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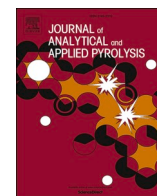
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# Reconsidering lab procedures for hydrothermal carbonization of biomass: The impact of pre-drying and stirring

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## ABSTRACT

Although industrial hydrothermal carbonization (HTC) uses wet feedstock, lab-scale studies tend to dry the feedstock under the assumption that the rehydration of the feedstock would restore its original properties. To the best of our knowledge, this assumption has not been thoroughly examined at the lab scale; therefore, its investigation is crucial to prevent any discrepancies that might affect the upscaling of HTC. This research aims to examine the effects of pre-drying biomass by comparing it to the use of wet biomass in HTC experiments, employing three different types of biomass (rejected tomatoes, rejected apples, and digestate). Additionally, the study investigates the influence of stirring on pre-dried and wet biomass under the selected HTC conditions. The results indicate a substantial disparity in studied hydrochar properties when using pre-dried biomass compared to wet biomass. For pre-dried biomass, there is a tendency for an increase in mass yield and solid carbon yield in most examined samples (5–10% dry basis) compared to the wet biomass. Regarding functional groups, wet tomatoes and apples exhibit more pronounced peaks than pre-dried samples. Conversely, digestate shows similar spectra across all examined scenarios. The effect of stirring appears insignificant for most of the studied scenarios; nevertheless, it reduced dehydration and decarboxylation reactions during HTC.

## 1. Introduction

The massive amounts of wet biomass produced by different activities have recently gained significant attention to develop sustainable waste management approaches. Dry thermochemical conversion processes, such as torrefaction, pyrolysis and gasification, are widely employed for valorizing low-moisture content biomass [1]. However, these processes are not the optimum approach for valorizing high-moisture biomass (>50 wt%) due to the high energy requirement for biomass pre-drying [2].

Hydrothermal carbonization (HTC) is regarded as a valuable thermochemical process for valorizing wet organic waste without a pre-drying step. HTC operates in a water medium at a temperature range of 180–260 °C, autogenic pressure (2–10 MPa), and the typical published residence time varied between 1 and 72 hours [3]. Under HTC conditions, water acts as a solvent and catalyst for several reactions, such as hydrolysis, dehydration, decarboxylation, aromatization, and

polymerization [3]. The main products associated with these conditions are a carbonaceous solid product called "hydrochar", a liquid byproduct rich in organics (acetic, levulinic, and formic acids) and leached inorganics, and small gaseous products, mainly CO<sub>2</sub> [4–6].

The absence of standardized lab procedures in HTC studies presents considerable challenges for researchers. This lack of standardization affects experiments' reproducibility and complicates comparisons between studies. Two of the most commonly overlooked lab procedure aspects are pre-drying and stirring.

Pre-drying biomass before HTC is a common practice in laboratory procedures to facilitate storage, handling, and prevent sample degradation [7,8]. It also aids in sample grinding, homogenization, and adjusting the biomass-to-water (B/W) ratio. However, the assumption that rehydrating the feedstock restores its original properties is most of the time unquestioned. This practice may lead to inaccurate scaling up of the HTC process, as large-scale reactors typically use biomass with its original moisture content. To our knowledge, only one study has

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compared pre-dried and wet biomass utilization (original moisture content). Using a 50 mL unstirred reactor, Volpe et al. [2] observed that pre-dried samples demonstrated a constant hydrochar mass yield when increasing the temperature. Additionally, it was noticed that a higher decomposition rate was observed at lower temperatures for pre-dried samples compared to the wet samples.

Stirring is another experimental lab procedure that is not standardized in HTC. Six experimental studies have investigated the influence of stirring rate on HTC. Remarkably, there is no consensus among the studies; three studies report an effect of the stirring rate [2,9,10], while the three other studies report its insignificance [11–13]. Several reasons exist for these discrepancies. Firstly, the reactor sizes differed for the stirred and unstirred tests. Secondly, the process conditions are different throughout the different studies. Thirdly, the feedstock encompasses different materials, from simple sugars to lignocellulosic biomass. Lastly, the previous studies did not compare the same outputs. For example, Volpe et al. [2] investigated the influence of stirring on product yield, organic composition, and HHV. On the contrary, Su et al. [10] and Jung et al. [9] focused their work on the morphological properties of hydrochar.

The present study systematically investigates the influence of overlooked HTC lab-scale procedures, particularly pre-drying and stirring. Different biomasses, such as rejected apples, tomatoes, and digestate, have been used. For that purpose, the study includes (i) product mass and carbon yields and (ii) extensive characterization of the compositional and morphological characteristics of the hydrochar and the liquid products.

## 2. Methodology

### 2.1. Feedstock

In this study, several types of biomass were used as feedstock for HTC. Rejected biomass, such as tomatoes and apples, were collected from the local market in Delft, Netherlands, to resemble food waste. Additionally, digestate was collected from a digester in a biogas plant with an input of animal feces, urine and manure, and corn silage [14]. Typically, the feedstock comprises 50 m<sup>3</sup> (tonnes) of pig waste and 2 tonnes of corn silage. The rejected wet biomass was stored for less than 5 days in a dark fridge at 4 °C before being used as a feedstock in the experiments. Due to experimental constraints, the digestate was stored for several months in the same conditions.

### 2.2. Experimental design

Based on the results of a previous study by Abdeldayem et al. [13], it was indicated that the stirring rate did not influence and interact with other process parameters in the typical HTC range. This study conducted HTC experiments in duplicate at 180 °C, with the residence time held constant at 30 minutes. These conditions were selected because, at lower temperatures and shorter residence times, water release starts, and HTC-associated reactions commence, thereby maximizing the potential impacts of stirring and pre-drying. The experiments were conducted at 0 and 200 rpm to investigate the influence of the stirring under laminar and turbulent flow conditions [13]. Based on Mendecka's [15] study, flow in unstirred cylindrical reactors relies on thermally driven natural convection, which leads to a laminar flow regime. Hence, the flow regime was assumed to be laminar for the unstirred experiments in our study. For stirred conditions, Eq. 1 was used to calculate the Reynolds number (Re) [16,17]; if the Re is above 10000, it is considered to be fully turbulent, which is the case at 200 rpm.

$$Re = \frac{Nd^2\rho}{\mu} \quad (1)$$

Where N (s<sup>-1</sup>) is the impeller's rotational frequency, d (m) is the

diameter of the impeller,  $\rho$  ( $\frac{kg}{m^3}$ ) is the density of the mixture, and  $\mu$  (Pa. s) is the dynamic viscosity of the mixture.

