



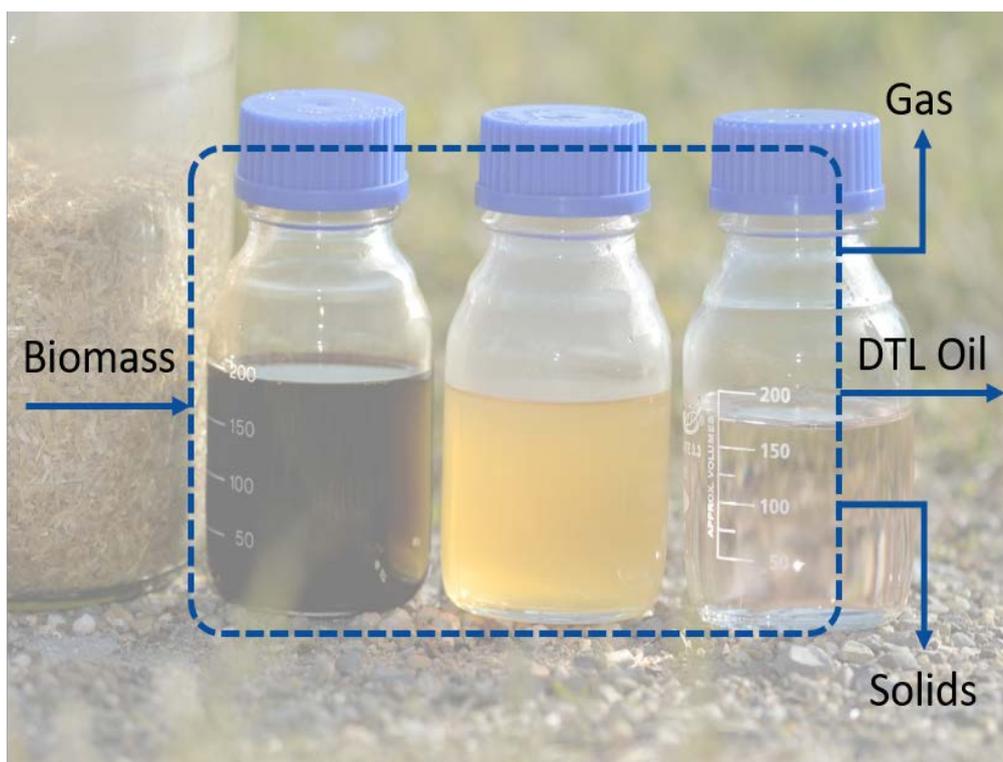
IEA Bioenergy
Technology Collaboration Programme

Mass balances for DTL processes

Considerations and best practice

IEA Bioenergy: Task 34

August 2022





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Considerations and best practice

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Introduction

The most basic approach to characterize DTL processes is by establishing mass balances to gain insight into product distribution. One important figure that is derived from these mass balances is the yield of the main product, the DTL bio-oil. Apart from being of fundamental importance to develop business cases based on DTL processes, this yield is also one important parameter to compare different process conditions and varying DTL process setups.

While there is little to argue how a mass balance should be calculated since this is subject to many textbooks, there are some specific considerations to be made when processing biomass in general as feedstock. Moreover, there are even DTL process specific issues that require attention due to their impact on the results of mass balances. This technical note aims at summarizing potential sources for inconsistencies and providing guidelines so that the reported values can be evaluated efficiently. Most of the recommended practices are already widely used in the scientific DTL community.

Main recommendations resulting from this report

- The three mass balances derived from the different biomass reference states hold important information to characterize DTL process and no recommendation is given of one over the other. The availability of data for the different mass balances is mandatory to enable comparison of different technologies and studies.
- In addition to the three reference states of biomass, carbon balances prove to be a reliable result to evaluate DTL processes, especially for the case of HTL.
- It is recommended to sample DTL products (and the feedstock) many times during the course of an experiment in order to increase accuracy of mass balances.
- The choice of solvent and how it is used to recover biocrude is a crucial consideration for HTL batch experiment balances.

