, processes such as percolation hydrolysis may lead to nearly complete dissolution of the biomass, leaving very little solid residue <sup>12</sup>. Conversely, increasing the solid loading by reducing the water content promotes the precipitation of dissolved organic compounds, thereby enhancing the formation of the solid phase. The highest hydrocoal yield (40.08 wt%) was obtained at 200 °C with a feed ratio of 50 g EO to 150 mL water. However, it should be noted that this relatively high yield at the lowest temperature does not necessarily indicate complete conversion of the EO into hydrocoal. Indeed, for all tested EO-to-water ratios, an increase in temperature led to a gradual decrease in hydrocoal yield. Elevated temperatures promote the decomposition of organic matter and the release of volatile compounds, thereby reducing the overall hydrocoal yield. Previous studies on the HTC of various biomass types-including lignocellulosic feedstocks <sup>13,14</sup>, algal biomasses <sup>15,16</sup>, and FWs <sup>17</sup>. have similarly reported decreases in hydrocoal yield with increasing temperature, in agreement with the present findings. The lowest hydrocoal yield (29.81 wt%) was observed at 250 °C with a feed ratio of 12.5 g biomass to 150 mL water. Figure 1b presents the influence of reaction time on hydrocoal yield. The maximum yield was obtained after the shortest applied reaction time (1.5 h) at all temperatures, whereas no significant changes were observed at longer reaction times. This observation suggests that most of the hydrothermal reactions reach completion within the first 1.5 h. It should also be emphasized that hydrocoal yields are strongly dependent on both the type of feedstock and the applied process conditions. Table 2 summarizes the physicochemical properties of the hydrocoals produced via the HTC of EO.

For all conditions, the hydrocoals exhibited lower volatile matter contents and higher fixed carbon contents compared to the raw feedstock. At the same residence time, increasing the temperature led to an increase in the fixed carbon percentage and a decrease in the volatile matter percentage. This can be attributed to the enhanced decomposition of organic material at higher temperatures, which promotes the release of volatile compounds and consequently increases the relative proportion of fixed carbon. Although changes in volatile matter with reaction time at a given temperature were not pronounced, at the highest temperature tested, extending the reaction time resulted in a further decrease in volatile matter and an increase in fixed carbon content. The fuel ratio (FR) of the raw feedstock was 0.20, whereas that of the hydrocoals ranged between 0.72 and 1.23. The highest fuel ratio was obtained under the most severe reaction conditions (250 °C and 12 h). Understanding the fuel efficiency of biochars and hydrocoals requires a thorough evaluation of their intrinsic combustion characteristics. The ash content of the raw material was 1.62 wt%, while the ash content of the hydrocoals ranged from 0.14 to 0.48 wt%. The significant reduction in ash content after HTC can be attributed to the dissolution of inorganic species into the aqueous phase under subcritical water conditions<sup>18</sup>. The low ash content and high fuel ratio (FR) of the hydrocoals indicate their suitability for use as solid biofuels. All hydrocoals exhibited higher carbon and lower oxygen contents compared to the raw material. The progression of coalification is commonly evaluated through the atomic hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios<sup>19</sup>. The hydrocoals exhibited atomic H/C and O/C ratios of 0.92–1.08 and 0.12–0.21, respectively, both lower than those of the raw material. Decreasing O/C ratios indicate decarboxylation, whereas decreasing H/C ratios reflect dehydration<sup>20</sup>. Figure 2 shows the Van

Krevelen diagram of H/C versus O/C ratios. It was found that most of the hydrocoals were in or near the bituminous coal region. It is clearly seen in the Van Krevelen diagram that the H/C and O/C ratios are reduced.

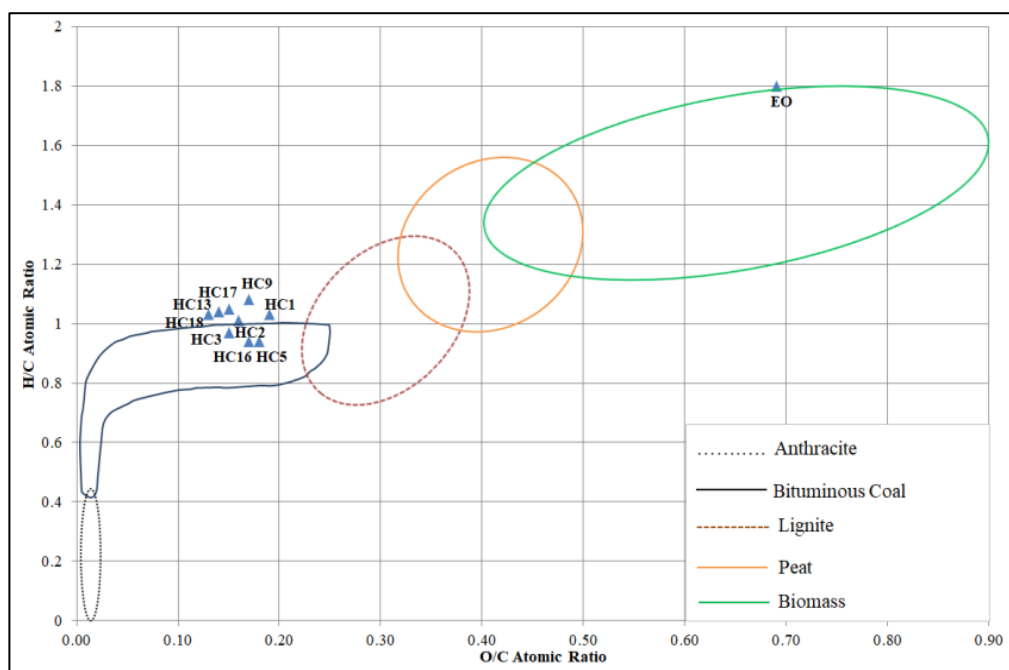


Figure 2. A van Krevelen diagram of EO and hydrocoals (HC1, HC2, HC3, HC5, HC9, HC13, HC16, HC17, HC18) obtained from the HTC of EO (codes refer to Table 2).

Notably, these decreases indicate increased aromaticity and decreased polarity of the hydrocoals, respectively <sup>20</sup>. Previous reports demonstrated that reduced O/C ratios increased chemical and microbial stability of biochars <sup>21</sup>. It was found that, under all conditions, the calorific values of the obtained hydrocoals were higher than that of the raw material, ranging from 29.6 to 32.3 MJ/kg, compared to 18.13 MJ/kg for the raw material. The EDR ranged from 1.61 to 1.78, while the energy yield ranged from 52.2% to 66.13%. The sulfur contents of the hydrocoals (0.15–0.26 wt%) are comparable to those of the raw feedstock and considerably lower than the typical sulfur content of commercial coals, which ranges from 1 to 3 wt% and can reach up to 11 wt% for high-organic-sulphur deposits,<sup>22</sup> indicating that SO<sub>2</sub>

emissions during combustion are not anticipated to pose a practical concern for energy recovery applications.

