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HYDROTHERMAL CARBONISATION OF ORGANIC WASTE FOR THERMAL ENERGY GENERATION

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ABSTRACT

There is currently no use of HTC in the energy sector, only in the waste sector to reduce the mass of sewage sludge before landfill. Different perspectives have been identified for HTC pretreatment technology in the energy sector including combustion, gasification and methanation. However, HTC can lead to a wide range of product quality considering the wide diversity in wet biowaste that can be used. In addition, as HTC is still an emerging technology on the market, there are limited references regarding the relevancy of using HTC as a thermal pretreatment from both the technical and economical point of view. To evaluate if HTC is a valuable pretreatment technology for the sake of thermal energy generation, a series of 15 different feedstock types have been tested in the HTC lab pilot of Laborelec, among which organic residues from the paper industry, food waste, green waste in summer and autumn, compost. The HTC lab pilot has a batch capacity of 100 kg wet feedstock. For each feedstock, a complete analysis of the mass and energy balances is provided together with the assessment of the final product quality. Based on the different tests realised, the methodology for mass and energy balance evaluation was also elaborated and improved to help future project managers in their project design and feasibility study. The 15 feedstock types were of very different nature and gave hydrochar of very different characteristics. However, it is possible to observe some general trends for the HTC products obtained from every feedstock type as alkalis were well reduced during the process and chlorine seems always decreased during HTC process. In most cases, based on the Van Krevelen diagram, HTC is first dominated by dehydration and then by decarboxylation. It appeared that energetic conversion of HTC products is strongly linked with the hydrochar quality. It is clear that HTC improves a lot the quality of low grade organic waste, especially wet feedstock with reasonably low ash content and makes it suitable as input to a boiler or a gasifier. It must also be noted that HTC does not bring added value for biomass that is already high grade like dry wood, as it can be directly used as a fuel. We could define three types of hydrochars for thermal conversion: high quality HTC black pellets with low ash and high calorific value that can be transported efficiently on long distances, average quality HTC black pellets with medium ash content and calorific value for which logistics should be limited to reasonable distances and low quality HTC black pellets that should not be transported and remain on their production site.

1. INTRODUCTION

Hydrothermal Carbonisation (HTC) is a thermal pretreatment process for organic waste and biomass (Hoekman et al., 2011), which is operated in saturated steam condition (between 180°C and 240°C) allowing to transform low grade organic waste into a carbon concentrated product that can be used as a renewable fuel in the energy sector.

At Laborelec, perspectives for the utilization of this process in the energy sector were drafted with the application within:

1. Combined heat and power (CHP) plants,
2. Circular green steam for district heating and industrial steam plants,
3. Thermal gasification for the generation of syngas.

In each application, HTC is first applied to a wet biowaste stream to produce a hydrochar i.e., a carbon concentrated product with high energy density, which can then be densified in black pellets. These black pellets can be transported efficiently and used as a fuel in thermal plants (Erlach et al., 2011).

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However, it should be noticed that the hydrochar quality may vary significantly depending on the biowaste type. Produced hydrochar has an ash content between 5 and 45%, a LHV between 10 and 25MJ/kg, variable chlorine and alkali concentrations, which might thus affect the efficiency of the energy conversion. Indeed, similarly to the inefficient transport of materials with a high moisture content, the transport of ash-rich materials must be avoided too as they correspond to a lower heating value and thus energy density and eventually they also generate costs for ash recycling.

Moreover, the fuel energy density has an influence on the asset performances and profitability (equipment size, OPEX, etc.). Depending on the feedstock, HTC product might then have preferred applications with optimized levelised cost of energy. When the hydrochar quality is low, some application should even be rejected to avoid unprofitability or because the potential hydrochar produced would have no interest for the market.

When a feedstock is considered for a project with an HTC pretreatment, the potential and optimal usage can be obtained by a small-scale HTC test at Laborelec: mass and energy balances between input and output streams can be quantified thanks to the analysis of both the raw material and the end-product (hydrochar).

This paper presents the analysis of 15 tests made with the HTC lab pilot at Laborelec. It gives also the interpretation of the mass and energy balances based on a specific methodology, which has been developed to provide all relevant information prior to a project development: hydrochar quality and possible usages, HTC plant sizing, required raw material quantity, etc. The results of this first part of the study are presented in section 3 and allow to have a first evaluation of HTC performances considering a wide range of feedstock types.

2. CHARACTERISATION OF FEEDSTOCK, HYDROCHAR AND DEASHED HYDROCHAR

For this assessment, the specifications of three types of products for each test were compared, all on dry basis (0% moisture content):

1. The raw feedstock,
2. The hydrochar produced and
3. The deashed hydrochar (simulated industrial quality by centrifugation, equivalent to 80% removal of Si and Al in ash, with 0% moisture content).

Some specifications were combined into relevant indexes for gasification, methanation and combustion to assess the suitability of those fuels (Erlach et al., 2012).