FEEDSTOCK CHARACTERIZATION

The most reported figure resulting from mass balances is the yield of a product, defined as

$$yield_{product,i} = \frac{mass_{product,i}}{mass_{feed}}$$

While this definition holds true for all processes, there are fundamentally important considerations when biomass is used as feedstock. Biomass is a complex mixture of components. In addition to organic biopolymers such as cellulose, hemicelluloses, lignin and extractives, there is always water/moisture present, as well as a variety of inorganic¹ compounds (see Figure 1). As a result of the types of components present, the following reference states are defined to characterize the feedstock; as received (ar), dry (d), and dry ash-free (daf). Each of these reference states are regularly used, equally valid, and

¹ The inorganic compounds are typically measured as ash content, which is made up of oxidized inorganic compounds. Consequently, there can be a notable difference between mass of inorganics and mass of ash. This difference is often neglected and both terms used to describe the amount of (unoxidized) inorganics because determination of ash content (instead of inorganics) is a valid pragmatic solution in many cases. We will follow this habit in this technical note since to ease reading.

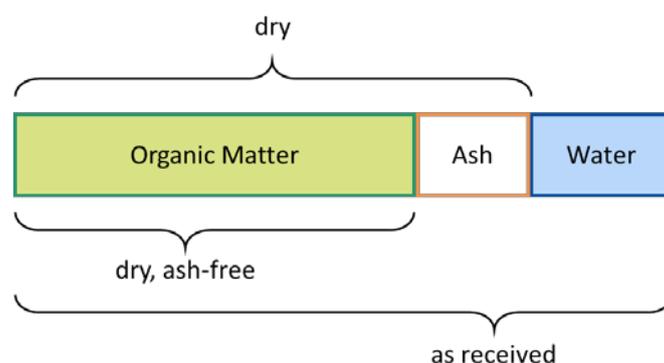


Figure 1: Biomass compounds and resulting reference states to report its weight.

are most useful under differing circumstances. From the definition of the yield, it can be observed that the choice of reference state directly affects the calculated yield(s). In fact, the different possible yields are calculated from different mass balances as explained in the next section. It follows that, depending on the type of mass balance performed, each of the feed and product materials must have certain compositional attributes quantified, specifically their water, ash, and carbon content. Provided that these product phases account for the entire material input and output across the system, and that their rate of consumption/production (in the case of continuous flow experiments) is accurately determined, an accurate mass balance can be obtained. DTL studies often investigate the influence of reactor conditions and/or a narrow range of feed compositions on DTL oil yield and quality. As a result, comparison of the efficacy of particular materials or reactor setups is often done across work conducted by different research groups. For the results to be accurately compared, the methods by which the feedstock and product phases are analysed and quantified need to be explicitly stated/ explained and as consistent as possible.

TYPES OF BALANCES

Before discussing the different types it is noted that mass balances will never be closed to 100% due to uncertainties in measuring weights of feedstock/ products and losses during handling (spilling, dead volumes etc). Typically, not all of the feedstock mass is detected in the products but it is also possible that there is an overrepresentation of products, i.e. a mass balances >100%. It is important to report any differences to 100% together with the mass balances because they convey crucial information for evaluation of the results.

For each of the three reference states of feedstock a separate mass balance, which derives different results and meanings from different calculative processes, is required. It follows that there can be an 'as received' balance², a 'dry' balance, a 'dry, ash-free' balance. Similar to the reference states, each different balance contains valuable information, and no one balance type is recommended over the other. Instead, each holds important complimentary information. Reporting the yield of product fractions on an 'as received' basis is advantageous for practical aspects such as economics, design of process/equipment and storage capacities, because it reports the actual product weight distribution to be expected. Reporting the 'dry' balance is useful to allow for a comparison between different studies as it eliminates the direct effect of moisture content of the feedstock. Similarly, the 'dry-ash-free' balance becomes important when feedstock of high ash content are used, to allow for a better comparison of solid product yield, which is directly affected by ash content (since the majority of this material is recovered as solids). The latter two approaches (dry and dry, ash-free) result in theoretical yields, but provide important

² In the context of a mass balance, 'as received' relates to the reference state of biomass as received by the process. This is an important difference over the 'as received' on site because there might be changes due to storage, pretreatment, and/ or additives. Some also refer to an 'as processed' balance for this case.

information on the fate of organic biomass compounds for a comparison between different feedstocks and process setups.