Comparison with studies on brewer's spent grain (BSG), a lignocellulosic brewery byproduct commonly used as an HTC feedstock, further contextualizes the fuel properties of the EO-derived hydrocoals obtained in this study. Arauzo et al. (2018) reported that HTC of BSG (43 wt% hemicellulose, 24 wt% cellulose, 29 wt% protein) at 180–220 °C yielded hydrocoal with carbon contents of 60–68 wt% and HHV of 26–30 MJ/kg, with O/C ratios declining from 0.53 to approximately 0.25–0.35 as a result of dehydration and decarboxylation reactions<sup>23</sup>. Lorente et al. (2020) using microwave-assisted HTC of BSG at 180–250 °C achieved HHV up to 32 MJ/kg and demonstrated that increasing temperature and reaction time shifted the Van Krevelen position progressively toward the bituminous coal region through enhanced aromatization<sup>24</sup>. Barontini et al. (2025) applied a design of experiments (DOE) approach to BSG HTC at 200–260 °C, obtaining carbon contents of 60.7–72.0 wt% and HHV up to 30.8 MJ/kg with lignite-like properties under optimized conditions<sup>25</sup>. Arauzo et al. (2019) further showed that protein extraction from BSG prior to HTC lowered the ash content to 1.52–1.72 wt% and altered the nitrogen distribution of the resulting hydrocoals, confirming that feedstock composition directly governs hydrocoal properties<sup>26</sup>. Against this backdrop, the EO-derived hydrocoals of the present study achieved comparable HHV values of 29.6–32.3 MJ/kg alongside markedly lower ash contents of 0.14–0.48 wt%, which can be attributed to the inherently lower mineral content of oatmeal relative to BSG. The O/C ratios of 0.12–0.21 and H/C ratios of 0.92–1.08 observed for EO hydrocoals fall within or below the range reported for BSG hydrocoals at comparable temperatures, suggesting that the carbohydrate-dominant composition of EO promotes efficient carbonization even under moderate process conditions, an outcome that becomes interpretable precisely because the feedstock composition is well-characterized.

The elevated carbon contents observed in the present study (69–77 wt% across all conditions) are further contextualized by comparison with oat-based and related carbohydrate-rich feedstocks reported in the literature <sup>27</sup> (Table 3). For whole oat grain, Zaccariello et al. (2022) reported carbon contents of 56–64 wt% at 180 °C and 68.1 wt% at 215 °C, reaching 72.8 wt% only at the considerably more severe condition of 250 °C <sup>27</sup>. For oat husk, a lignocellulosic agricultural residue, Murillo et al. (2022) reported a carbon content of 51.2 wt% at optimal HTC conditions (219 °C, 30 min), corresponding to only ~11% carbon enrichment relative to the raw feedstock (C = 46.0 wt%)<sup>28</sup>. Similarly, Singh et al. (2026) reported a hydrochar content of 52.4 wt% from oat hull HTC at 180 °C using fresh water, which increased to 65.5 wt% only when nutrient-rich HTL process water was employed as the reaction medium, with the accumulated dissolved organics effectively supplementing the carbon precursor pool<sup>29</sup>. These comparisons demonstrate that, even among oat-derived feedstocks, the carbon enrichment achievable under mild-to-moderate HTC conditions is strongly governed by the macromolecular composition of the feedstock. The higher carbon contents obtained in the present study at 200 °C, already exceeding those reported for whole oat grain at 215 °C and lignocellulosic oat husk/hull at any tested condition, can be attributed to several synergistic factors specific to EO. First, unlike lignocellulosic oat-derived residues such as oat husk and oat hull, EO is produced from dehulled oat groats and contains negligible lignin content, as the outer husk is removed during milling. This substantially reduces the physical barrier that in lignocellulosic biomasses shields the carbohydrate matrix from rapid hydrothermal hydrolysis, enabling complete and more efficient carbonization at 200 °C. Second, the high proportion of readily hydrolysable carbohydrates efficiently undergoes HMF-mediated dehydration, condensation, and polymerization reactions even at 200 °C<sup>30</sup>. Third, the protein content of EO promotes Maillard-type reactions between amino acid degradation products and carbonyl intermediates beginning at temperatures as low as 180 °C,

directly incorporating nitrogen-containing aromatic heterocycles into the hydrocoal matrix and further contributing to carbon densification<sup>23,31</sup>. The data compiled in Table 3 confirm that, at equivalent temperatures, EO consistently yields higher carbon contents and comparable or superior HHV values relative to lignocellulosic oat and BSG feedstocks, validating the approach of using a compositionally well-characterized non-lignocellulosic food waste as a model feedstock.

### *Structural Characteristics of Hydrocoals*

Typical functional groups of carbonized materials can be clearly seen in the FTIR spectra of the hydrocoals (Figure 3). The absorption region between 3600 and 3200  $\text{cm}^{-1}$  is mainly due to the stretching of O–H and N–H bonds. It is clearly seen from the FTIR spectra of the hydrocoals that dehydration and denitrogenating occurred with increasing temperature, as the broad absorption band observed at the lowest temperature became narrower and less intense at higher temperatures. Hydrocoals displayed aliphatic C–H stretching vibrations ( $\text{CH}_2$  and  $\text{CH}_3$ ) in the 3000–2800  $\text{cm}^{-1}$  region, and the intensities of these absorption bands decreased with increasing temperature. The peak observed around 1640  $\text{cm}^{-1}$  is attributed to Amide I, arising from C=O stretching<sup>32</sup>. The band near 1515  $\text{cm}^{-1}$  corresponds to C–N stretching and N–H in-plane bending, characteristic of the Amide II vibration of secondary amides in proteins<sup>33</sup>. Additionally, peaks in the 650–900  $\text{cm}^{-1}$  range, associated with wagging vibrations of aromatic C–H bonds, confirm the retention of aromatic carbon structures under all HTC conditions.

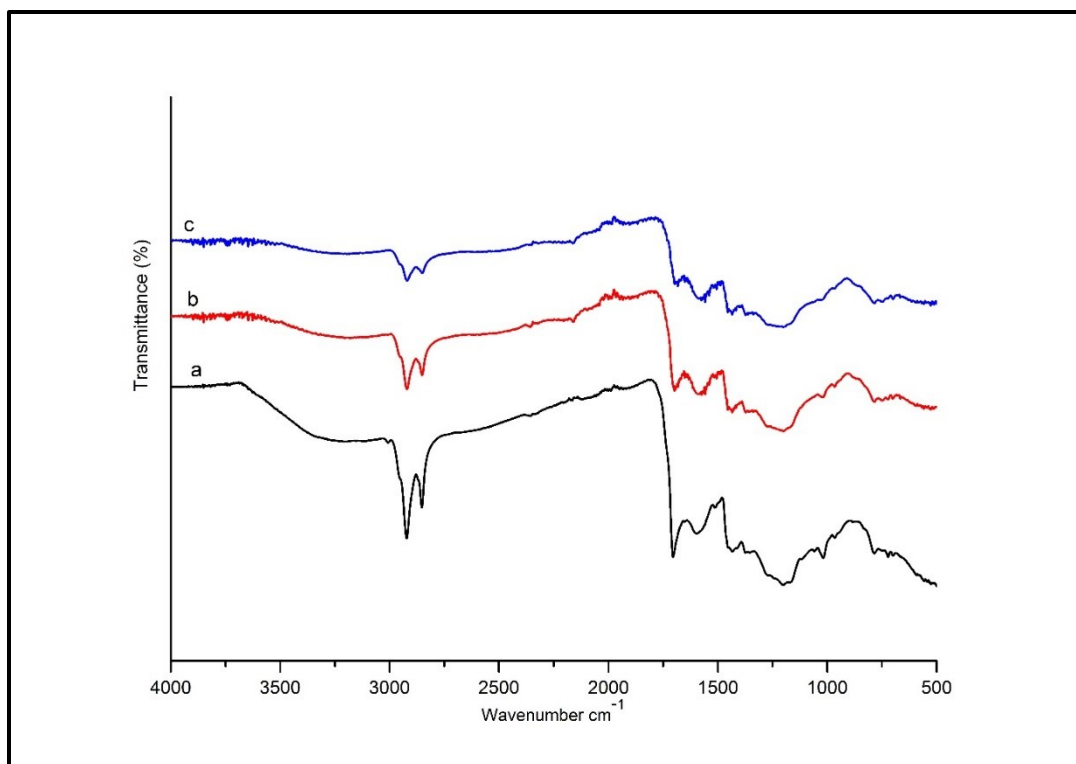


Figure 3. FTIR spectra of hydrocoals obtained from the HTC of EO (a) HC5 (b) HC9 (c) HC13 (codes refer to Table 2).