1. In order to assess the suitability of test samples for gasification, the gasification performance was first assessed by combining the following parameters and indexes.
   a. The volatiles (in % of dry matter): when lower than 50%, the volatile content is considered too low (and probably already too carbonised) for an efficient gasification. (50% is a rule of thumb).
   b. The H/C and the O/C (atomic) ratios in the corresponding Van Krevelen diagram: the higher the better for the gasification performance.
2. Next to the gasification performance, the risk of bed agglomeration in fluidised bed reactors was also assessed by combining the following parameters and indexes (Steurera & Ardissonea, 2015).
   a. Alkali (K+Na) in the fuel (in ppm in dry matter): the lower the better (and thus the less risky for bed agglomeration), considering a typical value of 2500 ppm and a limit value of 6000 ppm, according to biomass boiler manufacturers.
   b. Na+K/1,7: the lower the better (considering the content in ash, normalised as oxides).
   c. Ca/P: the higher the better (considering the content in ash, normalised as oxides).
   d. Ca/(Na+K): the higher the better (considering the content in ash, normalised as oxides).
   e. Si/Al: when lower than 1.5 the silicon is mainly in the form of clay (the quartz being negligible), and when above 3 the silicon is mainly in the form of quartz with risks of bed agglomeration. This ratio was computed considering the content in ash normalised as oxides and treated when normalising it as if 1.5 was the typical value and 3 the limit value (see explanations hereafter).
3. The ash removal system in combustion plants is an electrostatic precipitator (ESP) and/or bag filter in the flue gas stream. It is limited to a fly ash content (in % of dry matter) of 30% and was assessed separately. The 30% is linked to the design value of the ash removal system. This can differ from project to project. The 30% is a typical value.
4. Methanation is the reaction by which carbon oxides and hydrogen, catalysed by nickel, are converted into methane and water. In industry, there are two main uses for methanation: to purify synthesis gas (i.e. remove traces of carbon oxides) and to manufacture methane. Engie has developed catalytic methanation in its Gaya pilot plant located in Lyon France. The suitability for catalytic methanation was assessed by combining the following parameters.
   a. N content (in % dry matter): typical value of 1%, limit value of 3%. N is an issue because, during condensation, ammonia will be formed in the syngas stream. It will be converted to N_2 and H_2 into the catalyst. The N_2 in biomethane is limited by regulation. 2G biomethane plant has generally no means to take out the ammonia out of the syngas stream. Technically, this is possible but will demand an extra investment. Also ammonia is very corrosive and materials will need to be adapted.
   b. S content (in % dry matter): typical value of 0.2%, limit value of 0.5%. Sulphur poisons the catalyst in methanation process.
   c. Cl content (in ppm dry matter): typical value of 1500 ppm, limit value of 8000 ppm. Chlorine poisons the catalyst in methanation process.
5. Finally, some combustion parameters and indexes were also computed.

a. For boilers with metal temperature <550°C, the S/Cl index is a relevant corrosion index: lower than 2 indicating a high risk of corrosion, and higher than 4 a low risk. Treated similarly as the Si/Al index.
b. For boilers with metal temperature >550°C, the corrosion is assessed with the alkali in the ash (normalised as oxides, the higher the riskier), and with the Na+K+Fe+S (all in %ash normalised as oxides, the higher the riskier for molten sulphate corrosion).
c. Finally, the (Ca+K)/Si index (all in %ash normalised as oxides, the higher the riskier) is computed as an indicator of slagging and fouling risks.

Remark. There is no absolute value regarding Cl of which one can say, when Cl is lower than this absolute value there is no risk of corrosion. It depends under which form the Cl will come free in the flue gases, the presence of heavy metals like Sn, Pb, etc., the atmosphere in the boiler (reducing, oxidizing), etc. The S/Cl is the only one considered parameter for the risk of corrosion.

All indexes and parameters cited hereabove were normalised from 0 (worse value) to 1 (best value) according to some rules.

3. METHODOLOGY FOR THE HTC LAB PILOT TEST

This section describes the main steps of a standard HTC test i.e. material preparation, HTC cycle description, data logging, etc. (Lucian & Fiori, 2017).

Then the methodology to estimate the mass and energy balances will be explained together with the indicators allowing to evaluate the "HTC test" quality.

3.1 Typical HTC test description

A typical HTC test starts with the raw material preparation aiming at conditioning the tested material in the right conditions before starting.

To the contrary of the industrial process, our HTC lab pilot works in batch. The material dimensions, its weight and the average moisture in the reactor need to be controlled before starting the operation (Figure 1). Those specifications have been set by Ingelia as the designer of our pilot plant.

- max. weight on dry base is 30kg,
- max. wet volume of 100L,
- max. particle size = 40 mm,
- average moisture in process condition = 80%, lower moisture does not allow proper working of the pilot.

Note that the quantity of water required to achieve the process conditions is adjusted directly in the reactor.

After preparation, the material is weighted and charged into the reactor. At this stage, the mass and moisture content of the fresh feedstock need to be noted down meticulously, such that those two essential parameters are available for further interpretations. The fresh sample mass is used as reference for the mass yield and an error on it would change the HTC process evaluation.

The mass and the moisture of the tested sample are both linked to the reactor capacity i.e. 30kg of dry material. Exceeding this capacity would lead to issues during the HTC process (too high level in the reactor). On the opposite, if a too small quantity of feedstock is inserted into the reactor, the quantity of material recovered at the outlet could be too low to conduct all necessary analyses.

After this preparation phase, the average moisture is adjusted to 80% and the reactor is closed with a flange. Demineralised water is supplied in both the condenser and the boiler, and the test can start.

From this moment on, the boiler starts heating up until it reaches the required pressure and temperature level for the test:

1. Heating up to 4bars steam pressure (minimum pressure requirement to start heating the reactor by steam injection),
2. Pressurisation of the reactor by steam injection until it achieves equal temperature in both the boiler and the reactor,
3. Heating up to the required test temperature and pressure (220°C / 23.5 bars, Figure 2).

FIGURE 1: Raw material preparation, in this case contaminated compost of green waste.