Since no recommendation can be given to use one type of balance over the other, it follows that product composition should always be stated in a way that the different balancing methods can be recalculated (i.e. by reporting the water and ash content of the feedstock and products). At the same time, it is of high importance to keep some sort of consistency within one balancing method, and in consequence with the reported yields. This is not trivial for biomass DTL and will be discussed in the following.

'Dry' balances require eliminating the water fed into the process through moisture content of the feedstock (also called physically mixed water). During DTL reactions water is being produced by chemical reactions and the amount of this reaction water can be determined by establishing 'dry' balances. However, one cannot attribute this reaction water to product fractions (e.g. bio-oil and uncondensed vapours, both of which typically contain a lot of water) which would be required for a consistent balance. Instead, it is recommended to report yields of all products on a dry basis and the reaction water as a separate fraction. This leads to the commonly reported 'organic liquid yield' which can be defined as follows:

$$yield_{OrgLiq} = \frac{\sum mass_{condensate,i} (1 - x_{condensate,i})}{mass_{feed,dry}}$$

Depending on the process, it is possible to get one or several condensates e.g. when the liquid product separates into organic and aqueous fractions or during fractionated condensation. That is why the water content of several condensate fractions is included in above definition, expressed as mass fraction $x_{condensate,i}$. This organic liquid yield allows to better compare different process conditions and setups since it eliminates the effects of water resulting from both the feedstock and the reaction on the reported liquid yield.

In case DTL feedstocks exhibit a significant ash content, further additional balances help to understand how product distribution is affected. Catalytically active ash compounds will affect organic products, and the weight of inorganic substances might significantly obscure how organic products are distributed. Reporting of 'dry, ash-free' balances can help to understand how the process is affected by ash compounds. Another possibility is to report elemental carbon balances, which *per se* exclude inorganic compounds (and water). They have the additional advantage of showing the fate of biogenic carbon, i.e., its distribution in the recovered product fractions. This is important for the evaluation of more complex conversion chains and/or Bioenergy with carbon capture and storage (BECCUS) concepts. Due to systematic challenges, carbon balances are an important tool to evaluate HTL experiments.