Solid-state  $^{13}\text{C}$  NMR analyses of the hydrocoals were conducted to investigate their structural characteristics, as shown in Figure 4. There were no significant differences among the hydrocoal samples. Signals observed in the 0–90 ppm range correspond to  $\text{sp}^3$ -hybridized carbon atoms, typically linked to aliphatic chains and hydroxylated carbon (C–OH) group<sup>32</sup>. The peak observed between 110 and 160 ppm can be attributed to aromatic and olefinic structures in the hydrocoals. The broad signals in the 170–225 ppm range are typically associated with carbonyl and amide functionalities.

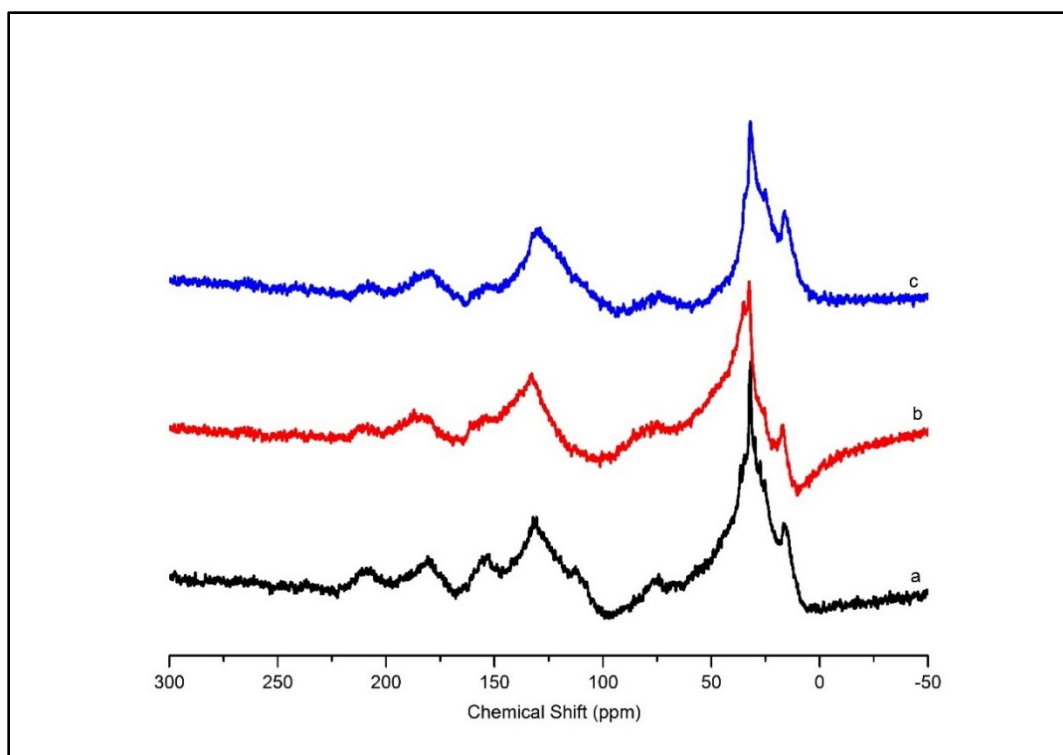


Figure 4. <sup>13</sup>C NMR spectra of hydrocoals obtained from the HTC of EO (a) HC5 (b) HC9 (c) HC13 (codes refer to Table 2).

As shown in Figure 5, the XRD patterns of hydrocoals derived from EO at 200 °C, 225 °C, and 250 °C exhibit a single broad peak near 21.5° (2θ). This feature is characteristic of amorphous carbon, in agreement with earlier findings.

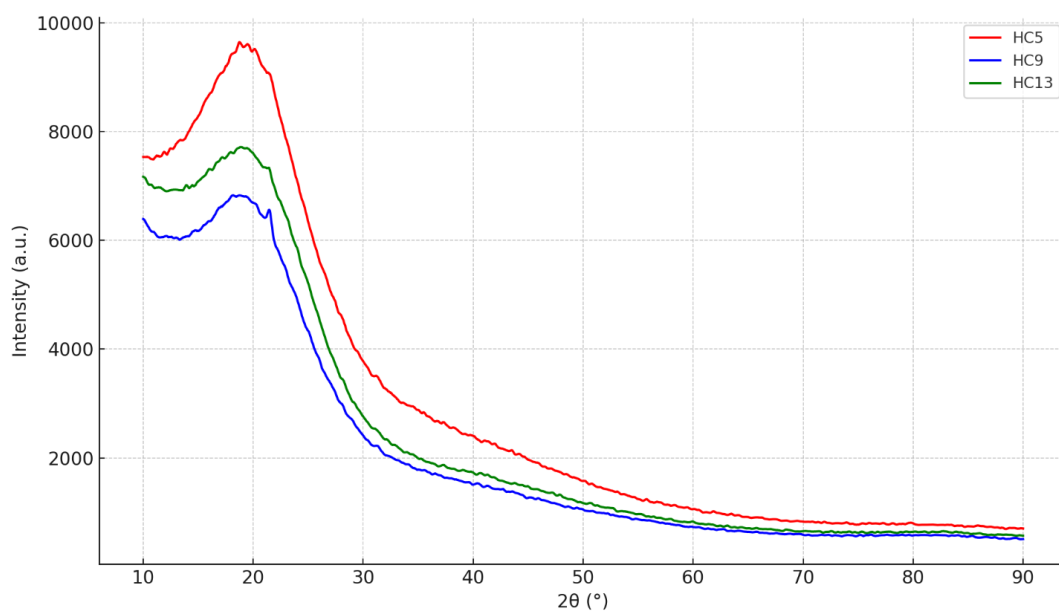


Figure 5. XRD patterns of hydrocoals (codes refer to Table 2).

Figure 6 shows the SEM images of EO and the hydrocoals. EO exhibited irregularly shaped particles with smooth surfaces. SEM analysis of EO-derived hydrocoals revealed the formation of carbon sphere structures in the hydrocoals, and it was found that with increasing temperature, the number of these carbon spheres increased. The diameters of the carbon spheres ranged from 1.65 to 2.78  $\mu\text{m}$  at 200  $^{\circ}\text{C}$ , from 1.2 to 3.4  $\mu\text{m}$  at 225  $^{\circ}\text{C}$ , and from 1.9 to 7.5  $\mu\text{m}$  at 250  $^{\circ}\text{C}$ . An overall increase in carbon sphere diameter was observed with increasing temperature.