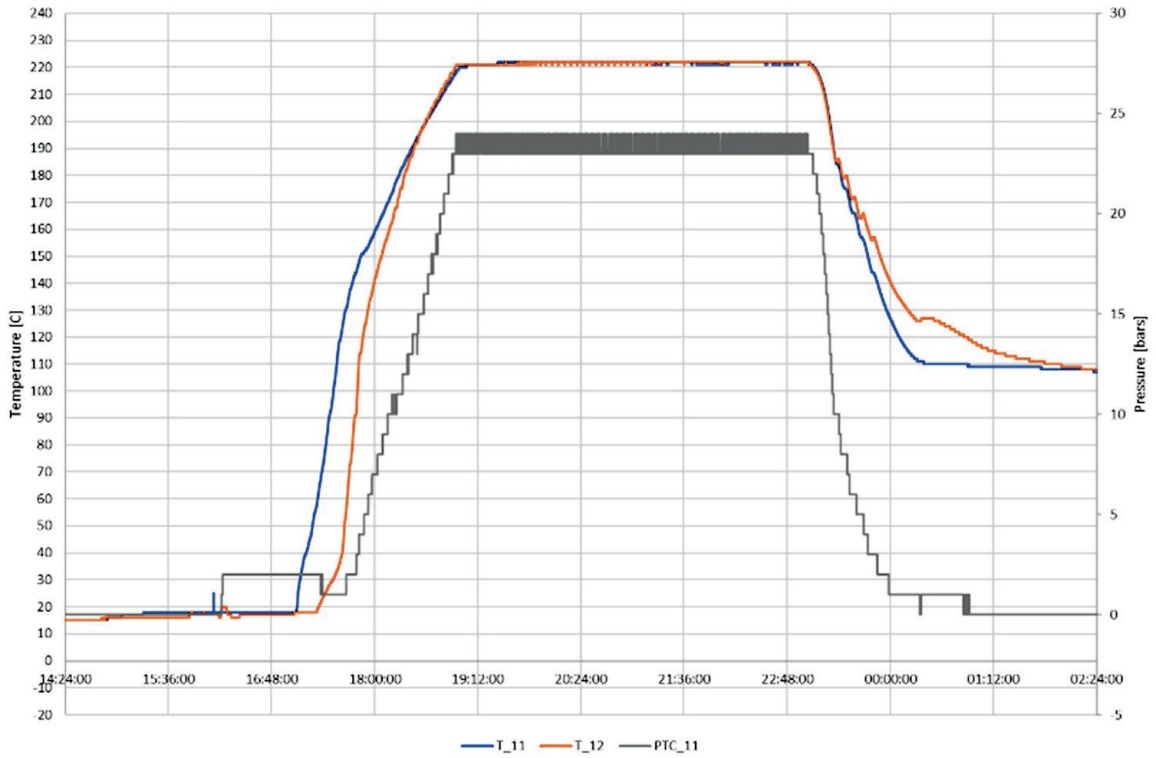


FIGURE 2: Temperature and pressure profile in a typical HTC test.

Note that to be representative of the commercial plant configuration, the test temperature and pressure were set to these values for all tests, as recommended by the designer of the HTC pilot.

After heating-up to carbonisation parameters, the reactor is maintained in steady state until the set residence time is reached i.e., typically 4 hours. In the test results presented in this paper, the residence time may vary between 3 hours or 4 hours depending on the test organisation. Sometimes technical issues resulted in a different residence time.

Then, the reactor is depressurised, and the carbonised sludge is discharged into a buffer tank by passing through the grinder. Finally, the slurry (composed of the process water and the grinded carbonised matter) is pumped into the filter press and after filtration, the carbonised material is recovered and weighted. The mass measured at this stage will be used for the mass yield computation for post-testing interpretation (Figure 3).

Finally, a hydrochar sample of 1-2kg is collected from the filtered weighted carbonised matter for lab analysis and the mass and energy (M&E) balances are obtained by comparing material properties and mass before and after the test.

3.2 Estimation of mass and energy balances

HTC is considered for its ability to pretreat wet biowaste with very low energy content into a higher value energy carrier that can be used as a fuel in thermal plant (Wang et al., 2018).

When HTC is considered as a circular fuel supply for a district heating, for industrial steam generation or for decarbonised fuel trading, the mass and energy balances are required to estimate the yield from a given feedstock and further on, to build a business model for the project including among others (Heidari et al., 2018):

- Sizing a boiler or a CHP,
- Evaluating the production cost and fuel price,
- Setting up a contract for green steam supply.

A detailed mass and energy balances assessment of the HTC process is required as its performance is highly dependent on the nature of the feedstock:

- Raw material analysis allows to have a first evaluation of the product characteristics and its adequacy regarding HTC process: moisture, carbon content, mineral load, etc.;

FIGURE 3: Carbonized material recovered after filtration.

- The analysis of the resulting hydrochar allows the assessment of the obtained energy content, carbon concentration, ash composition, chlorine and alkali reduction, etc.;
- The comparison of both analyses delivers the mass and energy yield, the elemental mass balance, any improvement in HHV/LHV and the Van Krevelen diagram.

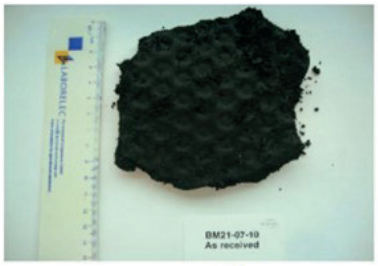
At this stage and considering the previous chapter, it should be noted that the lab analyses are carried out respectively on the raw material as received and, on the hydrochar cakes recovered at the outlet of the filter press. However, the HTC lab pilot presents significant differences compared to an industrial HTC plant. Indeed, due to its scale, the HTC lab pilot does not include the different post-treatment steps of the reactor outflow as it exists for the industrial HTC plant, namely:

- A hydro cyclone allowing to remove small stones and small metal pieces from the mainstream containing the carbonised material (Figure 4);
- A spiral separator allowing to remove fine mineral particles from the mainstream richer in carbon;
- The final thermal drying step occurring between the filter press and the pelletisation unit;
- The pelletisation unit.

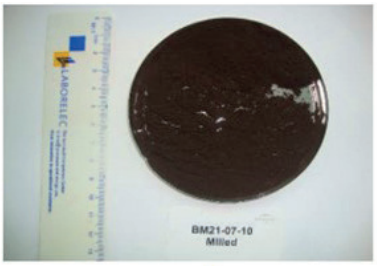
Drying and pelletisation steps have an influence on the final moisture and the density but not on the elemental composition (except for water), as opposed to both the hydro-cyclone and the spiral separator that contribute to the fuel quality improvement with an ash reduction.

Consequently, it appears that the mass and energy balances of the HTC lab pilot cannot be used straightaway in the perspective of an industrial project. Since the product obtained after a test is still in a "raw" state, compared to what we would have obtained with an industrial plant, mainly a dry and "de-ashed" pelletised hydrochar (Zhang et al., 2019). This is why, in the meanwhile Laborelec added a 3kW pelletiser to the HTC lab pilot for future tests. Figure 5 shows a direct analysis of a HTC lab pilot hydrochar product made from green waste. As can be seen, lower heating value is increased around 23,5 MJ/kg on dry basis and volaties decrease under 60% on dry basis, though ash content is slightly increased. Moisture measured at the outlet of the filter press is 64% where typical pellets moisture would be about 6%.