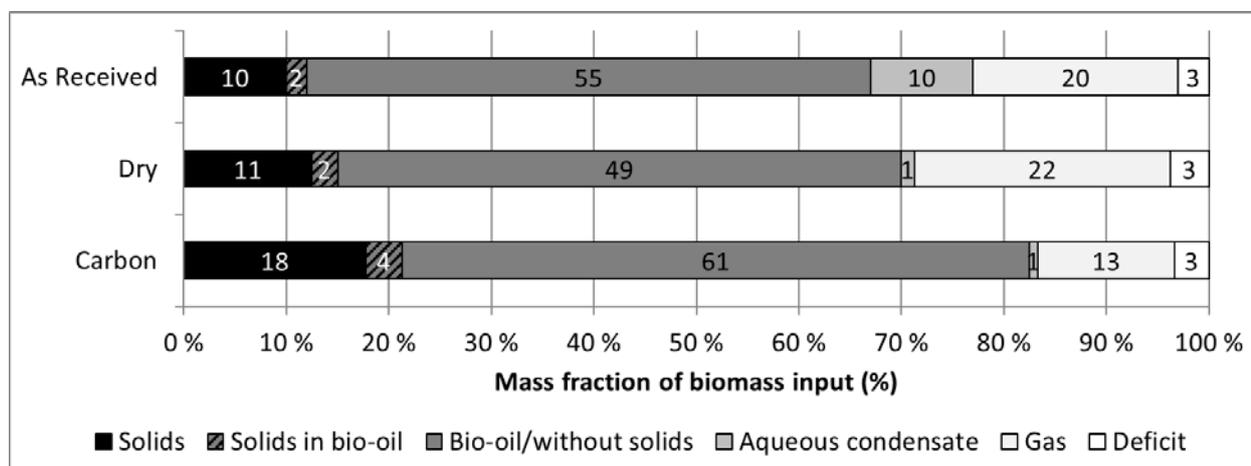


Figure 2: Results from different balances for the example of fast pyrolysis with fractionated condensation. In analogy, this can be conducted for HTL but with different shares of each product fraction. The deficit corresponds to the amount of mass not recovered, i.e. when the mass balance is less than 100%.

Best practice for fast pyrolysis

In addition to the more generic considerations for biomass DTL balances, there are some specific issues for fast pyrolysis processes. They primarily emerge based on extending biomass feedstocks to biogenic residues, which often contain significant amount of inorganic compounds. In most cases, this results in increased solids (which might end up in solid and liquid product) and reaction water yields (from ash catalytic effect). In terms of mass balancing it is important to report the amount of solids recovered with the liquid product because a high solids load in the fast pyrolysis bio-oil will obscure the liquid yield. Preferably, solids content is subtracted when calculating the liquid yield (see Figure 2). Also, high ash content biomass might demand an increase in condensation temperature to avoid phase separation, which leads to an increased amount of organic compounds to remain uncondensed or contribute to aqueous condensates. In order to properly compare these different conditions it is recommended to apply the concept of organic liquid yield and combine organic liquids obtained from different condensates. Naturally, condensation conditions, especially temperatures, are important to report. The analytical tests required to establish dry, dry ash-free and carbon balances are summarized in Table 1. Most of these tests are not established for online monitoring of fast pyrolysis products. Given the heterogeneous nature of many biogenic feedstocks, and the resulting heterogeneity of the products, it is highly recommended to enable multiple sampling over the course of one experiment in order to increase accuracy of the calculated balances.

Table 1: Listing of mandatory and additional analytical tests for fast pyrolysis feed and product phases in order to conduct standard mass balance procedures

Material	Mandatory analytical tests	Additional analytical tests
Feedstock	C content (CHNS analysis) Dry solids and ash content (drying/ashing gravimetric)	Complete elemental analysis (O analysis & ICP) Proximate analysis
Fast pyrolysis bio-oil	C content (CHNS analysis) Water content (Karl Fischer titration) Solids content	Complete elemental analysis (O analysis & ICP) Additional analyses according to ASTM D7544 or EN 16900 Molecular composition analysis (GC-MS)
Residual solids	C content (CHNS analysis) Dry solids and ash content (drying/ashing gravimetric)	Complete elemental analysis (O analysis & ICP)
Gases	C content (gas chromatography)	
Aqueous phase (if any)	Water content (Karl Fischer titration) Total organic carbon (TOC)	Molecular composition analysis (GC-MS)

Best practice for hydrothermal liquefaction

It is also important to consider specific aspects for the calculation of a hydrothermal liquefaction (HTL) mass balance before any activity is performed. A typical HTL experiment includes the preparation of a slurry with biomass, water, catalyst (in some cases) and/or other conditioning additives, and the processing of this slurry at the desired hydrothermal conditions (typically moderate temperatures and high pressure) for a given duration of time. HTL also produces solid, liquid and gaseous products; however there is always a liquid aqueous phase together with the main product biocrude, which is gravity separable after the solids are removed. Being able to perform a meaningful mass balance requires that these phases are, first of all, separated in an accurate manner. The different separation approaches applied may significantly influence the outcome of these measurements, therefore it is useful to refer to common guidelines. Here, we will illustrate some best practices, reflecting the best approaches adopted in the field.