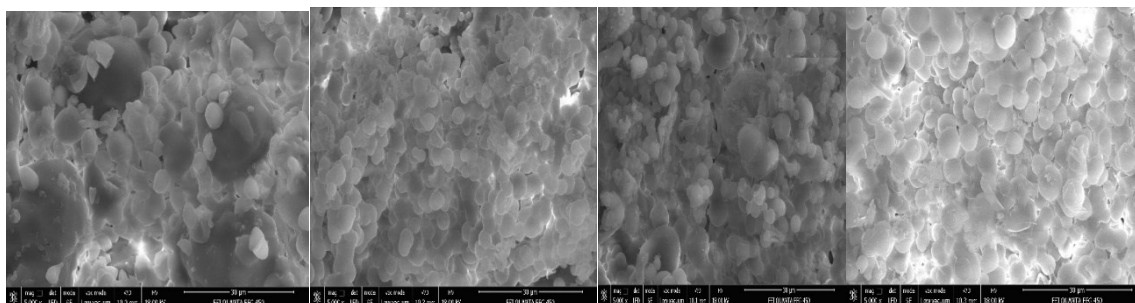


Figure 6. SEM images of (a) EO and hydrocoals obtained from the HTC of EO at (b) HC5 (c) HC9 (d) HC13 (codes refer to Table 2).

The well-defined macromolecular composition of EO, comprising 68.66 wt% carbohydrates, 12.99 wt% protein, and 7.25 wt% lipids, provided a mechanistic basis for interpreting the observed structural and physicochemical transformations. The high carbohydrate content is directly responsible for carbon sphere formation observed in SEM images: HTC of carbohydrates proceeds via hydrolysis to hexoses, dehydration to HMF, and subsequent polymerization and aromatization, producing the spherical carbonaceous particles whose diameter increased progressively from 1.65–2.78  $\mu\text{m}$  at 200  $^{\circ}\text{C}$  to 1.9–7.5  $\mu\text{m}$  at 250  $^{\circ}\text{C}$ . The persistence of Amide I ( $1640\text{ cm}^{-1}$ ) and Amide II ( $1515\text{ cm}^{-1}$ ) bands in FTIR spectra at lower temperatures, and their gradual attenuation at 250  $^{\circ}\text{C}$ , is mechanistically attributable to the protein fraction undergoing hydrolysis and partial denitrogenation. The retention of aliphatic C–H stretching bands ( $3000\text{--}2800\text{ cm}^{-1}$ ) at all temperatures reflects the hydrothermal resistance of the lipid fraction. This compositional traceability, linking each structural feature to a specific macromolecular fraction, is not achievable with heterogeneous, undefined food waste mixtures.

#### *Thermal Decomposition of Hydrocoals and raw EO sample*

Figure 7 illustrates the TG and DTG curves of hydrocoals HC5, HC9, and HC13, produced at 200, 225, and 250  $^{\circ}\text{C}$  for 3 h, respectively, as well as the raw EO sample.

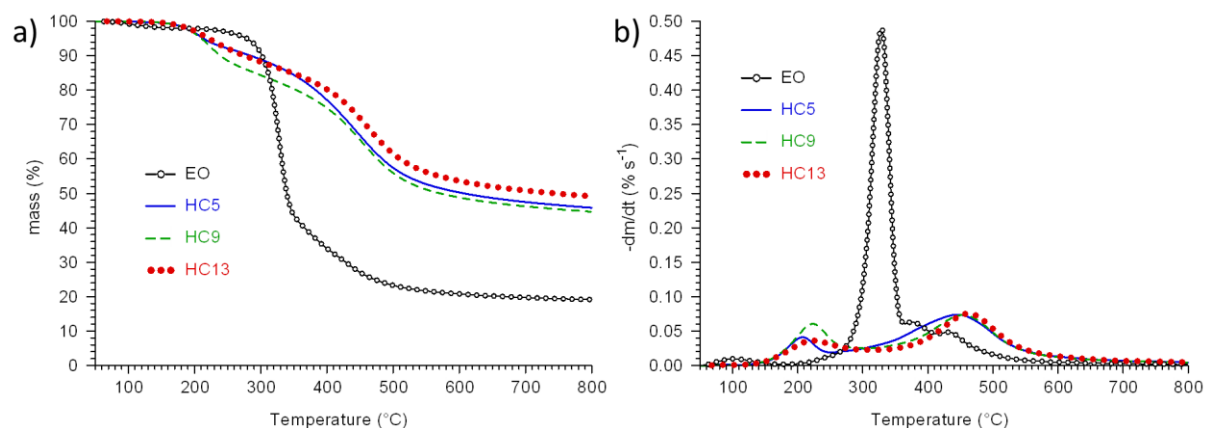


Figure 7. TG/DTG curves of EO and hydrocoals obtained from the HTC of EO (codes refer to Table 2).

The first weight loss event, observed below 120 °C, corresponds to the evaporation of physically adsorbed moisture remained in the sample after the 40 min inertization period by 140 ml/min Ar flush. The remaining moisture content of the raw EO sample was about 3%, while the weight loss of hydrocoals were negligible up to 120 °C, indicating the more hydrophobic nature of the hydrocoal. The second event, with a DTG peak at approximately 220 °C, is attributed to the release of fatty acids from the sample, which was proved by a 250 °C Py-GC/MS measurement discussed in detail later this chapter. The weight loss in this step was more remarkable for the hydrocoal samples reflecting the accumulation of the fatty acid content of EO in the solid hydrophobic hydrocoal. The thermal decomposition of the carbohydrate content of the raw EO sample, which accounts for its 69 % (Table 1) is takes place around 330°C, and indicated with the main DTG peak of the raw EO sample. In the case of the three hydrocoal samples no DTG peak was observed in this range, which indicates the complete decomposition of the carbohydrate fraction during the HTC processes, even at 200°C temperature. The next event of the hydrocoal samples, centered at approximately 400–500 °C corresponds to the main thermal degradation of the aromatic hydrocoal matrix. The development of the carbonization process at higher HTC temperatures reflected in the narrowing peak shape and shift to higher temperature. Increasing HTC production

temperature progressively shifted the onset of this decomposition event to higher temperatures, confirming enhanced thermal stability of hydrocoals produced under more severe conditions, in agreement with earlier studies<sup>11,33</sup>. A gradual low-intensity mass loss continues up to 700 °C, associated with the decomposition of thermally stable condensed aromatic structures. The total mass losses of HC5 (54.9%), HC9 (55.3%), and HC13 (50.8%) were consistent with the volatile matter contents determined by proximate analysis, confirming the reliability of the thermal decomposition data.

TG/MS analysis was performed to identify the volatile species responsible for the mass loss events observed in the DTG curves. Figure 8 compares the evolution profile of characteristic  $m/z$  ions.