Table 1 illustrates the experimental design adopted in this study. All experiments used the feedstock with its original moisture content and B/W ratio. Additional experiments using the same feedstock were performed after drying the raw biomass at 105 °C for 24 hours. Table 1 illustrates the HTC experimental conditions that were conducted in duplicate. The wet tomatoes and apples were blended using a kitchen blender before being used as a feedstock for the HTC experiments. The dried feedstocks were milled to a 1–2 mm particle size. The B/W ratio differed for each feedstock based on its as-received moisture content.

### 2.3. HTC setup and procedure

The HTC experiments were conducted in a 2 L high-pressure reactor vessel. The full description of the reactor can be found in Abdeldayem et al. [13]. The biomass was introduced into the HTC reactor with its original B/W ratio, occupying 70% of its total volume (1.3 L). The reactor vessel underwent a 3-minute purging process using grade-6 nitrogen gas to remove the air from the headspace and replace it with inert nitrogen. The reactor was then heated at a 4 °C/min rate and cooled down using compressed air.

After cooling down, 20 mL of gaseous samples (triplicates) were collected from the HTC outlet. The total released gas volume was measured using a gas meter. Subsequently, the reactor was opened, and its contents were removed to be further processed.

A sieve of 100  $\mu$ m was used to filter the solid-liquid mixture; the resulting liquid was further filtered by passing it through 0.45  $\mu$ m filter paper. The obtained hydrochar was dried in an oven at 105 °C for 24 hours for characterization. The liquid sample was preserved by acidifying the sample to a pH less than 2 and was then stored for less than 7 days at 4 °C in a dark fridge until further analysis. Diluted sulfuric acid was used for dissolved organic carbon (DOC) samples, while diluted nitric acid was used for inorganic elements samples [18,19].

### 2.4. Product mass yield

The solid mass yield was calculated based on the solid product's ratio to the raw biomass's initial mass (dry basis (db)). The ideal gas law was used to calculate the mass of the produced gas. The temperature at the degassing of the reactor was used for the ideal gas calculation, and it ranged between 40 and 50 °C for each experiment. Then, the gas yield was calculated based on the ratio between the mass of the produced gas and the raw biomass's initial mass. The liquid yield was determined by subtracting the solid and gas yields from the initial mass of the raw biomass.

### 2.5. Gas, liquid, and solid characterization

#### 2.5.1. Gas and liquid characterization

SCION 456-GC gas chromatograph was used to analyze the gas samples using helium as a carrier gas. The calibration was performed using a CarlTech standard gas (50% CO<sub>2</sub> and balanced CH<sub>4</sub>). A 25 m (length), 0.53 mm (inner diameter), and 10  $\mu$ m (film thickness) PoraBOND-Q column was used with a run time of 2 min.

The Shimadzu TOCv-cpn analyzer and its accompanying module, Shimadzu TN, were used to analyze the DOC in the liquid phase. For the inorganic elements, Avio 200 Perkin Elmer Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used for its analysis. All the liquid samples were measured in triplicates to calculate the mean and the standard deviation values. The associated measurement error was 0.5 mg/L for the DOC, and ranged between 2  $\mu$ g and 60  $\mu$ g in the ICP OES, depending on the measured element

**Table 1**  
Experimental design.

| Sample name       | Feedstock | Wet or pre-dried | Temperature (°C) | Residence time (h) | Stirring rate (rpm) | B/W ratio (%) |
|-------------------|-----------|------------------|------------------|--------------------|---------------------|---------------|
| App 200           | Apples    | Wet              | 180              | 0.5                | 200                 | 14.4          |
| App 0             |           | Wet              | 180              | 0.5                | 0                   | 14.4          |
| Dry App 200       |           | Pre-dried        | 180              | 0.5                | 200                 | 14.4          |
| Dry App 0         |           | Pre-dried        | 180              | 0.5                | 0                   | 14.4          |
| Tom 200           |           | Wet              | 180              | 0.5                | 200                 | 4.5           |
| Tom 0             | Tomatoes  | Wet              | 180              | 0.5                | 0                   | 4.5           |
| Dry Tom 200       |           | Pre-dried        | 180              | 0.5                | 200                 | 4.5           |
| Dry Tom 0         |           | Pre-dried        | 180              | 0.5                | 0                   | 4.5           |
| Digestate 200     |           | Wet              | 180              | 0.5                | 200                 | 2.3           |
| Digestate 0       |           | Wet              | 180              | 0.5                | 0                   | 2.3           |
| Dry Digestate 200 | Digestate | Pre-dried        | 180              | 0.5                | 200                 | 2.3           |
| Dried Digestate 0 |           | Pre-dried        | 180              | 0.5                | 0                   | 2.3           |

### 2.5.2. Solid characterization

All the solid hydrochar samples were measured in duplicates to measure the mean and the standard deviation. The National Renewable Energy Laboratory (NREL) standards were used to determine the contents of lignocellulosic sugars, lignin, and extractives [20,21]. Solvent water is used to determine the water-soluble extractives and 95% ethanol is used to determine ethanol soluble extractives. To determine full extractives, the samples are first extracted with water and then extracted with 95% ethanol. The lignin is considered as the summation of Klason lignin and the acid soluble lignin (ASL). The Klason lignin is determined by the difference between the acid insoluble residue (the solid particles in hydrolysate after treatment with the 72% H<sub>2</sub>SO<sub>4</sub>) and the acid insoluble ash [22]. The acid soluble lignin is measured by taking an aliquot of the hydrolysate and measuring the absorbance at 240 nm. The absorbance is then converted to the ASL composition using the Beer's Law [22,23]. To determine the structural sugars, the biomass is hydrolysed with 72% H<sub>2</sub>SO<sub>4</sub> to reduce the polymers to monomers [22, 24]. The monomeric sugars liberated in the hydrolysate are measured using ion chromatography. The summation of the C6 sugars is representative of cellulose.

The proximate analysis was conducted for all the hydrochar and raw biomass samples. The EN15148–2009 and EN147741:2009 standards were used for the volatile matter and moisture content, respectively. The NREL procedure was used to determine the ash content, while the fixed carbon was calculated based on the difference in dry basis [25].

The EN15289–2011 standard was used to determine the C, H, N, and S content using an Elementar Macro Cube elemental analyzer. The O content was determined based on the difference. The measurements were done in duplicates for accuracy. The hydrochar and raw biomass samples were microwave-digested according to the ISO11466 standard. The Agilent ICP-OES 51110 was then used to analyze the digested samples to identify and quantify the major and minor inorganic elements.