FIGURE 4: Representation of a hydro-cyclone.



as received



milled

Results

direct analysis

	unit	standard	as received	dry base	dry & ash free
total moisture	%	ISO 18134	64,2	-	-
ash content @550°C	%	ISO 18122	3,2	9,0	-
ash content @815°C	%	ISO 18122	3,0	8,4	-
volatile matter	%	ISO 18123	21,4	59,9	65,3
fixed carbon	%	calculated by difference	11,4	31,8	34,7
higher heating value (HHV)	MJ/kg	ISO 18125	8,83	24,66	26,91
lower heating value (LHV)	MJ/kg	ISO 18125	6,86	23,53	25,68

FIGURE 5: Direct analysis of green waste hydrochar obtained in the HTC lab pilot.

Considering the current pilot infrastructure, it is not possible to directly measure the real mass and energy balances of the corresponding industrial plant. Interpretations or hypotheses have been used to extrapolate them.

The two main options to achieve this objective are then as follows.

1. Considering only the analyses made on the real physical products, sampled at the HTC lab pilot inlet and outlet without any interpretation. The mass balance can be done between the raw material "as received" and the hydrochar in "dry base". There will be a small error due to the moisture (which is 0 in the dry base reference), but the most important approximation is due to the ash content because it has a significant influence on the energy content and on the boiler operation later on. Neglecting the efficiency of the particles separation system will then lead to a less attractive result:
   - Higher mass balance will lead to more transportation, larger handling system, larger boiler, etc;
   - Lower energy balance and higher ash content will lower the resulting fuel price and increase marginal transformation cost, resulting in a degraded business model, etc.
2. Estimating what could be the industrial product quality based on the operational experience of an HTC plant. This would allow to improve the mass and energy relevancy compared to 1., but the risk is to over-estimate the HTC product quality conducting to a too optimistic business model. Indeed, while assuming a different final moisture is not that risky, the particles separation system will not simply reduce linearly the ash content but impact mostly the heavy and unbounded minerals concentrations (SiO_2 and Al_2O_3).

Obviously, the ideal solution would be to perform the assessment directly on an industrial HTC plant including the entire post-treatment. However, the fresh material required for such a test would be 10 tonnes (depending on the moisture), which is difficult to manage at the prefeasibility stage. Moreover, when different feedstock types or when a combination of feedstock types needs to be tested, the time and cost of such qualification tests become prohibitive. Nevertheless, this has in the meanwhile been considered at a later stage, when project perspectives are confirmed, to validate the project business model on a larger industrial testing facility, like the one available in Náquera, Spain with Ingelia company (HTC process owner).

Considering the purpose of these tests in our field activity, the second approach (simulating an industrial HTC plant on the basis of the hydrochar obtained at the outlet of the HTC lab pilot) is the preferred option. Estimate the efficiency of the particles separation will be continuously improved thanks to the return of experience.

So, from the abovementioned discussion, a methodology has been built to assess the HTC process on different input materials.

1. In any case, the material quality cannot be higher than the "dry ash free" reference. This seems obvious but it gives an easy and direct asymptote when post-treatment is discussed. This remains also valid when further chemical treatment to improve quality is envisaged.
2. The reference material at the HTC process inlet is always the raw material as received because this is the one that must be handled and processed.
3. The moisture of the final product is always considered at 6% corresponding to the average moisture in resulting black pellets. This low moisture is very important for logistics but higher moisture could be considered when the fuel is fired locally.
4. Only the default post-treatment path is considered, including hydro-cyclone and spiral separator only. Its efficiency has been established by Ingelia to 80% in the removal of unbounded minerals measured in the ash analysis of the hydrochar i.e. alumino-silicates SiO_2 and Al_2O_3. This efficiency was set on the basis of the experience of the equipment providers and Ingelia.
5. Clean water recirculation in the process is considered to avoid recirculation of chlorine and alkali that would lead to a higher concentration in the final product.

In the following, this extrapolation of the industrial product quality from the pilot quality will be identified as "industrial properties".

The elemental ash are re-estimated considering the new normalised values and their weighted average.

All formulas used to compute the parameters of the different sample types (dry, dry ash free, as received, industrial quality, industrial dry quality) are described as follows.

$$A_{moist} = A_{dry} * (1 - MC_{new})$$

$$A_{moist,changed\ ash} = A_{dry} * (1 - MC_{new}) * \left(\frac{1 - AC_{new}}{1 - AC_{old}}\right)$$

$$AC_{new} = AC_{old} * (1 - MC_{new}) * \alpha$$

$$\alpha = \frac{\sum ash\ elements\ in\ \%\ ash\ @815\ as\ oxides\ in\ new\ sample}{\sum ash\ elements\ in\ \%\ ash\ @815\ as\ oxides\ in\ old\ sample}$$

$$H/C_{atomic} = \frac{H\ content}{C\ content} * \frac{atomic\ weight\ C}{atomic\ weight\ H}$$

$$O/C_{atomic} = \frac{O\ content}{C\ content} * \frac{atomic\ weight\ C}{atomic\ weight\ O}$$

$$B_{fuel} = B_{ash@815\ as\ oxides} * AC$$

with

- A_{dry} being any parameter coming from the direct or the elemental analysis (but not from the analysis of the major elements in the ash), in a "dry" sample (moisture content equal to zero);
- A_{moist} being any parameter coming from the direct or the elemental analysis (but not from the analysis of the major elements in the ash), in a "moist" sample (any sample with a moisture content different from zero);
- $A_{moist,changed\ ash}$ being any parameter coming from the direct or the elemental analysis (but not from the analysis of the major elements in the ash), in a "moist" sample (any sample with a moisture content with a moisture content different from zero) where the ash composition was changed;

- MC being the moisture content, measured on the basis of ISO18134 standard;
- AC being the ash content measured at 815°C like fossil coal;
- B_{fuel} being the percentage of any of the major elements in the ash, measured at 815°C like fossil coal, and reponderated as oxides;
- $B_{ash@815\ as\ oxides}$ being the percentage of any of the major elements in the ash, measured at 815°C, and reponderated as oxides;
- Atomic weight C = 12.01, of H=1.08, of O=16.00.