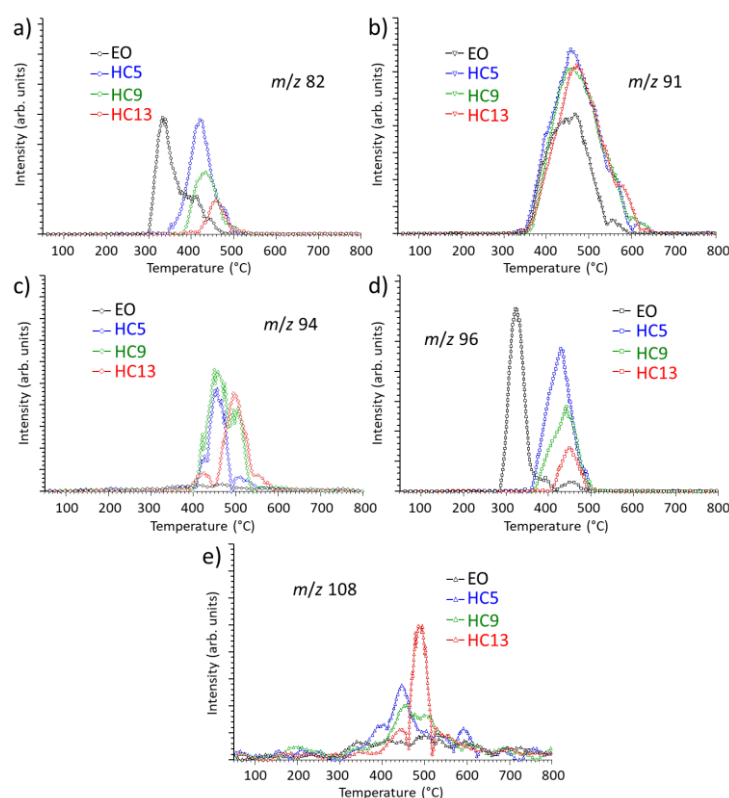


Figure 8. TG/MS ion intensity profiles of EO and hydrocoals obtained from the HTC of EO (codes refer to Table 2).

No specific ions were detected during the release of fatty acids in a temperature range of 150–300°C. The absence of fatty acid-specific ions in this region is attributed to the high molecular weight and low volatility of lipid-derived species, which do not reach the MS detector under the applied conditions. In contrast, the second and most prominent decomposition event of hydrocoals (420–460 °C) was clearly associated with the release of aromatic and furan-derived compounds, as evidenced by the detection of characteristic ions including e.g. methylfuran ( $m/z$  82), toluene ( $m/z$  91), phenol ( $m/z$  94), dimethylfuran ( $m/z$  96), and cresol ( $m/z$  108). Comparing the  $m/z$  82 and  $m/z$  96 ion signals shows that both exhibit similar temperature-dependent trends. These ions are characteristic molecular ions of carbohydrate-derived products: 2-methylfuran and cyclopentanone (both  $m/z$  82) as well as 2,5-dimethylfuran and furfural (both  $m/z$  96). Based on the Py-GC/MS results, the  $m/z$  96 profile mainly reflects the release of 2,5 dimethylfuran from the hydrochar samples (max between 420 and 450°C), whereas formation of furfural in the raw EO sample (max at 320°C) due to cellulose and hemicellulose decomposition. For the hydrocoals, the evolution of furan-derived compounds shifted to higher temperatures (from 420 to 455°C) and their relative abundance decreased as the HTC treatment temperature increased. The evolution profile of the detected aromatic compounds (toluene ( $m/z$  91), phenol ( $m/z$  94) and cresol ( $m/z$  108)) showed higher release intensities from the hydrocoals compared with the raw EO sample, while did not exhibit clear temperature shift. The detection of these aromatic and furan derivatives in the main decomposition stage is consistent with the aromatic character of the hydrocoal matrix confirmed by FTIR and  $^{13}\text{C}$  NMR analyses, and corroborates the formation of a thermally stable, aromatic-rich solid product during HTC of EO.

Py-GC/MS analysis of HC9 hydrocoal at 250 °C was performed to identify the molecules releasing in the first weight loss step between 150 and 250°C (Figure 9). The chromatogram is dominated by saturated and unsaturated lipid derived products, namely palmitic acid (C16:0),

stearic acid (C18:0), oleic acid (C18:1) and octadecadienoic acid (C18:2). In addition to fatty acids, small amounts of long n-alkanes (C24-C34) were also detected, probably of plant wax origin.

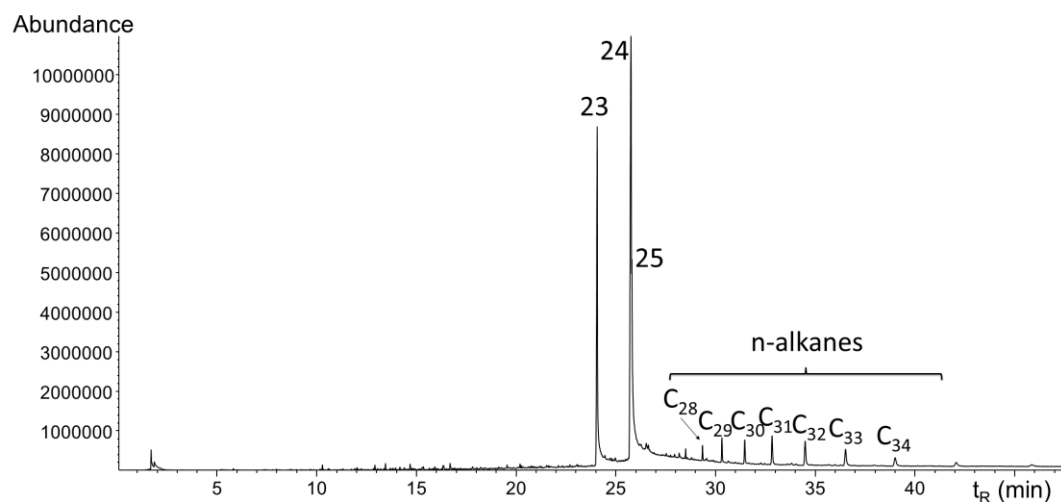


Figure 9. Py-GC/MS chromatogram of HC9 hydrocoals using 250°C pyrolysis temperature (peak No. refers to Table 4).

Py-GC/MS analysis at 500 °C was performed to further characterize the organic composition of the hydrocoals matrix and to track the fate of individual macromolecular fractions during HTC (Figure 10).