The Brunauer-Emmet-Teller (BET) surface area was calculated using the DIN ISO 9277 standard and N<sub>2</sub> as an adsorption gas. For surface morphology examination, a JHC-1300 JEOL sputter coater was used to apply a dual layer of gold, approximately 4–6 nm thick, on the stubs. This was followed by using the JEOL JSM-6010LA scanning electron microscope (SEM) to investigate the surface morphology of the hydrochar and the raw biomass.

The functional groups were examined using a Bruker Alpha II Fourier-transform infrared analysis instrument equipped with a platinum attenuated total reflection (ATR) crystal. The spectral range covered the range from 4000 to 400 cm<sup>-1</sup> with a precision of 4 cm<sup>-1</sup>.

### 2.6. Carbon and inorganics balance

The carbon balance was calculated by assuming that carbon exists in the gaseous, liquid, and solid products of the HTC, as shown in Eq. 2. The carbon measurements from the elemental macro cube analyzer, Shimadzu TOCv-cpn analyzer, and the GC were used to calculate the

amount of carbon in the solid, liquid, and gaseous phases, respectively. Further information regarding the carbon balance measurement can be found in Abdeldayem et al. [13].

$$C_{Raw \text{ biomass}} = C_{hydrochar} + C_{Gas} + C_{liquid} \quad (1)$$

It was assumed that the inorganics exist in the solid and liquid phases and will not volatilize under HTC conditions. Hence, the elemental balance was conducted as Eq. 3, except for the P and Si, where the liquid product is calculated based on the difference.

$$I_{Raw \text{ biomass}} = I_{hydrochar} + I_{liquid} \quad (2)$$

## 3. Results and discussions

### 3.1. Feedstock

The fiber analysis of the raw biomass is shown in Table 2. The cellulose content is the highest in tomatoes (8.68%), followed by apples (4.82%) and digestate (4.32%). The hemicellulose content is the highest for

**Table 2**  
Fiber analysis and ash content of raw biomass on a dry basis.

| Feedstock | Biomass composition |          | Percentage (wdb %) |
|-----------|---------------------|----------|--------------------|
| Apple     | Cellulose           |          | 4.82± 0.15         |
|           | Hemicellulose       | Xylan    | 0.88± 0.05         |
|           |                     | Arabinan | 0.24± 0.02         |
|           |                     | Galactan | 0.56± 0.02         |
|           |                     | Mannan   | 0.31± 0.01         |
|           |                     | Rhamnan  | 0.16± 0.01         |
|           | Lignin              |          | 17.97± 0.55        |
|           | Ash                 |          | 1.90± 0.17         |
|           | Extractives         |          | 70.77± 0.40        |
|           | Moisture Content    |          | 86.98± 0.45        |
| Tomatoes  | Cellulose           |          | 8.68± 0.06         |
|           | Hemicellulose       | Xylan    | 1.23± 0.01         |
|           |                     | Arabinan | 0.35± 0.02         |
|           |                     | Galactan | 0.70± 0.01         |
|           |                     | Mannan   | 1.72± 0.07         |
|           |                     | Rhamnan  | 0.13± 0.01         |
|           | Lignin              |          | 12.28± 1.42        |
|           | Ash                 |          | 9.69± 1.19         |
|           | Extractives         |          | 72.68± 0.44        |
|           | Moisture content    |          | 95.55± 0.15        |
| Digestate | Cellulose           |          | 4.32± 0.22         |
|           | Hemicellulose       | Xylan    | 3.74± 0.33         |
|           |                     | Arabinan | 2.00± 0.03         |
|           |                     | Galactan | 0.70± 0.05         |
|           |                     | Mannan   | 0.22± 0.05         |
|           |                     | Rhamnan  | 0.36± 0.02         |
|           | Lignin              |          | 43.39± 6.22        |
|           | Ash                 |          | 34.00± 0.98        |
|           | Extractives         |          | 18.83± 0.01        |
|           | Moisture content    |          | 97.71± 0.18        |

digestate (7.02%), followed by tomatoes (4.13%) and apples (2.15%). For lignin, it was found that the digestate has the highest content with 43.39%, which might be due to its corn silage content, while apples had 17.97% and 12.28% for tomatoes. The digestate has the highest moisture content with 97.71%, while apples and tomatoes had 86.98% and 95.55%, respectively. The digestate has the highest ash content (34.0%) among the studied biomass, which might be mainly attributed to its manure and animal feces content, aligned with the literature [26]. The ash content of tomatoes and apples was 9.69% and 1.90%, respectively, aligned with previous findings in the literature [27,28].

### 3.2. Mass and carbon balance

The product mass balance is illustrated in Fig. 1a. Upon looking at the biomass with its original moisture content and the pre-dried ones; it was found that the tomatoes had the lowest solid mass yield for both scenarios, which can be attributed to attaining a relatively high composition of extractives that leach starting at a temperature of 160 °C [29]. Even though it has a very high lignin composition, digestate had the second lowest mass yield, possibly due to its relatively higher composition of hemicelluloses that mainly degrade at 180 °C and its low