Note that hypotheses 3 and 4, can always be challenged and optimised based on further experience. Indeed, when the prefeasibility study with the HTC lab pilot confirms the interest of a specific fuel supply chain, it is recommended to confirm it by a test on an industrial plant (in continuous operation mode as available with Ingelia) including the complete post-treatment. This real scale test also allows to measure the OPEX of the plant and to confirm the preliminary business model. In parallel, the efficiency of the particles separator can also be measured and the hypothesis on its efficiency will be improved for each project.

3.2.1 Presentation of the test results and interpretation

Giving the wide diversity of material that can be treated by HTC and the potential process effect on the specific elemental composition that may also vary for a same feedstock coming from different locations, both the presentation and the interpretation of an HTC test results are not easy.

Moreover, a certain level of discussion will remain depending on the material tested. Indeed, it will always be easier to make results interpretations on well-known and simple feedstock (fresh wood for instance) when similar tests results are available and can be compared. Inversely, interpretations of tests are less straightforward when the feedstock is tested for the first time, and with no repetition of the test on this feedstock.

It was then required to build a systemic methodology to be used for every HTC test and based on our own perspective for the energy sector. In the next chapter, test results will be then always presented as follows. When required, highlight of potential error propagation in the measurement chain will be also given.

- In Table 2 mass and energy results can be found: the direct analysis, the elemental analysis (including chlorine and alkali) and the main ash composition are given for the fresh material as received and the industrial product (see Appendix). As a reminder, the industrial product is estimated considering a moisture of 6% for pellets and minerals separation system with efficiency of 80% on SiO_2 and Al_2O_3 concentration in the “dry hydrochar” that comes out of the HTC lab pilot.
- The detailed mass balance description: the global mass yield is presented: mass of the fresh material sample (measured), mass of the industrial product recovered (estimated from the mass measured at the filter press outlet).

The evolution of the elemental composition is presented on both the concentration and the absolute mass. Both views are required to understand the effect of HTC on the material. Indeed, the decrease in absolute mass causes an increase in concentration. The opposite is never possible of course as the absolute mass balance is always either zero or negative (no creation of material).

Note that for both concentration and mass balance, the elements were all compared based on their relative proportion in the fuel (and not on their proportion in the ash at 815°C), necessitating that the content of some elements (major elements in the ash) were multiplied by the corresponding ash content at 815°C in the sample.

However, in some case, a mass gain can be observed on some specific element like, for instance, iron (Fe) or others. This can be explained by different reasons depending on the element considered.

- The error propagation in the measurement chain. Indeed, when HTC has no effect on a given element, the concentration increases because of the global mass reduction but the mass of the element is constant. In the balance estimation, this brings division by very small number giving the impression of a mass gain, but this is false. In any case, a mass gain will have to be interpreted as no absolute mass variation for this specific element.
- Value obtained by difference. This is typically the case for the fixed carbon in the direct analysis or the oxygen in the elemental analysis. The reason for this is similar than previously. Difference in close number can lead to big error propagation.
- The sampling technique.

Of course, these phenomena are even more impacted by the quantity of material recovered at the filter press outlet. Therefore, the mass of the fresh material sample is key to ensure the test result quality. Indeed, using less material is better to avoid problems during the test but, on the other hand, a too low quantity will give more uncertainty on the mass balance. The biggest challenge being with very wet materials (>85% moisture) as the maximal volume in the reactor is reached with a very small amount of dry material. In this case, the test should be repeated, and the M&E balance made on the average measurement.

Van Krevelen diagram is usually used by the coal industry or solid fuel traders to evaluate their product maturity based on the atomic carbon concentration related to volatile compounds (Figure 6). It is also very appropriate to compare the hydrochar with the degree of fossilation of reference coal types anthracite, subbituminous coal and lignite.

As HTC is close from the fossile coal formation process, this diagram is well adapted to evaluate HTC process performance on a given feedstock.

Moreover, it also allows to compare different feedstock types before and after HTC or with references found in the literature.

Effects of process parameters can also be evaluated thanks to this diagram as different residence times or tem-

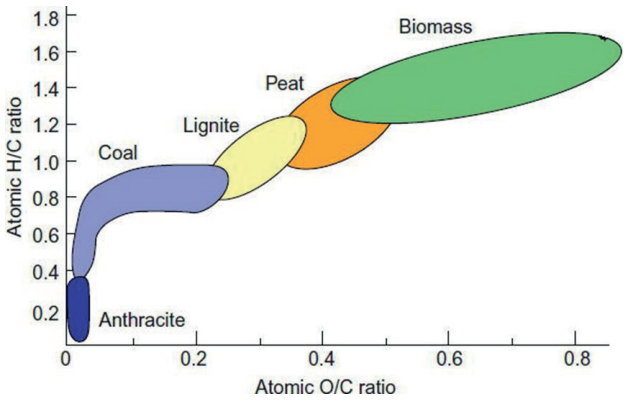


FIGURE 6: Representation of a hydro-cyclone.

perature levels will lead to a different product transformation.

The "demethanation" corresponds to a decrease in CH_4 molecules in the hydrocarbonate chain, the "dehydration" corresponds to a decrease of H_2O molecules and the "decarboxylation" corresponds to a decrease of CO_2 molecules. HTC is mainly dominated by dehydration.

LHV evolution can also be deducted from the Van Krevelen diagram. Indeed, LHV will increase when the ratio H/C increases and when ratio O/C decreases.

The change in high heating value (HHV) and low heating value (LHV) is described together in the detailed energy balance with the evolution of the ash fusion temperature or AFT (HT, hemispherical). Then, the "higher energy balance" and the "lower energy balance" are presented considering the weight of both the input raw material and the output HTC product (estimated). Both values are presented because the "high energy balance" represents the real material transformation. In contrast, the "low energy balance" represents the gain of the feedstock in market value.