DRY, ASH-FREE AND CARBON BALANCE

Differently from pyrolysis, HTL involves two co-reactants: biomass and water. It is more common in the field that dry or dry ash-free (daf) mass balances are reported, therefore not including water in the equation. This enables comparison between experiments with varying feedstock water content and avoids unfavourable propagation of uncertainties when water is included in the balance. Still, an “as received” mass balance is crucial to design a process. Since water is taking active part in the reactions, it can be expected that the overall closure of the mass balance (i.e. the sum of the amounts collected in the different phases) is higher than 100%. Moreover, it is intrinsically difficult to separate the organic products within the aqueous phase if solids are not removed (as is the case with batch experiments), in order to quantify the organics that are dissolved in water. Therefore, a common choice is that of determining the amount of biocrude, solids and gases and calculate the amount of products in the aqueous phase by difference. Consequently, any information on the actual closure of the mass balance is lost but one gets at least an idea of the distribution of the different product phases.

A more rigorous approach to observe the distribution of the products is to determine the carbon balance, therefore tracking the amount of carbon contained in each phase. In this case, the amount of carbon in the aqueous phase can be determined via total organic carbon (TOC).

MASS BALANCE FOR BATCH HTL TESTS

Typical batch experiments are carried out in units like autoclaves where a certain amount of reacting mixture (biomass/water slurry) is placed in a reactor, which is sealed and brought to reaction conditions. After the desired time is elapsed, the unit is quenched and products can be collected.

Mass balance is normally conducted on dry, ash-free base (daf). This requires that the biomass feedstock is fully characterized to determine moisture content and ash content. This being known, the amount of biomass fed to the reactor is m_{bio} . While batch experiments require solvent extraction on the back end to separate biocrude, which has the possibility of influencing the aqueous/oil separation and recorded biocrude yield.

After the batch test is completed, products are recovered. The first phase to be collected is the gas phase. Its quantification can follow different methodologies. A common approach is that of referring to the differential pressure between the end (P_2) and start (P_1) of the reaction and using the gas law to determine the gas volume at atmospheric conditions:

$$V_{gas,atm} = \frac{(P_2 - P_1)}{P_{atm}} V_{gas,react}$$

Where $V_{gas,react}$ represents the volume of the reactor occupied by gases, which can be assumed as the difference between the reactor volume and the volume of the loaded slurry. As an alternative, gas volume

could be also directly measured by venting process gases through a gas measurer or in a water-displacement column. In order to obtain the mass of gas, its composition needs to be determined by a gas analyzer, typically a GC with a TCD. Once the gas composition is known, the density of the mixture ($\rho_{gas,atm}$) can be determined as the weighted average of the densities of the different components. Alternatively, is possible to obtain a reasonable estimate by assuming that the whole gas is composed by CO_2 if a high precision is not needed. This assumption is more accurate the lower HTL temperature is.

$$m_{gas} = V_{gas,atm} \times \rho_{gas,atm}$$

Another approach to directly quantify the gas yield is that of weighing the reactor before and after venting the gases and recording the weight difference. However, this approach is only viable for relatively small units (e.g. micro-batch).

Once gases are vented, the reactor will typically display some free-flowing liquids and a bottom product represented by a mixture of biocrude and char (oil sand). Recovering the products from the reactor will involve the utilization of one or more solvent. It is indeed of utmost importance that all products are carefully recovered, especially when processes with very reduced amounts of sample are involved.

The first operation involves the separation of most of the aqueous phase, which will be present as a free-flowing liquid. This can be simply obtained by pouring the content of the vessel in a collection flask. Whatever remains in the reactors after pouring the aqueous phase includes biocrude, further aqueous phase and solids, which are intimately mixed. In order to collect these products, the reactor should be washed with a proper solvent. There could be different strategies to do that. In this technical note we recommend to utilize acetone in this step. Acetone is a polar solvent with a relatively low boiling point, which allows an easy recovery by means of evaporation. Compared to other solvents, it presents less hazards for human health and its disposal can be conducted in a simpler way with respect to, for example, halogenated solvents.