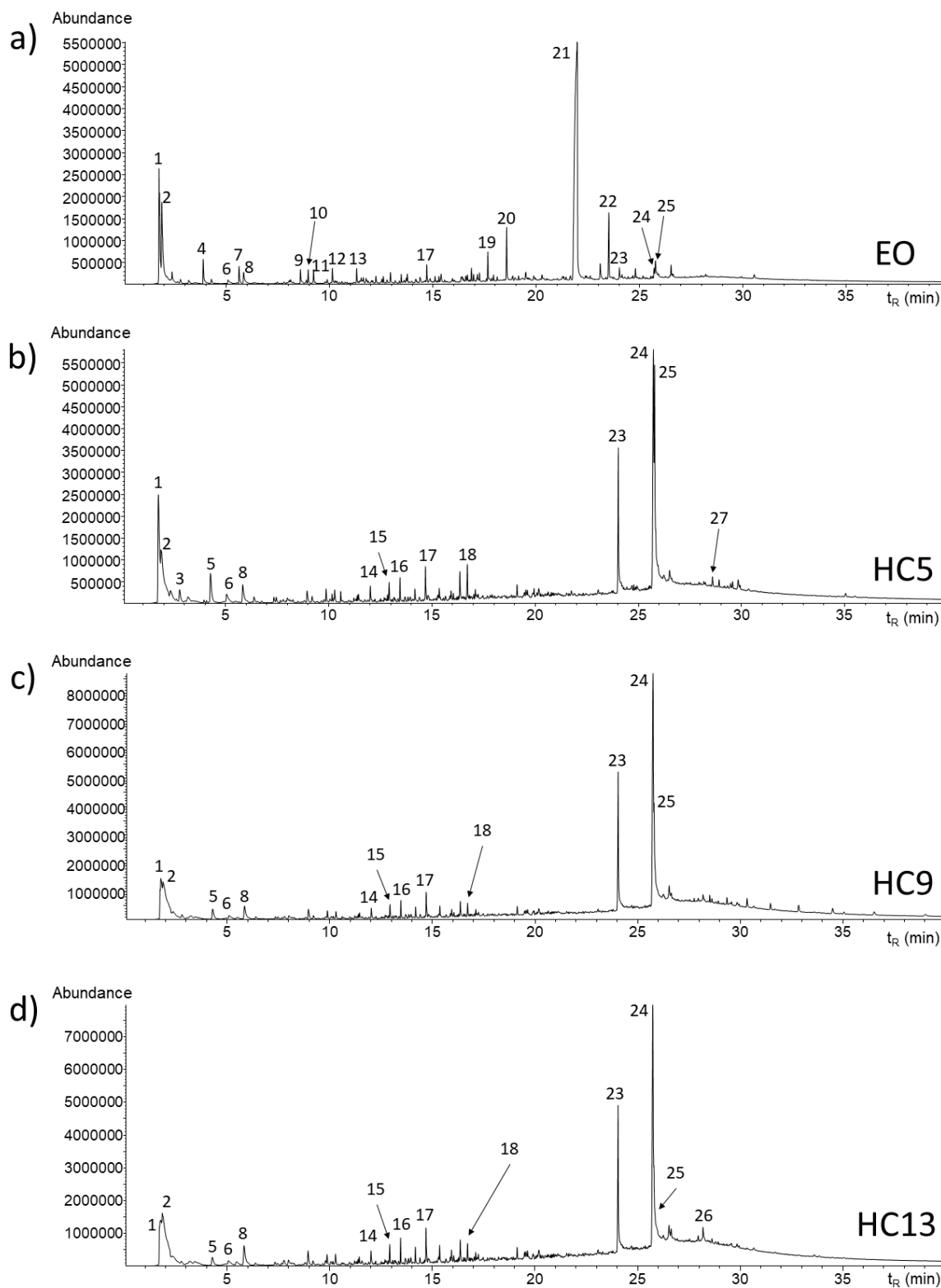


Figure 10. Py-GC/MS (pyrolysis T: 500°C) chromatograms of EO and hydrocoals obtained from the HTC of EO (codes refer to Table 2, peak No. refers to Table 4).

**Table 2.** The list of the identified pyrolysis products of EO and hydrocoals (sample No. refers to Figures 9 and 10)

| No. | t <sub>R</sub> (min) | Compound                                               | m/z                  |
|-----|----------------------|--------------------------------------------------------|----------------------|
| 1   | 1,74                 | Carbon dioxide                                         | 44,28                |
| 2   | 1,86                 | Water                                                  | 18,17                |
| 3   | 2,76                 | 2-Methylfuran                                          | 82,81,53             |
| 4   | 3,87                 | Hydroxyacetaldehyde                                    | 31,32,29             |
| 5   | 4,26                 | 2,5-Dimethylfuran                                      | 96,95,43             |
| 6   | 5,07                 | Acetic acid                                            | 43,45,60             |
| 7   | 5,59                 | 1-Hydroxy-2-propanone                                  | 43,31,74             |
| 8   | 5,82                 | Toluene                                                | 91,92,65             |
| 9   | 8,58                 | Furanone                                               | 84,54,53             |
| 10  | 8,95                 | Methyl-pyruvate                                        | 43,102,31            |
| 11  | 9,21                 | Furfural                                               | 96,95,39             |
| 12  | 10,13                | Furfuryl alcohol                                       | 98,81,97             |
| 13  | 11,30                | Methyl-furanone                                        | 98,55,69             |
| 14  | 12,02                | 3-Methyl-2-cyclopenten-1-one                           | 96,53,67             |
| 15  | 12,92                | 2,3-Dimethyl-2-cyclopenten-1-one                       | 110,67,82            |
| 16  | 13,46                | Phenol                                                 | 94,66,65             |
| 17  | 14,69                | <i>p</i> -Cresol                                       | 107,108,77           |
| 18  | 16,72                | 6-Methyl-3-pyridinol                                   | 109,80,53            |
| 19  | 17,64                | 5-Hydroxymethylfurfural                                | 97,126,41            |
| 20  | 18,55                | 2-Hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one | 144,87,97            |
| 21  | 21,95                | Levoglucosan                                           | 60,57,73             |
| 22  | 23,48                | 1,6-Anhydro- $\alpha$ -D-galactofuranose               | 73,69,85             |
| 23  | 24,00                | Palmitic acid                                          | 73,60,129            |
| 24  | 25,67                | Oleic acid                                             | 55,69,264            |
| 25  | 25,75                | Stearic acid + Octadecadienoic acid                    | 43,73,129 + 67,81,95 |
| 26  | 28,19                | 9-Octadecenamide                                       | 59,72,281            |
| 27  | 28,60                | Phe-Val DKP                                            | 91,127,246           |

The list of the identified pyrolysis products is presented in Table 4. The total ion chromatogram of raw EO exhibited a complex profile comprising compounds derived from all three macromolecular fractions: carbohydrate-derived products including levoglucosan, hydroxyacetaldehyde, hydroxypropanone, furfural, furfuryl alcohol, hydroxymethylfurfural (HMF), and furan derivatives; protein-derived products including phenol, *p*-cresol, toluene, 6-methyl-3-pyridinol, and a phenylalanine-valine diketopiperazine (Phe-Val DKP); and lipid-

derived products including palmitic acid (C16:0), oleic acid (C18:1), stearic acid (C18:0), octadecadienoic acid (C18:2), and 9-octadecenamide. The detection of these compounds is consistent with the fatty acid profile of EO (Table 1), in which oleic acid (C18:1) and linoleic acid (C18:2) are the dominant C18 fatty acids. With increasing HTC temperature, carbohydrate- and protein-derived pyrolysis products became less prominent in the chromatographic profiles, while lipid-derived compounds, particularly the long-chain fatty acids, became the dominant species in the hydrocoal matrix, confirming the accumulation of fatty acids due to the hydrothermal resistance of the lipid fraction. At 250 °C (HC13), the chromatographic profile was markedly simplified, with fatty acids representing the most prominent species. This trend confirms that the lipid fraction of EO exhibits the highest resistance to hydrothermal carbonization among the three macromolecular fractions, consistent with the persistence of aliphatic C–H stretching bands (3000–2800 cm<sup>-1</sup>) observed in the FTIR spectra across all HTC temperatures.

Figure 11 shows selected ion chromatograms obtained by Py-GC/MS analysis of the raw EO and hydrocoal samples. The relative distribution of C18 fatty acids — diunsaturated linoleic acid (m/z 280), monounsaturated oleic acid (m/z 282), and saturated stearic acid (m/z 284) — was compared across HTC temperatures. The hydrocoal produced at 200 °C exhibited a C18 fatty acid distribution similar to that of the raw EO feedstock, with diunsaturated species (linoleic acid) present as the dominant fraction. With increasing HTC temperature, the relative abundance of diunsaturated octadecadienoic acid decreased progressively, while the relative abundances of monounsaturated oleic acid and saturated stearic acid increased correspondingly, indicating the progressive saturation of carbon–carbon double bonds during hydrothermal carbonization at elevated temperatures.