It results that every material tested has its own and complete HTC identity card offering a complete overview of both technical aspects entering in the thermal asset conception and business data to evaluate the business model performances.

3.2.2 Calculation of HHV and LHV

According to ISO-18125, the gross calorific value or high heating value HHV is measured. A weighed portion of the analysis sample of the solid biofuel is burned in high-pressure oxygen in a bomb calorimeter under specified conditions. The effective heat capacity of the calorimeter is determined in calibration experiments by combustion of certified benzoic acid under similar conditions, accounted for in the certificate.

HHV is calculated from the corrected temperature rise and the effective heat capacity of the calorimeter, with allowances made for contributions from ignition energy, combustion of the fuse(s) and for thermal effects from side reactions such as the formation of nitric acid (Dashti et al., 2019). Furthermore, a correction is applied to account for the difference in energy between the aqueous sulphuric acid formed in the bomb reaction and gaseous sulphur dioxide, i.e. the required reaction product of sulphur in the biofuel. The corresponding energy effect between aqueous and gaseous hydrochloric acid can be neglected due to the usually low value for the correction regarding solid biofuels.

The net calorific value at constant pressure $q_{p,net,m}$ or low heating value LHV is calculated from the measured HHV or $q_{v,gr,d}$ with the following formula.

$$q_{p,net,m}=\{q_{v,gr,d}-212*w(H)_d-0.8*[w(O)_d+w(N)_d]\}*(1-0.01*M))*24,43*M$$

$$q_{p,net,d}*(1-0.01*M)-24.43*M$$

where

- $q_{p,net,m}$ is the net calorific value at constant pressure in joules per gram (or kJ/kg) of the biofuel with moisture content M (usually as received M_{ar});
- $q_{v,gr,d}$ is the gross calorific value at constant volume in joules per gram (or kJ/kg) of the moisture-free fuel.
- When fuel composition is affected by pretreatment, HHV can also be recalculated on the basis of the elemental composition together with the specific elemental heating values:

  $$HHV=0.3491*[C]+1.1783*[H]+0.1005*[S]-0.0151*[N]-0.1034*[O]-0.0211*Ash_{dry}$$

- But ash composition of biomass fuels must be estimated at 550°C according to ISO-18122 for biomass, in order to keep the volatiles in the ash for further detailed ash analysis e.g. by ICP. Indeed some of those volatiles like KCl play an important role in slagging and fouling generated by the combustion in a boiler. But when carbonates in ash @550°C remain significant, then the formula is no longer correct. This occurs e.g. when Ca in ash is high. In that case the following formula's will give the best estmate:

  $$HHV=0.01*[carbonates]+0.3491*([C])-[carbonates]+1.1783*[H]+0.0151*[N]-0.1034*[O]-0.0211*A_{dry}$$

  where

  $$carbonates=(Ash_{dry@550°C}-Ash_{dry@815°C})*12.011/28$$

This shows that the contribution to the heating value is not the same when C is bounded in carbonates or elemental.

4. MASS AND ENERGY BALANCE FOR THE 15 HTC TESTS IN LAB

The mass and energy balances of the feedstock types that have been tested in the HTC lab pilot can be found in Table 1 and in Figure 7. The mass yield is the ratio between the mass hydrochar as industrial (kg) and the mass feedstock as received (kg).

It appears that:

- The main driver of the mass yield is the initial moisture content as feedstock of very different nature having similar initial moisture are in the same range.
- The energy yield is more variable depending on the feedstock characteristics.
  - Energy yield of degraded feedstock is below the average (food waste, raw compost, etc.). However, exceptions can be found when the feedstock is pollut-

TABLE 1: Mass and energy balance of the feedstock types that have been tested in the HTC lab pilot pilot.

Feedstock	Mass feedstock as received (kg)	Mass hydrochar as industrial (kg)	Mass yield	Lower Energy yield	Higher Energy yield
Bark	25	7.3	29.2%	70.8%	62.8%
Primary paper sludge	42.5	12.2	28.7%	188.2%	86.3%
Biological paper sludge	30.0	8.3	27.8%	125.3%	68.4%
Mixed paper sludge	42.5	9.3	21.9%	85.3%	60.1%
Green waste in summer	14.5	3.4	23.5%	147.5%	98.3%
Dead leaves	14.5	2.0	13.7%	104.2%	62.0%
Jelly residues	94.78	2.39	2.5%	30.5%	29.0%
Food waste	86.9	3.8	4.3%	123.9%	35.2%
Shredded root residues	13.6	5.8	42.8%	57.4%	55.4%
Raw compost	15.5	3.5	22.5%	44.2%	40.2%
Compost refusal	7.2	4.1	52.2%	82.4%	78.9%
Compost grade 20-80	10.1	5.4	53.3%	80.3%	76.1%
Aerobic sludge from potatoes industry	43.7	4.7	10.8%	346.5%	73.0%
Grey starch from potatoes industry	46.3	10.9	23.4%	319.3%	140.2%
Grey starch from potatoes industry	59.3	5.6	9.4%	345.8%	73.7%

ed with plastics (like compost 20-80 and compost refusal). Plastics being not degradable, this may explain the lower impact of the material degradation on the energy yield.

- When fresh biowaste is treated, energy yield is higher than average. This shows why it is important to treat feedstock as fresh as possible to keep as much as possible carbon and energy before degradation starts (see green waste).
- When moisture is very high (>85%) like for food waste (in this case) and jelly residue, the energy yield is very low. However, these tests should be repeated because of respectively, the material degradation initiated before the test and the very low mass yield. Small measurement errors can have big consequences.