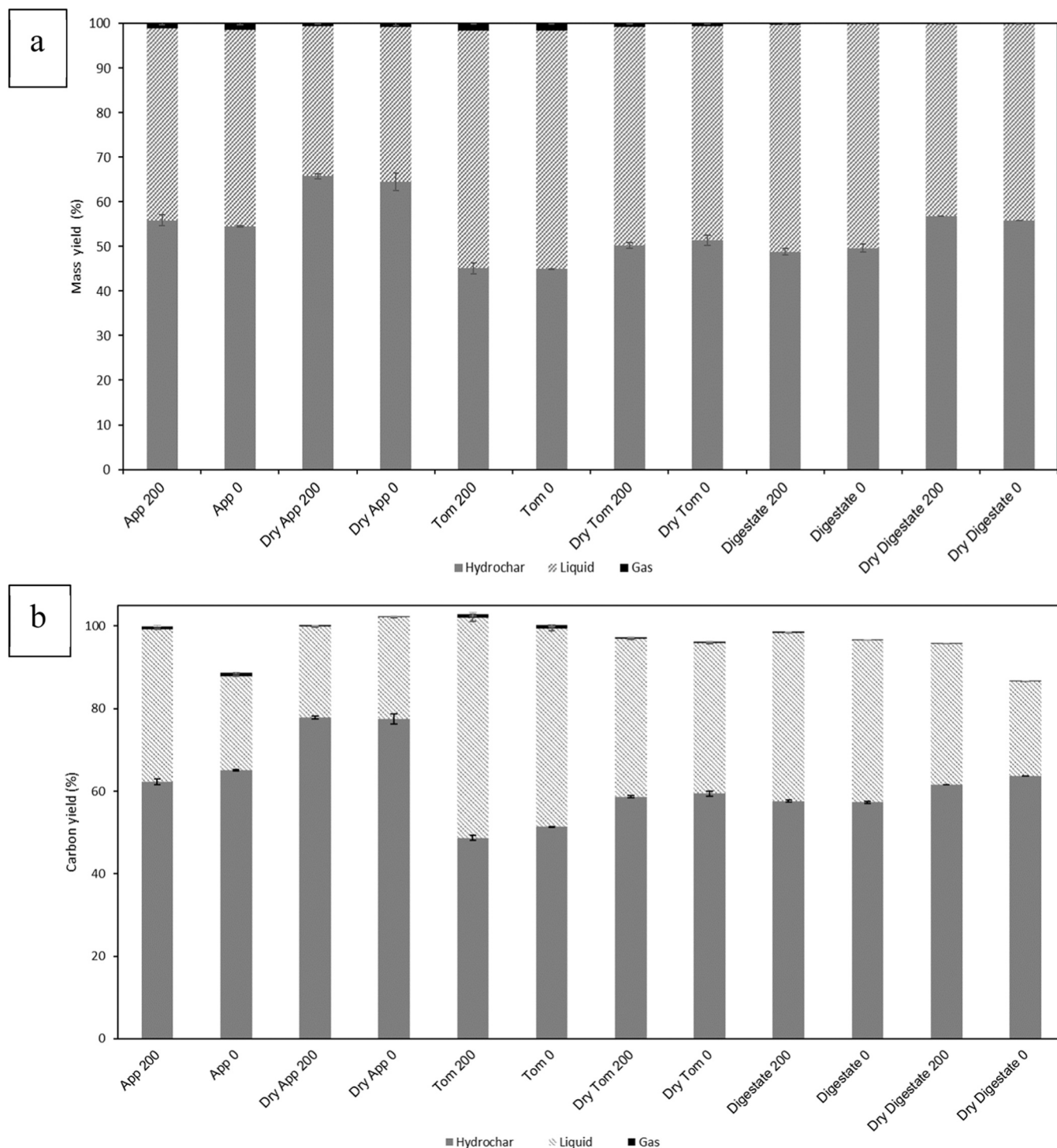


Fig. 1. (a) Mass yield (b) Carbon yield of different types of biomass.

B/W ratio [30]. Apples had the highest solid mass yield, which might be due to its relatively high B/W ratio [30].

Upon comparing the wet and pre-dried biomass experiments, it was noticed that the solid mass yield tends to increase for the pre-dried biomass. The absolute magnitude of the increase was around 10%, 5%, and 7% for apples, tomatoes, and digestate, respectively. For the wet biomass, the water is bound in its cellular structure [31]; therefore, during HTC, the impact of hydrolysis might be more substantial than the pre-dried biomass, leading to a significant mass leaching from the solid to the liquid phase [3]. Up to the author's knowledge, no studies were conducted on the influence of drying on the biomass structure at 105 °C as most of the studies are concerned with the food industry. However, studies on convective drying (20–60 °C) indicated that the structure can be altered upon drying the biomass, decreasing cell size, roundness, compactness, and increasing elongation [31–34]. These consequences lead to poor water retention after rehydration [31]; hence, less bounded water inside the rehydrated biomass. Therefore, less severe HTC reactions occur inside the pre-dried biomass, leading to a higher solid mass yield. Besides that, it is worth noting that the gas yield components are almost negligible due to the low severity of the operating condition at 180 °C and 30 mins of residence time [35].

The influence of stirring has been investigated on the product mass yield for several wet and pre-dried biomasses. Overall, as seen in Fig. 1a, there were no significant differences in the obtained product yields for the wet and pre-dried experiments, indicating the insignificance of the stirring under the studied conditions. These results corroborate the previous findings by Abdeldayem et al. [13] on pre-dried *Typha australis*. The lack of significance of the stirring can be attributed to several reasons. Firstly, water is an excellent heat transfer and storage medium, minimizing local peaks [3]. Secondly, the heating-up phase (45 mins) might be a long enough period for natural convection to transfer heat homogeneously under the applied operating conditions [13].

The carbon balance was also conducted for the studied feedstocks at wet and dry conditions using 0 and 200 rpm, as shown in Fig. 1b. The carbon balance ranged between 88% and 103%, in agreement with previous studies in the same reactor [36,37]. The apples' solid carbon yield was the highest due to the high B/W ratio [30].

The solid carbon yield was higher for the pre-dried samples compared to the wet ones, showing an average increase of 13%, 9%, and 5% for apples, tomatoes, and digestate, respectively. This can be attributed to the pre-dried biomass having a limited rehydration capacity, resulting in less bound water within its structure than the wet biomass. Consequently, this leads to milder HTC reactions within the pre-dried biomass, reducing carbon leaching into the liquid phase and enhancing carbon retention in the solid phase. In contrast, the wet biomass naturally contains bound water within its structure, leading to more severe HTC reactions, which decrease the proportion of carbon in the solid phase and increase it in the liquid phase.

Regarding the influence of stirring, it was noticed that the stirred samples exhibited a slightly lower solid carbon yield than the unstirred ones, with a magnitude around 2.5% lower than the unstirred experiments for apples and tomatoes. However, no significant effects were observed for their pre-dried samples. This indicates that stirring might have slightly influenced the HTC reactions for wet lignocellulosic biomass. For the digestate, no significant difference was noticed between the wet and dried experiments.

### 3.3. Ash content and inorganic element distribution

The ash content has been measured for all the studied hydrochars, as shown in Table S1 in the supplementary file. Several observations were made for the ash content of hydrochar produced for apples, tomatoes, and digestate. On the one hand, the ash content of the hydrochar produced from pre-dried tomatoes and apples was lower than the ash content of the hydrochar from the wet biomass. On the other hand, the pre-dried digestate-based hydrochar tended to have a higher ash content

than the wet digestate sample. Hence, these observations indicate that the pre-drying effect might depend on the type of feedstock used in the experiment. The stirring did not significantly influence the ash content in any of the studied pre-dried or wet conditions, confirming its lack of significance for the ash content.