Upon mixing with acetone, a homogeneous liquid phase including biocrude and water will be formed, with low viscosity. Washing the reactor several times will allow removing all reaction products. The obtained liquid must therefore be filtrated, using common filtration apparatus (e.g. paper filter and an Erlenmeyer vacuum flask), in order to separate the solid phase (char). The quantification of the yield of char should be obtained by drying the filter containing the solids in an oven at 105 °C until constant weight is reached (typically overnight), and measuring the weight afterwards. Acetone should now be removed from the filtered solution by means of evaporation. A common rotary evaporator can be utilized to this purpose,

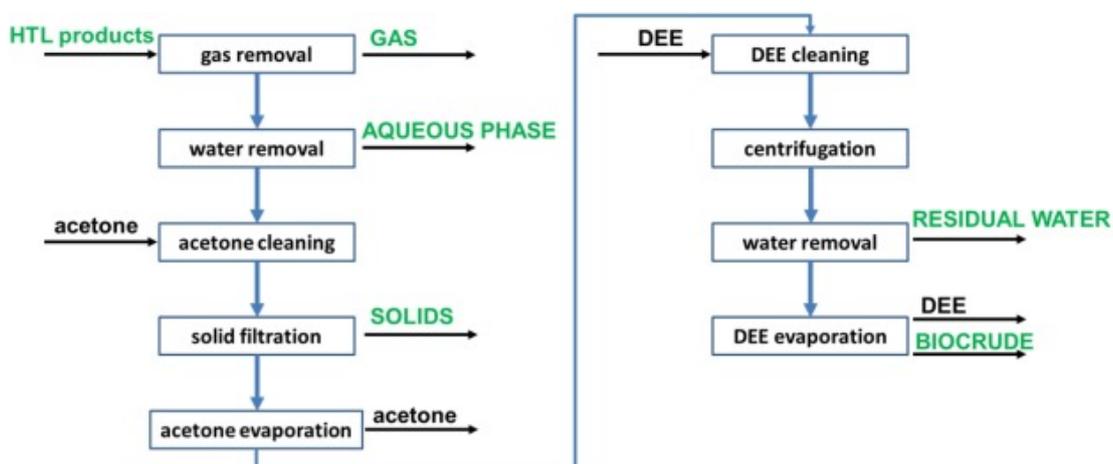


Figure 3: Procedure for the recovery of reaction products during batch experiments³.

³ Conti, F. et al. "Valorization of Animal and Human Wastes through HTL for Biocrude Production and Simultaneous Recovery of Nutrients." Energy Conversion and Management 216 (2020) 112925.

transferring the solution to a round bottom flask and adopting a temperature of 60 °C and operating a slight vacuum (640 kPa).

After this operation, two immiscible liquid phases will be observed: a biocrude phase and a small amount of residual aqueous phase. Although they could be, in principle, separated only by gravity, this operation is typically not straightforward, especially due to the small amount of aqueous phase and the difficulty to operate with the round bottom flask used for the evaporation. Therefore, it is convenient to add a small amount of a non-polar solvent, such as diethylether (DEE) or dichloromethane (DCM). These solvents are immiscible with water and therefore two immiscible layers will be obtained. In the case of DEE, there will be an upper layer of solvent+biocrude, with a lower layer of aqueous phase. In the case of DCM, the position of the two layers is inverted. In both cases, the two layers can be separated gravimetrically, for example by using a separation funnel. When small scale tests are concerned, the solvent can also be mixed in a plastic tube and centrifuged to speed up phase separation. Then the phases can be collected by means of a syringe with a needle. In both cases, the solvent must be removed by evaporation, which can be achieved again in a rotary evaporator or other similar devices working under vacuum.