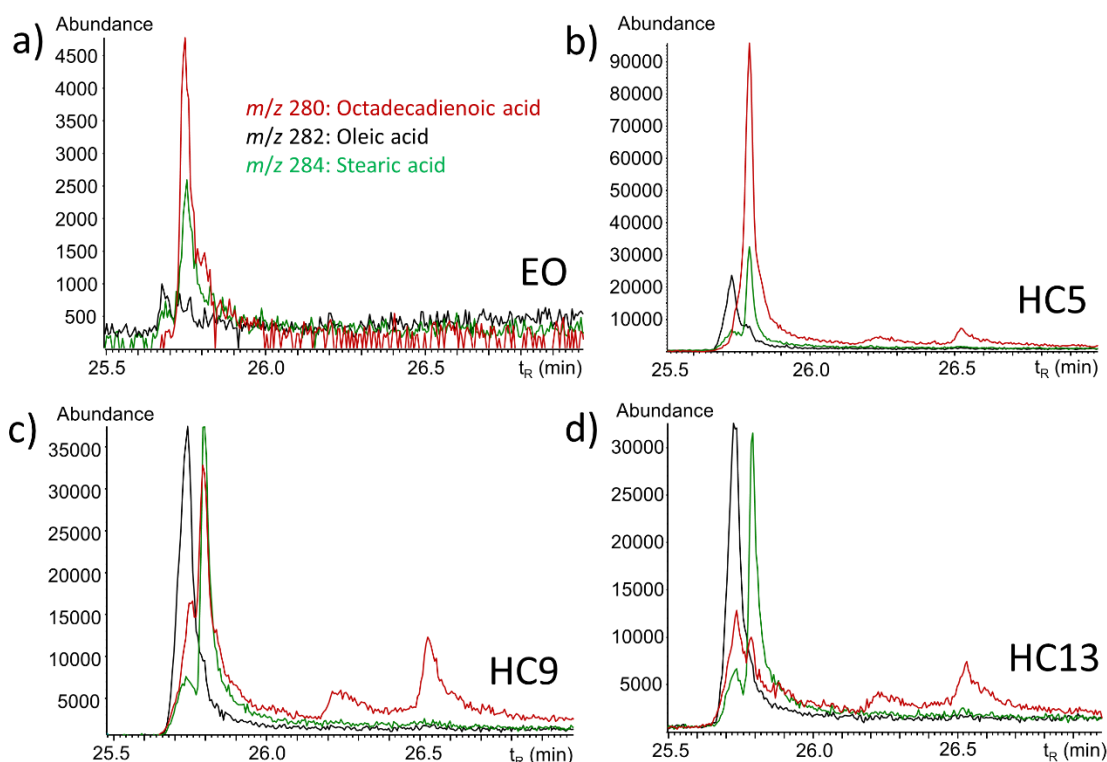


Figure 11. Selected ion intensity curves of Py-GC/MS (pyrolysis T: 500°C) of EO and hydrocoals obtained from the HTC of EO (codes refer to Table 2).

**Table 3.** GC-MS analysis of aqueous phases obtained from the HTC of EO (codes refer to Table 1).

| Retention Time (min) | Compounds                                  | Area (%) |       |       |
|----------------------|--------------------------------------------|----------|-------|-------|
|                      |                                            | HC5      | HC9   | HC13  |
| 5.43                 | Cyclohexanone                              | 0.26     | -     | -     |
| 5.90                 | 2-Methyl-2-cyclopenten-1-one               | 3.54     | 11.04 | 10.94 |
| 6.16                 | 1-(2-Furanyl)-ethanone                     | 4.50     | 8.64  | 8.79  |
| 7.86                 | Dihydro-5-methyl-2(3H)-furanone            | -        | 0.92  | 1.16  |
| 8.30                 | 3-Methyl-2-cyclopenten-1-one               | 1.22     | 4.73  | 7.07  |
| 10.85                | 3,4-Dimethyl-2-cyclopenten-1-one           | -        | 0.51  | 0.63  |
| 11.27                | Limonene                                   | 6.36     | -     | -     |
| 11.75                | 2,3-dimethyl-2-Cyclopenten-1-one           | 0.49     | 4.08  | 4.78  |
| 12.66                | 3,4-Dimethyl-2-hydroxycyclopent-2-en-1-one | 0.48     | -     | -     |
| 12.94                | 3,4,4-Trimethyl-2-cyclopenten-1-one        | -        | 0.40  | -     |
| 12.96                | 2,6-Dimethyl-2,4-heptadiene                | -        | -     | 0.37  |
| 13.21                | 2-Pyrrolidinone                            | -        | -     | 1.95  |
| 14.17                | 2,3,4-Trimethyl-2-cyclopenten-1-one        | -        | 0.70  | -     |
| 14.19                | Mequinol                                   | -        | -     | 0.79  |
| 15.15                | 3,5,5-Trimethyl-2,4-Imidazolidinedione     | -        | 1.80  | 1.73  |
| 18.75                | 2-Acetoncyclopentanone                     | -        | 1.21  | 1.15  |
| 22.08                | 1,3-Bis(1,1-dimethylethyl)-benzene         | 1.60     | -     | -     |
| 25.13                | (2Z)-3,4,4-Trimethyl-5-oxo-2-hexenoic acid | -        | 3.40  | 3.48  |
| 25.16                | 1,3,5-trimethyl-1H-Pyrazole                | 0.67     | -     | -     |
| 27.69                | 4-Methyl-1,3-benzenediamine                | 1.69     | -     | -     |

|              |                                                                           |       |       |       |
|--------------|---------------------------------------------------------------------------|-------|-------|-------|
| <b>29.75</b> | 1,4-Diacetylbenzene                                                       | 0.83  | -     | -     |
| <b>31.15</b> | 2,6-di-t-Butyl-p-benzoquinone                                             | 0.67  | -     | -     |
| <b>31.59</b> | 2,5-Dimethyl-benzothiazole                                                | 0.87  | -     | -     |
| <b>33.24</b> | 2,4-Bis(1,1-dimethylethyl)phenol                                          | 1.31  | -     | -     |
| <b>43.75</b> | 3,5-Dihydroxy-4,4-dimethyl-2,5-cyclohexadien-1-one                        | -     | -     | 1.27  |
| <b>43.78</b> | Dimethoxyphenol*                                                          | 1.34  | -     | -     |
| <b>44.62</b> | Dimethoxyphenol*                                                          | -     | -     | 8.62  |
| <b>44.67</b> | 2,6-Dimethoxyphenylacetate                                                | 3.85  | -     | -     |
| <b>45.10</b> | 4-(3,4-Dimethoxybenzylidene)-1-(4-nitrophenyl)-3-phenyl-2-pyrazolin-5-one | 3.53  | -     | -     |
| <b>47.62</b> | 5-Isopropylidene-3,3-dimethyl-dihydrofuran-2-one                          | -     | 15.20 | -     |
| <b>47.63</b> | 1-Methyl-3-iso-propyl-2,4,5-trioxoimidazolidine                           | -     | -     | 11.92 |
| <b>47.99</b> | Dimethoxyphenol*                                                          | -     | -     | 14.88 |
| <b>48.08</b> | Cyclo(leucylopropyl)                                                      | 19.93 | 17.49 | -     |
| <b>59.23</b> | 3-Benzyl-6-isopropyl-2,5-piperazinedione                                  | 4.89  | 3.52  | 2.08  |
| <b>63.39</b> | Cyclo-Phe-Pro-diketopiperazine                                            | 13.71 | 11.45 | 9.68  |
| <b>64.15</b> | Cyclo-(l-leucyl-l-phenylalanyl)                                           | -     | 1.07  | -     |
| <b>66.88</b> | Tetracosane                                                               | 0.94  | -     | -     |