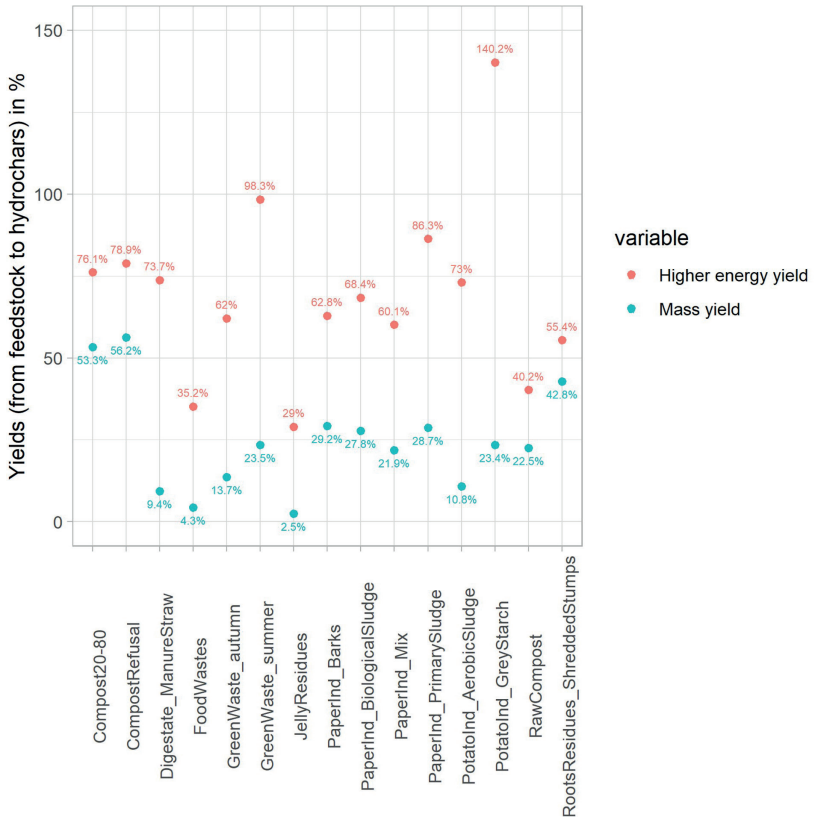


FIGURE 7: Overview of mass and energy balances for the performed HTC tests.

- In most cases, when feedstock is not already degraded or not too wet, energy yield varies from 60% to 85%, which is coherent with references found in the literature.

Energy yield on LHV is more variable and should be interpreted as product quality/value evolution through HTC with respect to the LHV and ash content achieved after transformation: As in any case HTC leads to an increase of LHV, the lower energy yield is above 100% when the initial moisture is about 70% or above. The lower energy yield of degraded material is very low (<60%). Exceptions are however, visible on degraded feedstock containing plastics. Probably because it is not degradable. The C losses are then lower.

Roots residues, jelly residues and food waste should not be considered because of either the problem met during the test or the very small mass measurement that may lead to potential errors.

Figure 8 presents every feedstock transformation on a single Van Krevelen diagram (round shape are the raw materials and square are the hydrochars).

Except very specific cases, it appears that most of hydrochars are in the lignite area i.e. O/C in the range of 0.2-0.4 and H/C in the range of 0.8-1.3.This is further illustrated in the figure showing the typical coal family area on the Van Krevelen diagram (Figure 6).

It appears that the O/C ratios of the tests are well concentrated around the average value of 0.3246 which is typical of lignite. Regarding H/C ratios, the values are more spread around the average of 1.2174. This may be explained by the main effect of HTC observed on the Van Krevelen diagram i.e., the dehydration corresponding to H_2O removal. Then, it seems that HTC has its main effect on the O/C ratio. The effect on the H/C ratio is then mainly due to the H_2O removal (2 atoms of H for 1 atom of O).

Note that this should be confirmed with more tests to increase the size of the database used for the Gauss curves (Khan et al., 2019).

Of course, dehydration is not the only transformation as it has been also observed that a small quantity of carbon is also released in the process water or as CO_2 with the COV released during the process.

HTC seems then dominated by dehydration with decarboxylation at the second order. For one specific feedstock (aerobic sludge from potatoes industry) decarboxylation was probably dominating but the reason might be the feedstock origin i.e., from lake water.

Regarding Ash Fusion Temperature (AFT), it seems that no general trend can be observed for every feedstock. However, it appears that the AFT is either constant or higher after transformation (no diminution).