As explained previously, the amount of collected aqueous phase does not enter directly into the mass balance. Nevertheless, it could be important to know the amount of aqueous phase produced, e.g. to elaborate a carbon balance. In this case, the amount of aqueous phase is represented by the sum of the free-flowing liquid plus the amount collected in the last step of separation.

INFLUENCE OF SOLVENTS FOR OIL RECOVERY

Especially for the case of batch reactions, the procedure to recover the different reaction products from HTL strongly relies on the usage of solvents. They are indeed necessary to transfer reaction products from the reactor to the different collection vessels and to allow their separation and quantification. The usage of solvents during the collection of the reaction products is something quite delicate, which must be carefully considered, as it can potentially alter the distribution of the products and thus their chemical composition. It is therefore important that the product collection procedure is always carefully described and that comparisons are done between products obtained with the same methodology.

There are several studies in the open literature documenting the effect of the most common solvents which have been used in HTL experiments. A first main difference resides in the point at which the solvent is introduced within the product collection process. This was explored in a study by Xu and Savage, where DCM was either mixed with the whole products in the reactor, or only utilized to extract specific phases⁴. This study highlighted that, when the solvent is put into contact with all phases, the amount of biocrude that is recovered is higher than the case where no solvent is utilized. This happens because the solvent extracts an aliquot of organics from the aqueous phase itself, which then contribute to the overall production of biocrude. A conclusion that can be drawn from this study is that, for a more realistic estimate of biocrude yields, it is important to avoid the solvent extraction of products from the aqueous phase. A possible solution is to separate the aqueous phase before starting the solvent collection of the product (as explained above).

Other studies have instead focused on the effect of the different solvents utilized in the separation train. Once again, these studies generally consider the extraction of all phases simultaneously, which is often adopted for sake of simplicity. The reported results of these comparisons did not lead to the same conclusions, and their output seems to be strongly related with the kind of biomass feedstock. For instance, comparing DCM, acetone and toluene for the extraction of HTL products from algae leads to the conclusion that extraction with non-polar solvents gives the highest yields, though with lower carbon content⁵. In another case it was concluded that results differ based on the type of feedstock, with

⁴ Xu, D. and Savage, P. E. "Characterization of Biocrudes Recovered with and without Solvent after Hydrothermal Liquefaction of Algae." *Algal Research* 6 (2014) 1-7

⁵ Valdez, P. J. et al. "Characterization of Product Fractions from Hydrothermal Liquefaction of *Nannochloropsis* Sp. and the Influence of Solvents." *Energy & Fuels* 25 (2011) 3235-43.

acetone giving the highest yields for high ash-containing, DCM for high carbohydrate-containing and toluene for high protein-containing feedstock⁶.

In any case, this intrinsic variability in the obtained results is a further argument that discourages the utilization of solvent for the simultaneous extraction of all product phases. Referring to the procedure described in the previous section, it can be noticed that the solvent is introduced only after the separation of a large part of the aqueous phase has happened in the first step. This is actually thought in order to avoid that the solvent extracts part of the organic compounds from the aqueous phase, which will be then transferred to the biocrude phase, leading to an overestimation error. The adopted procedure does not remove this possibility, but it greatly reduces it, by exposing only a minimal amount of aqueous phase to the solvent extraction.

CONTINUOUS HTL PROCESS BALANCES

The majority of published HTL studies apply a batch reactor process, with subsequent organic solvent extraction to separate the biocrude from the aqueous phase products (see above). In order for HTL to be adopted at a commercial scale, a continuous flow reactor system, capable of isolating the biocrude via gravitational separation, will need to be utilized. Batch HTL studies are common due to the far lower complexity and cost of the reactor systems required. Differences between batch and continuous HTL oil separation, further necessitate the need for strict mass balance calculations.