Overall, the elemental mass balance was satisfactory for the majority of the experiments conducted. However, for a few elements in some experiments, the mass balance was not well closed due to the heterogeneity of the used feedstocks or the low concentration of the elements in the studied biomass, which is close to the detection limit. Upon looking into the element distribution for HTC products in Fig. 2a and 2b, it was observed that the majority of K and Na leached into the liquid phase for the studied runs. Neither the pre-drying procedure nor the stirring showed any significant effect, confirming previous findings on stirring by Abdeldayem et al. [13] for pre-dried biomass (*Typha australis*). Smith et al. [38] indicated that K and Na exist as ionic salts (alkali metal salts) inside the biomass. Hence, these alkali metal salts easily dissolve in water during HTC [38]. Moreover, the acidic conditions created by the release of organic acids during HTC facilitate the leaching of K and Na into the liquid phase [39].

In contrast to K and Na, the distribution of Ca, Mg, and P varied between the studied biomass, as illustrated in Fig. 2c, 2d, and 2e. A significant portion of Ca and Mg leached from solid to liquid phases for tomatoes and apples. However, the P tended to leach significantly to the liquid phase in the case of tomatoes only. On the other hand, these elements have slightly leached from the solid phase to the liquid phase in the digestate case.

The Ca concentration slightly increases in the apple-derived hydrochar using the pre-drying procedure. Regarding Mg, there were no significant differences between the runs conducted on apples using the pre-drying procedure. However, it was noticed that the Mg tends to leach more from the solid phase to the liquid phase for the pre-dried tomatoes and pre-dried digestate. For P, the drying procedure did not significantly affect the migration of elements in the case of apples; however, the migration of P from the solid to liquid phase was higher for the pre-dried tomatoes and digestate. Overall, it was noticed that the stirring did not significantly influence the fate of inorganics in the wet and pre-dried conditions for Ca, Mg, and P.

The difference in behavior between feedstocks can probably be attributed to the form in which the elements are present in the biomass. For example, Ca exists in the form of ionic salts in the lignocellulosic biomass (similar to Mg), where a minor amount is incorporated in the macromolecules, and the rest are mainly in the form of calcium oxalate, which is an acid-soluble compound [40]. Hence, the acidic and subcritical conditions could potentially facilitate the migration of Ca to the liquid phase at 180 °C [36]. Ca and Mg are also detected inside the cell walls of the biomass, potentially bonded to carboxyl groups, which are susceptible to degradation during HTC through decarboxylation [36]. At low temperatures, the hydrolysis of organic matter is initialized where P in the form of pyrophosphates, polyphosphates, phytic acids, and phosphate diesters are broken down into orthophosphates, which tend to dissolve in the liquid phase [41]. In the liquid phase, the organic functional groups are substituted by inorganic elements, forming inorganic phosphorous that tends to precipitate and re-incorporate in the hydrochar [42,43]. Ghanim et al. [44] indicated that P precipitates majorly consist of Ca and Mg phosphates ( $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_3(\text{PO}_4)_2$ ) and apatites.

On the one hand, Si was found to be the highest in digestate, as shown in Fig. 2f, which might be due to the corn silage component in the digestate [36] or sand contamination in the manure component of the digestate. On the other hand, Si in apples and tomatoes might be attributed to the silicic acid uptake from the soil [45]. Fig. 2f shows that the Si concentration was higher for wet apples, tomatoes, and digestate in the solid phase than that obtained from the pre-dried biomass. Similar to previous observations, stirring did not influence the migration of elements.

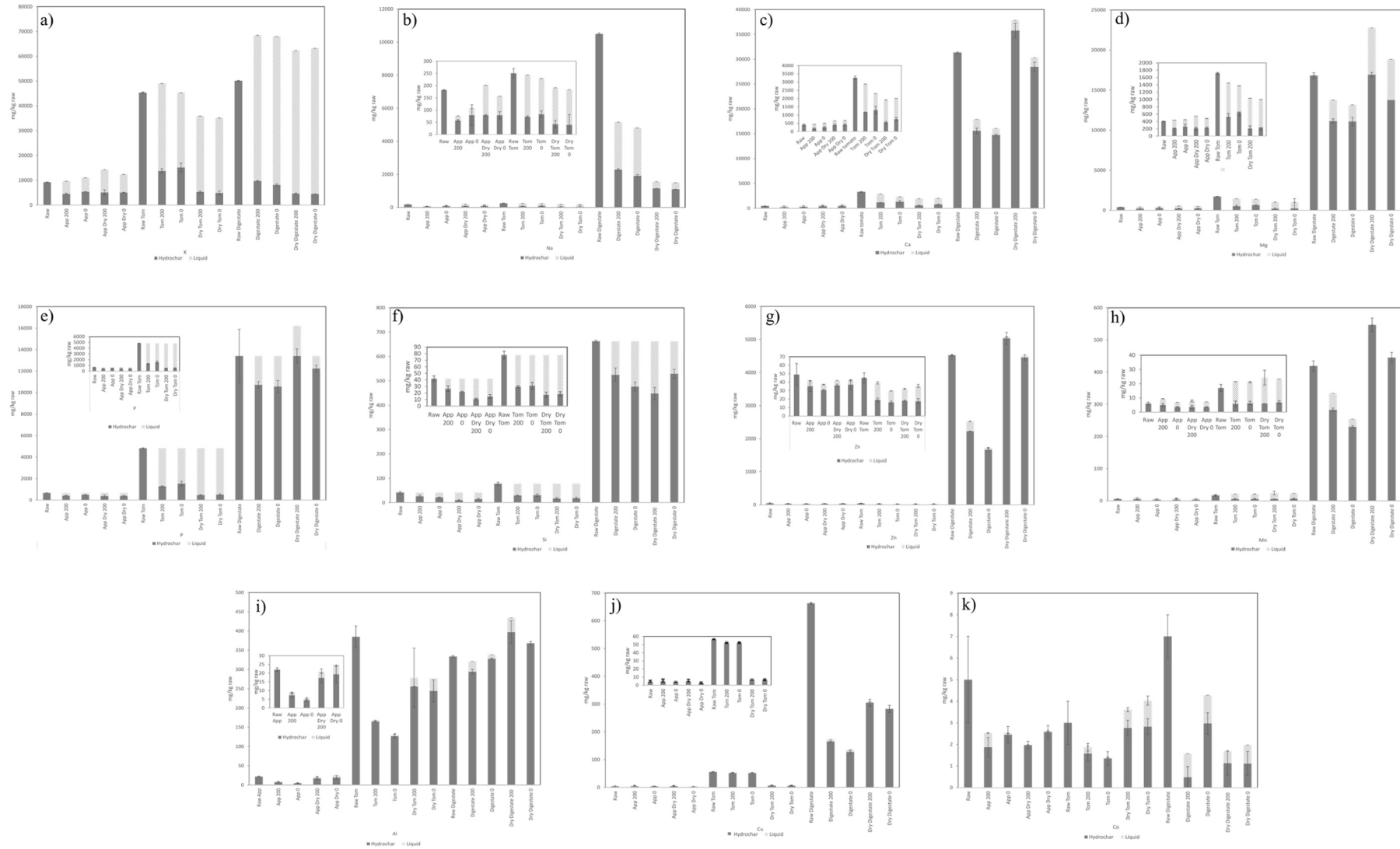


Fig. 2. Fate of inorganics for different feedstocks, wet, dry, stirred, and unstirred.