\*Isomers

### *Aqueous Phase Characteristics*

The process water was acidic, with pH levels ranging from 3.89 to 4.38, and no obvious trend was observed. The pH of the process water is thought to be influenced both by the material used in HTC and the initial pH of the water in the system. In our experiments, the deionized water employed for HTC runs had an initial pH of 6.51. Table 5 shows the TOC and COD measurements of the process water generated during the HTC of EO. TOC and COD analyses of the aqueous phase indicated that increasing the HTC temperature led to a decrease in TOC and COD values. A study on the HTC of chicory roots (*Cichorium intybus L.*), an agricultural residue from salad production, also reported decreases in TOC and COD with increasing temperature <sup>34</sup>. Therefore, the results obtained in this study are consistent with this previous report. However, it should be noted that some studies in the literature have reported no clear trend in TOC and COD changes with increasing HTC temperature <sup>32,35</sup>. In our experiments, the lowest COD and TOC values in the aqueous phase were obtained at the lowest HTC temperature. Since higher COD values enhance biogas production, the aqueous

phase from EO of HTC at the lowest temperature appears to be the most suitable process water for anaerobic digestion.

The compounds present in the organic phase isolated from the aqueous phase are summarized in Table 6. Many oxygen- and nitrogen-containing compounds were observed in the aqueous phase. Among the oxygen-containing compounds, cyclopentenone derivatives and phenolic compounds were prominent, while among the nitrogen-containing compounds, diketopiperazines (DKPs) and imidazolidine derivatives stood out. The cyclopentenone derivatives are attributed to the carbohydrate fraction, arising from dehydration and cyclization reactions of hexose intermediates during HTC. The phenolic compounds are likely derived from Maillard-type reactions between protein degradation products and carbohydrate intermediates, as well as from the thermal decomposition of aromatic amino acids such as tyrosine and phenylalanine. The nitrogen-containing compounds originate from protein decomposition through two concurrent pathways. The DKPs, including cyclo(leucyl-prolyl), cyclo(Phe-Pro), and 3-benzyl-6-isopropyl-2,5-piperazinedione, are formed through hydrothermal cyclization of amino acids released during protein hydrolysis: lysine and other amino acids first cyclize to form intermediate pipecolic acid derivatives, which subsequently undergo dimerization and dehydration to yield the corresponding DKP structures, as described by Fan et al. (2022)<sup>36</sup> The imidazolidine derivatives, including 3,5,5-trimethyl-2,4-imidazolidinedione and 1-methyl-3-isopropyl-2,4,5-trioxoimidazolidine, represent Maillard reaction products formed through the interaction of amino acid degradation products with carbonyl intermediates derived from carbohydrate dehydration, consistent with the reaction pathways proposed by Fan et al. (2018).<sup>37</sup> With increasing HTC temperature, the relative abundance of DKP compounds decreased progressively, while imidazolidinedione derivatives became more prominent at 250 °C, suggesting a temperature-dependent shift in protein degradation pathways from cyclic dipeptide formation at lower temperatures toward more

oxidized N-heterocyclic structures at higher temperatures. It is also noted that the nitrogen-containing compounds identified in the process water, including DKPs and imidazolidine derivatives, may influence the biodegradability of the aqueous phase and should be considered in the design of downstream treatment strategies. Alternatively, recirculation of the process water as the reaction medium in subsequent HTC runs has been reported to enhance hydrocoal carbon content and energy yield while reducing water consumption,<sup>29</sup> representing a promising valorization strategy for future work.

## **Conclusion**

The hydrothermal carbonization of expired oatmeal (EO), a compositionally defined, non-lignocellulosic food waste with a precisely known macronutrient profile (68.66 wt% carbohydrates, 12.99 wt% protein, 7.25 wt% lipids), was systematically investigated under varied temperature (200–250 °C), solid-to-water ratio (12.5–50 g per 150 mL), and residence time (1.5–12 h) conditions. The following key findings were established.

All hydrocoals exhibited substantially enhanced fuel properties relative to the raw feedstock, with HHV values of 29.6–32.3 MJ/kg compared to 18.1 MJ/kg for raw EO, carbon contents of 69–77 wt%, and ash contents of 0.14–0.48 wt%, remarkably low compared to both the raw feedstock (1.62 wt%) and typical commercial coals (6–12 wt%). H/C and O/C atomic ratios of 0.92–1.08 and 0.12–0.21 placed all hydrocoals in or near the bituminous coal region of the Van Krevelen diagram, confirming their suitability as drop-in solid biofuels.

The well-defined macromolecular composition of EO enabled direct attribution of observed structural and physicochemical transformations to specific macromolecular fractions. Carbon sphere formation in SEM images (diameter 1.65–7.5 μm, increasing with HTC temperature) was mechanistically linked to HMF-mediated polymerization and aromatization of the

carbohydrate fraction. Progressive attenuation of Amide I ( $1640\text{ cm}^{-1}$ ) and Amide II ( $1515\text{ cm}^{-1}$ ) bands in FTIR spectra confirmed hydrolysis and denitrogenation of the protein fraction with increasing temperature. The persistence of aliphatic C–H stretching bands ( $3000\text{--}2800\text{ cm}^{-1}$ ) across all HTC temperatures confirmed the hydrothermal resistance of the lipid fraction, further corroborated by Py-GC/MS analysis, which demonstrated the accumulation of long-chain fatty acids, including palmitic, oleic, stearic, and octadecadienoic acids, in the hydrocoal matrix across all HTC temperatures, consistent with the surface adsorption of lipid hydrolysis products rather than their full incorporation into the aromatic carbonaceous network.

TG/MS analysis of the hydrocoals identified methylfuran ( $m/z\ 82$ ), toluene ( $m/z\ 91$ ), phenol ( $m/z\ 94$ ), dimethylfuran ( $m/z\ 96$ ), and cresol ( $m/z\ 108$ ) as the primary volatile species released during the main thermal decomposition event at  $420\text{--}460\text{ }^{\circ}\text{C}$ , confirming the aromatic character of the hydrocoal matrix. The total mass losses of hydrocoals ( $59.5\text{--}61.7\%$ ) and the enhanced onset temperatures of the main decomposition event with increasing HTC temperature confirmed the significantly improved thermal stability of the hydrocoals.

The aqueous phase was acidic ( $\text{pH}\ 3.89\text{--}4.38$ ) and contained a diverse array of oxygenated and nitrogenated organic compounds identified by GC-MS, including cyclopentenones, furan derivatives, phenolic compounds, and diketopiperazines. COD analysis indicated the greatest biogas production potential for process water generated at the lowest HTC temperature.

Overall, this study demonstrates that the use of a commercially expired food product with a known macronutrient composition as a model HTC feedstock enables a level of mechanistic interpretability not achievable with heterogeneous, undefined food waste matrices, providing a robust compositional framework for designing and optimizing HTC processes for food waste valorization at industrial scale.

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