Preparing a mass balance for a continuous flow HTL process is more complicated than that of an equivalent batch process. Batch experiments benefit from the simplicity of being a closed system. In the case of a continuous flow process, not only must the feed composition and rate of addition be determined and maintained, but the production rate of each of the 4 product phases must also be monitored and determined, and periodically sampled for analysis. It is recommended to continuously collect both the liquid product stream (biocrude and aqueous phase) and the residual solids, throughout the entire duration of an HTL experiment. In addition to this, liquid product samples (~1L) could be obtained from the reactor system at pre-determined sampling times during steady-state conditions. This procedure allows for multiple large samples to be obtained throughout a single campaign, improving the accuracy of the analyses and the subsequent mass balance. The sampling period used can then be converted to a fraction of the entire runtime, to determine the quantity of residual solids and gases produced during the sample collection period. Throughout the run, the composition of the gas mixture produced should be continuously analysed via gas chromatography, allowing for determination of the molecular and associated elemental composition. The production rate of the gas mixture should be determined using an online wet test meter.

In a continuous flow HTL reactor, the feed is pumped into the reactor as a slurry. To maximise biocrude production efficiency, the carbon content of this slurry should be high, however this is limited by the physical pumpability of high-solids mixtures. The result is that a feedstock will likely need dilution or concentration from the as-received state to achieve the ideal solids content. It is of particular importance to reflect this in any mass balance. In contrast to batch HTL experiments, the mass balance of continuous flow HTL experiments can also be presented on an as received basis. By determining the mass balance in this way, the results are presented in terms of the actual feed slurry processed, instead of the more theoretical dry, ash-free basis. Such data is useful for comparing the volume of various materials to be processed, and how this relates to the throughput and efficiency of a proposed HTL refinery system.

In a best case scenario, the yield results for each product stream are reported in 4 different ways to compare mass balance data obtained from HTL of a range of feedstocks: The minimum analytical data required in order to present mass balances on an as-received, dry, dry ash-free and carbon basis is: solids and ash content of the feed slurry, residual solids, aqueous phase, and biocrude, as well as the carbon content of the feed slurry and each of the product phases. In the case of the biocrude product, the water

⁶ Watson, J. et al. "Effects of the Extraction Solvents in Hydrothermal Liquefaction Processes: Biocrude Oil Quality and Energy Conversion Efficiency." *Energy* 167 (2019): 189-97.

Table 2: Listing of mandatory and additional analytical tests for HTL feed and product phases in order to conduct standard mass balance procedures

Material	Mandatory analytical tests	Additional analytical tests
Feedstock	C content (CHNS analysis) Dry solids and ash content (drying/ashing gravimetric)	Complete elemental analysis (O analysis & ICP) Density and viscosity Proximate analysis pH, COD, ammonium content
Biocrude	C content (CHNS analysis) Water content (Karl Fischer titration) Ash content (ashing gravimetric)	Complete elemental analysis (O analysis & ICP) Density and viscosity Filterable solids Higher heating value Total acid number
Residual solids	C content (CHNS analysis) Dry solids and ash content (drying/ashing gravimetric)	Complete elemental analysis (O analysis & ICP)
Aqueous phase	C content (CHNS analysis) Dry solids and ash content (drying/ashing gravimetric)	Complete elemental analysis (ICP, O determined by difference) Molecular composition analysis (HPLC) pH, COD, ammonium content Chloride, sulfate and phosphate content (IC)
Gases	C content (gas chromatography)	

content is determined via Karl Fischer titration. A range of further analytical tests are also generally performed in order to produce a more comprehensive experimental balance (e.g. balancing elements other than C), as well as a compositional profile of each product phase. A listing of the mandatory and additional analytical testing for each material is provided in Table 2.

An important consideration for ensuring a maximum accuracy mass balance is to directly measure properties wherever possible and not rely on derived values. It is also common practice to sample the feed and product phases at several points throughout an HTL experiment, to ensure that the results are consistent. If for example the solids content of the feed slurry is observed to shift throughout the process (e.g. from settling/dewatering in the feed tank), this can be accounted for in the mass balance, provided that the change is measured via periodic samples throughout the experiment.



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