Regarding minor inorganic elements in apples and tomatoes based on raw biomass and hydrochar, they were present in low concentrations close to or below the detection limit. In contrast, the digestate had a significantly higher concentration of minor inorganic elements in its hydrochar and raw biomass. For example, it was noticed that Zn and Mn were present mainly in the solid phase for digestate, as demonstrated in Fig. 2g and 2h. However, these elements slightly leached into the liquid phase after the HTC of apples and to a higher extent for tomatoes. The severe HTC reactions lead to the hydrolysis of proteins [46]; hence, Mn is released from the biomass matrix to the liquid phase. However, it re-accumulates in the solid phase as it is associated with the precipitation of non-apatite inorganic P [47]. In Fig. 2j, Cu tended to remain in the hydrochar for all of the studied samples, which is aligned with the findings of Michel et al. [36] using different types of dried waste. Overall, there were no significant differences due to pre-drying or stirring.

### 3.4. Dehydration, decarboxylation, and demethanation reactions

Dehydration, decarboxylation, and demethanation reactions

Fig. 3 exhibits van Krevelen's diagram illustrating the H/C and O/C atomic ratios for the raw biomasses and different hydrochars, where dehydration, decarboxylation, and methanation reactions can be visualized from the arrows. As expected, Fig. 3 shows that all the hydrochar exhibits lower O/C and H/C than the original raw biomass upon undergoing HTC, which occurs mainly due to dehydration and decarboxylation reactions, as previously illustrated by Sharma et al. [48].

First of all, it can be noticed that the wet and pre-dried feedstocks behaved differently. For example, hydrochar produced from wet apples and tomatoes had higher H/C and O/C ratios for the stirred experiment than the unstirred ones. This indicates that stirring decreases the dehydration and decarboxylation reactions inside the wet apples and tomatoes. However, this was not the case for the digestate, where the stirring did not influence its reactions in wet conditions. Hence, stirring's influence on reactions might depend on the type of biomass and the form in which water is bound to it.

Secondly, the stirred and unstirred pre-dried samples had almost the same H/C and O/C ratios, indicating that stirring did not affect the pre-dried biomass during HTC. These results are aligned with several studies [12,13]. This might be explained by the fact that pre-drying had dehydrated the raw biomass to a degree in which stirring cannot influence dehydration and decarboxylation reactions.

Overall, the results indicated that stirring influences the process by reducing dehydration reactions when the wet biomass such as apples and tomatoes are used as a feedstock. At the same time, lab scale results

from pre-dried biomass might provide wrong indications and insights for scaling up, as the influence of stirring might be hidden by the experimental pre-drying procedure in the lab due to the poor rehydration of the pre-dried biomass.

### 3.5. Hydrochar surface characterization

#### 3.5.1. Surface functional groups

The FTIR spectra have been investigated for the different biomass and hydrochar produced, as shown in Fig. 4. Fig. 4a shows that wet and pre-dried apples exhibited several differences in the obtained spectra. For wet apples, it is observed that there is a strong peak at  $3000 - 3600 \text{ cm}^{-1}$ , indicating the O-H stretching of the hydroxyl groups [49]. However, this peak was lacking in the dried apples, indicating that the pre-dried samples were dehydrated compared to the wet ones. For the wet and pre-dried samples, the peaks for the C=C and C=O existed at the ranges of  $1610 - 1620 \text{ cm}^{-1}$  and  $1650 - 1680 \text{ cm}^{-1}$ , respectively [50]. However, the peaks were slightly stronger in the wet samples compared to the pre-dried ones. The C-O peak obtained around  $1020 \text{ cm}^{-1}$  [51] was the strongest for the wet; however, it was less significant for the pre-dried hydrochar and raw biomass, indicating the influence of pre-drying. Upon comparing the stirred and unstirred hydrochar, it can be noticed that they are similar in all cases. Hence, this indicates that the stirring did not have an observable impact on the obtained spectra while pre-drying the biomass had a significant impact.

The tomatoes in Fig. 4b exhibited a similar trend to apples, where the stirred and unstirred hydrochar produced from wet biomass exhibited similar spectra. In addition, the stirred and unstirred dried hydrochar were similar; however, they differed from the hydrochar produced from wet biomass. The symmetric and asymmetric C-H stretching peaks lie between  $2800$  and  $2970 \text{ cm}^{-1}$  [52]. The magnitude of the peaks was higher for the wet biomass and slightly higher for the unstirred wet hydrochar and raw biomass; however, they were very weak for the pre-dried samples. The peaks at  $1740 \text{ cm}^{-1}$  and  $1130$  resemble the C=O and C-O stretchings [53,54]. For the hydrochar produced from pre-dried tomatoes, it is observed that the magnitude of peaks is very low compared to the hydrochar obtained from directly using wet tomatoes, indicating the significant effect of the pre-drying on the obtained functional groups.

The spectra digestate is demonstrated in Fig. 4c. Overall, it can be noticed that the spectra for raw, wet, pre-dried, stirred, and unstirred hydrochar are almost identical for each feedstock, indicating that pre-drying and stirring did not significantly influence the obtained spectra. The reasons for the absence of observed differences for digestate are poorly understood; however, it might be due to the form in which water is bound to it, which is different from the tomatoes and apples. These results align with the dehydration and decarboxylation reactions, where digestate behaved differently than apples and tomatoes, indicating that the feedstock type influences its behavior. Hydrochar for digestate demonstrated peaks at  $2800 - 2970 \text{ cm}^{-1}$ ,  $1610 - 1620 \text{ cm}^{-1}$ ,  $1650 - 1680 \text{ cm}^{-1}$ ,  $900 - 110 \text{ cm}^{-1}$ , for the C-H, C=C and C=O, C-OH respectively [49,50,52].