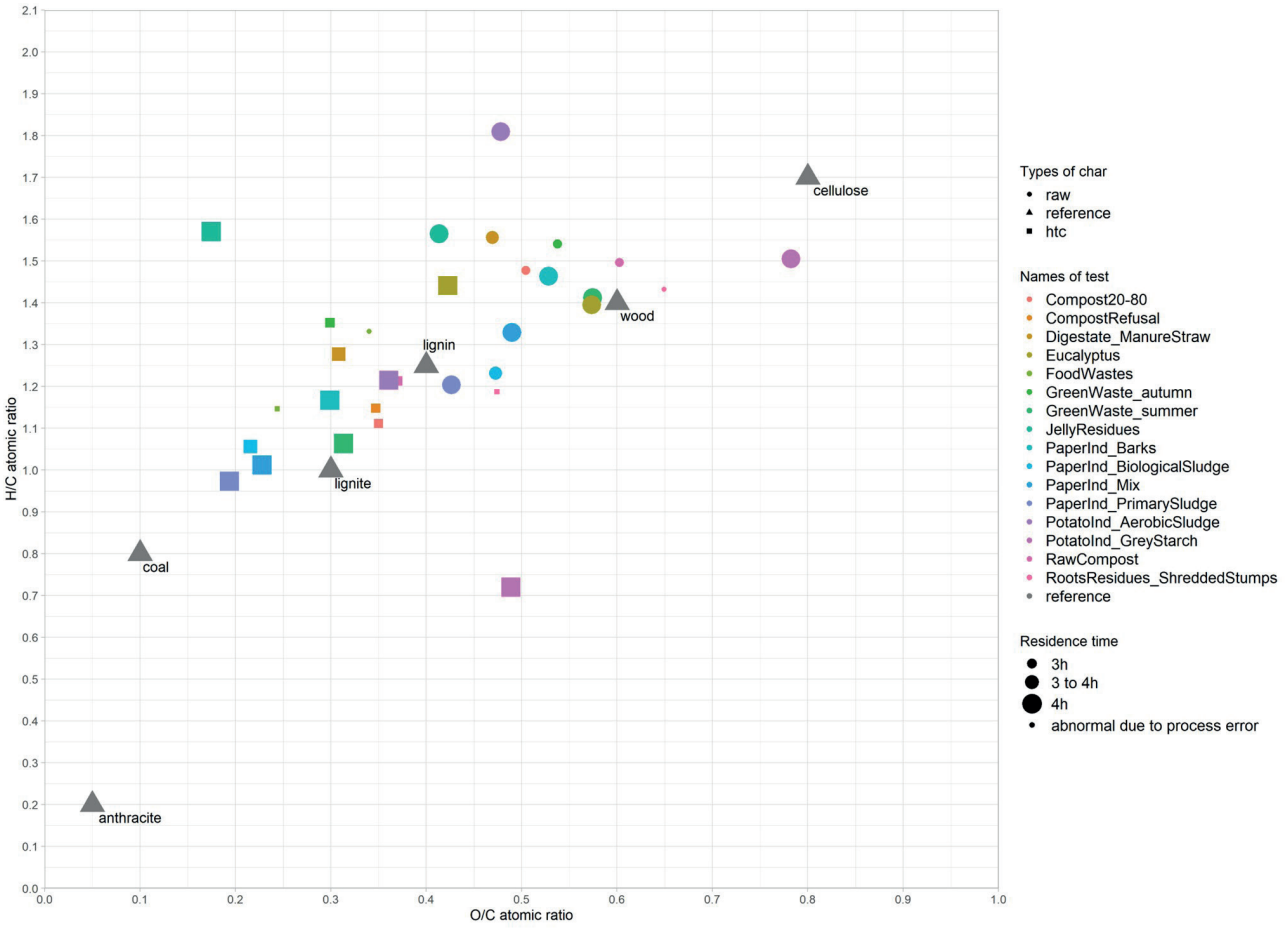


FIGURE 8: Van Krevelen diagram with all performed HTC tests.

5. CONCLUSIONS

The 15 tested feedstock types were of very different nature (Surup et al., 2020) and gave hydrochar with very different characteristics (Table 2 in Appendix). However, it is possible to observe some general trends for the HTC products obtained from every feedstock type.

- Alkalis are greatly reduced during the process, which is a positive effect considering Ash Fusion Temperature. When alkali were not decreased (see grey starch), additional test should be performed on the feedstock with the 'process water to dry matter' ratio as parameter to verify if improvement is possible.
- Cl seems always decreased during HTC process. When the decrease is smaller, the process water over dry matter ratio should also be tested to verify if improvement is feasible.
- In most cases, based on the Van Krevelen diagram, HTC is first dominated by dehydration and then by decarboxylation. Different trends have also been observed on very specific feedstock (aerobic sludge), but this may be due to the origin of the raw material i.e., earth, soft water, or marine water. Indeed, depending on the origin, the C, H, O elements have different initial ratios and might be bounded differently with, as a consequence, a different behaviour in the HTC process.

Note that all these interpretations have been confirmed in the meanwhile with additional tests to extend the database representativity and the trends reported in this report have been confirmed.

Regarding the methodology described in this paper, some adaptations are required to improve the readability of the mass balance. Indeed, in this methodology, the initial statement was to provide to future project developers a clear view of the mass and energy balances related to a specific project i.e., the ratios between the raw material and the product obtained after transformation in an industrial plant.

However, by doing so, the elemental mass balance is affected by the initial water concentration. Indeed, water remains the main compound in mass in every case as most of the feedstock tested are meant to be wet and have above 50% moisture. Then, when considered in the elemental mass balance, all other species seem very slightly affected by the HTC process and it is hard to make conclusions about the migration of certain species towards the hydrochar or the effluent. Indeed, it would have been interesting to see if some trends could be identified in this perspective to evaluate if and in which proportion every element are either bounded to the solid phase or can be leached out in the liquid phase.

For further HTC test, it is then recommended to make the elemental mass balance analysis on dry basis. This will allow to have the picture of what remains in the solid phase after HTC treatment. By definition, what is not in the solid phase will be retrieved mainly in the liquid effluent (whith typically 65-70% of the HTC output) or in the volatiles released during the process (generally 2-4% of the raw material dry mass). In this paper, this can be done by consulting tables given in every material overview. For further reporting, the elemental mass balance will be presented on a dry basis only.

Considering the mass and energy balances evaluated for every tested feedstock, the chemical composition of the feedstock plays an important role in the HTC performance as well as in the energetic conversion of its products. Therefore, it is important to examine the complete pretreatment process of the fuel including its optional posttreatment with chemicals. This can help us understanding what could be the final product quality or if some molecules are present as organics or inorganics, the latter will be easily "washed out".

RECOMMENDATIONS

Depending on the origin of the raw material, some of the parameters of the HTC process, such as:

- the residence time in the reactor,
- the process temperature,
- or the ratio of the process water and the dry matter in the reactor,

can be adapted.

It is then recommended to repeat some of the tests presented in this paper with different process conditions to optimise the HTC pretreatment.

The results obtained with the HTC lab pilot have been validated against the industrial HTC demo plant of Ingelia with success. But It is still recommended to test some of the feedstock types in such a facility. This will allow to assess the:

- the reactor size,
- the batch vs continuous process,
- the efficiency of the particles separation system for ash reduction,
- the final HTC product quality.

It would also be interesting to figure out how the quality of some hydrochar (e.g., from the paper industry) could be further improved by the implementation of chemical treatment after the process. Indeed, those kinds of post-treatment are often referenced in the literature to extract components of interest such as the phosphorus (Milotti et al., 2020). HTC is well adapted to such a process because of the liquid form of the product after treatment and before filtration, which eases chemical treatment. In particular, acid leaching aiming at reducing ash content could be further studied. Some preliminary test realised in the frame of a master thesis at LBE showed promising results in this perspective at lab scale. Further investigations could determine how to implement such a process at industrial scale and if this additional operation can be profitable i.e. the cost of operation vs the additional market value of the product (Papa et al., 2021).

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