#### 3.5.2. Surface morphology

SEM imaging was employed to examine the surface morphology of the raw biomass and hydrochar samples, as depicted in Fig. 5. Raw apples and tomatoes (Figs. 5a and 5f) display hard and smooth surfaces with homogeneous characteristics. In contrast, raw digestate in Fig. 5k exhibits rougher and more heterogeneous surfaces, which might be due to their distinct sources.

The HTC of the raw tomatoes and apples resulted in surface degradation in the produced hydrochar, a phenomenon linked to hemicellulose degradation at  $180^\circ\text{C}$  [55]. Notably, the hydrochar produced from wet apples (Figs. 5b and 5c) and wet tomatoes (Fig. 5l and 5m) displayed rougher surfaces than their pre-dried counterparts. The presence of bound water within the biomass structure likely intensified the severity

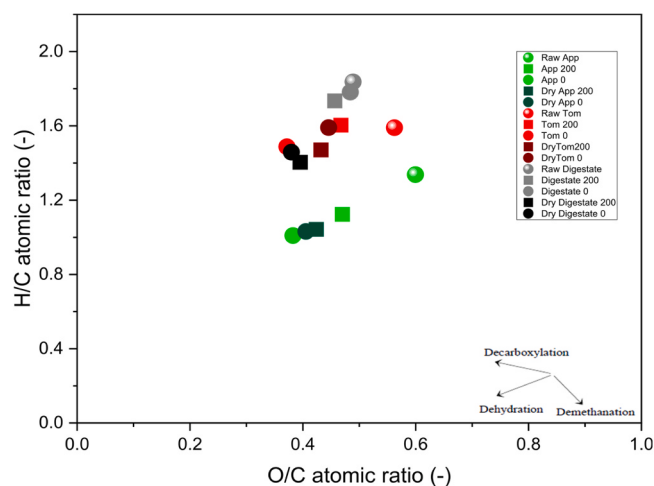


Fig. 3. Dehydration, decarboxylation, and methanation reactions for different types of feedstocks at wet, predried, stirred, and unstirred conditions.

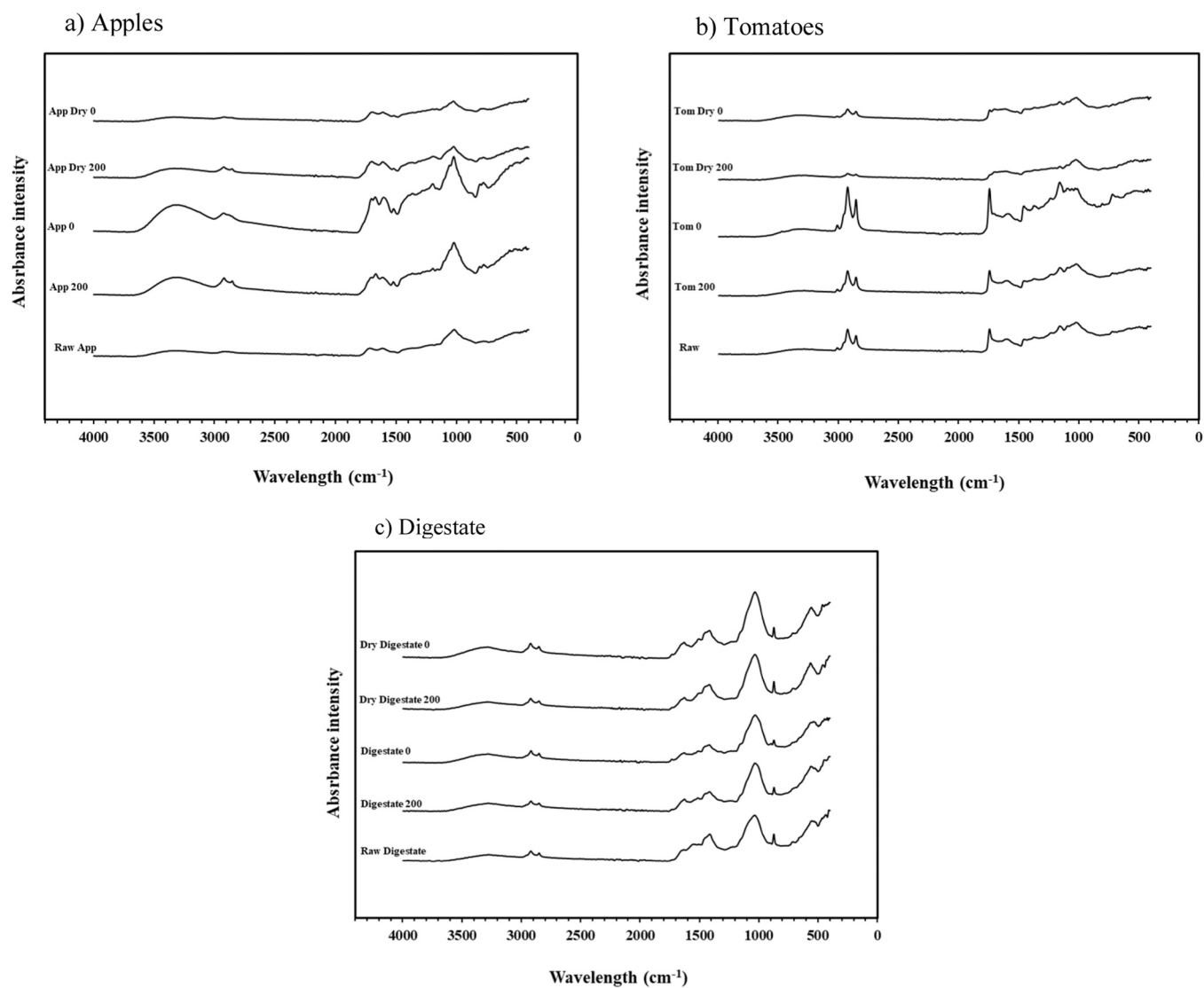


Fig. 4. FTIR spectra for different feedstocks at wet, pre-dried, stirred, and unstirred conditions.

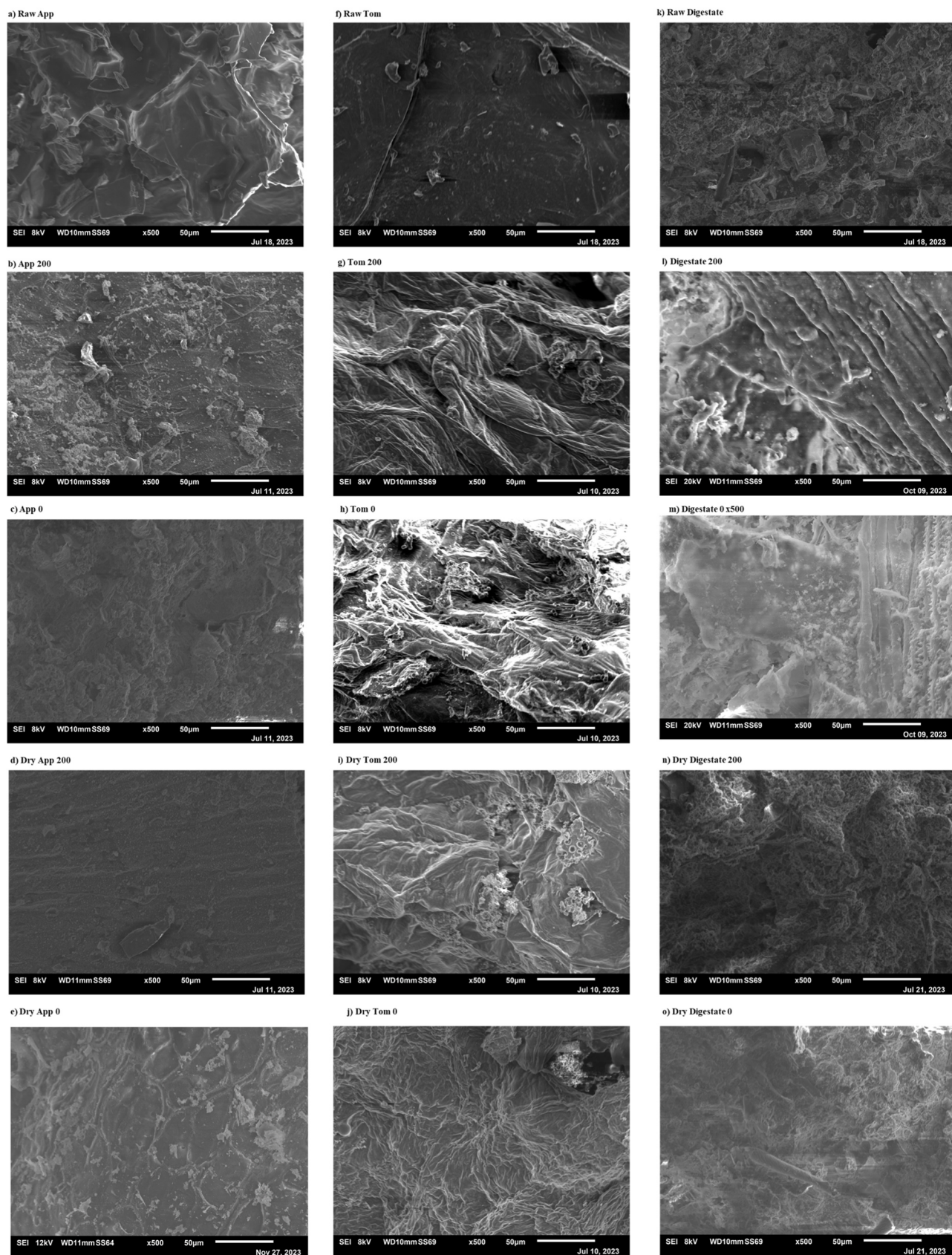


Fig. 5. Morphology of raw tomatoes and tomato-derived hydrochar from wet, pre-dried, stirred, and unstirred conditions.

of the HTC reactions, thereby yielding rougher surface structures. In contrast, pre-dried biomass exhibited limited water retention after rehydration [31], resulting in milder HTC reactions within the biomass and minimal alteration in surface morphology. As for stirring, no significant differences were observed between the stirred and unstirred hydrochar produced from the wet or the pre-dried biomass, confirming and extending the findings of Abdeldayem et al. [13] on *Typha australis* to other types of biomass. Interestingly, the tomato-based hydrochar for the wet and pre-dried scenario revealed the existence of small spherical particles known as microspheres. During HTC, sugars breakdown forming a 5-hydroxymethylfurfural (HMF) intermediate. The HMF polymerizes, forming the microspheres [56]. The existence of microspheres for the tomato-based hydrochar only indicates that the type of biomass influences the production of microspheres.

Fig. 5n and 5o show that the hydrochar from digestate displayed smoother surfaces, unlike dried digestate, which had rougher surfaces. Consistent with earlier observations, no significant differences were noted when comparing the stirred and unstirred samples.

## 5. Conclusions

This study has examined the impact of two overlooked HTC procedures at the lab scale: the pre-drying of biomass and the stirring using 3 different types of biomass. The pre-drying of biomass has impacted the HTC process, including mass and carbon balance, fate of inorganic elements, dehydration and decarboxylation reactions, and surface functional groups and morphology within the specified experimental conditions. The effect of using pre-dried biomass was observed across all studied responses for tomatoes, apples, and digestate. In contrast, stirring had a minimal effect on most of the examined responses for all feedstock materials. Stirring has reduced the dehydration reactions in the case of wet apples and tomatoes. For future laboratory tests of biomass HTC, it is recommended to use the feedstock with its original moisture content without pre-drying to have reliable results and facilitate upscaling. The reactor can be stirred, but the effect seems rather limited under studied conditions.

These findings lead to the following conclusions and perspectives:

- Adding water on a pre-dried feedstock cannot be assumed to be equivalent to using directly wet feedstock when performing HTC laboratory-scale experiments.
- Stirring, while having no apparent effect on results in most studied cases, influences the extent of reactions that occur during the HTC experiments of wet biomass.
- There is a need to study the detailed effects of pre-drying on HTC reaction pathways, which result in significant changes in hydrochar surface morphology and functional groups, and the mass leaching from the solid to liquid phase.

## Declaration of Generative (AI) and AI-assisted technologies in the writing process

During the preparation of this work, the authors used Grammarly and ChatGPT in order to improve the *English* of the Manuscript. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

## CRediT authorship contribution statement

**Omar M. Abdeldayem:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Maria Kennedy:** Writing – review & editing, Supervision, Formal analysis. **Lat Grand Ndiaye:** Writing – review & editing. **David Ferras:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Capucine Dupont:** Writing –

review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2024.106459.

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