THE ROLE OF CARBOHYDRATES AND LIPIDS IN HYDROTHERMAL CARBONISATION

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ABSTRACT: This paper presents the hydrothermal carbonization (HTC) of a wide variety of wet resources such as microalgae, sewage sludge and food wastes. HTC was applied to these resources to produce a bio-coal (hydrochar) that can be dried more effectively, has a superior heating value and is suitable for gasification. Gasifiers have constraints on the quality of the feedstock. There are constraints on ash content, heating value, fixed carbon and volatile matter content. The properties of the resources are compared to the properties of the hydrochar, in particular the fixed carbon content. The results show insights in the conversion and the calculation of product yields.
Carbohydrate content is an important parameter in the carbonisation process. A large proportion is hydrolysed and dissolved in the aqueous phase together with the proteins. High lipid content resources, low hydrocarbon content, also favours hydrochar yield, by associating the insoluble lipids and the solids. High yields from lipid rich resources show however a very low fixed carbon content in the hydrochar, making these hydrochars unsuitable for gasification. This work shows how the biochemical composition of the resources are a determining factor in the quality and yield of the hydrochars, more so than temperature and reaction time.
Keywords: Hydrothermal carbonisation; Hydrochar; Fixed carbon; Sewage sludge; Algae; Biochemical composition

1 INTRODUCTION

Many resources are available in large quantities but not directly suitable for direct valorisation without significant pre-processing. This is the case for gasification of algae, sewage sludge and many food wastes. Gasification needs a dried form of biomass and produces a syngas (or producer gas) suitable for use in fuel synthesis processes and fuel cells. Hydrothermal carbonisation (HTC) increases the energy density of the resources (much like torrefaction) and facilitates dehydration and drying. It improves generally the gasification properties of the resources. The EU funded project Niagara [1] studies the full chain from algae cultivation, hydrothermal carbonisation, gasification and valorisation of the synthesis gas in fuel cells. One of the objectives of this project is to produce a high quality hydrochar with optimal yields from sewage sludge and algae cultivated on waste water for this purpose.

The body of knowledge in the literature on HTC is quite large but most authors focus on one specific property of the products. Generally, not much data is presented on how the resource composition [2] influences the final result in terms of yield and hydrochar quality. This work presents a complete compositional analysis of the resources together with their fixed carbon and volatile matter content. The products are also extensively analysed evaluating a large number of product qualities.

These detailed analyses are necessary to be able to evaluate the products for suitability in a specific gasifier. Not all resources are suitable for gasification and HTC does not allow all resources to be compliant. It also allows the project to gather an extensive experimental database to train machine learning models. These models are integrated in a large modelling platform at EPFL

This study concentrates on the HTC of a wide variety of resources, including algae cultivated on waste water as part this project. These resources are subject to hydrothermal conditions, between 200 and 300 °C. The hydrochar is extensively analysed and compared to the constraints of the gasifier to be used in the project, the ARIANE gasifier at Gazotech (France) [3]. The collected data include conversion yields and product properties. The data is compiled into a large database that serves as a basis for a machine learning model. This model predicts the results from the biomass composition and properties and the operating conditions. This paper concentrates on the influence of the biochemical composition, and in particular the carbohydrate and lipid content of the resource on the hydrochar yield.

This work will contribute to the body of knowledge on HTC and present the way forward to analyse studies on HTC. The machine learning models of HTC and the other process bricks will allow efficient modelling of the overall process of the Niagara process chain.

2 EXPERIMENTAL

2.1 Resources

A wide variety of resources was converted in this study, including micro-algae, (sewage-) sludges, food wastes and some dry resources as pruning waste. The objective of this work is to maximise hydrochar yield and quality. The resources in this project are presented in Table I.

Table I: Overview of biomass resources

Biomass	Details	Humidity (%)
CS4	Chlorella sorokiniana	71.5 %
UAL1	Algae from fertilizer	79.2 %
UAL2	Algae from fertilizer	74.7 %
UAL3	Algae from urban waste water	88.9 %
UAL4	Algae from pig slurry	85.1 %
Fango 1	Slaughterhouse - Sewage sludge	70.7 %
Fango 2	Meat processing - Sewage sludge	80.6 %
ISW3	Industrial Sludge snacks	92.8 %
ISW4	Industrial Sludge soda	85.5 %
NDUSW	Non digested urban sludge	98.2 %
CDUSW	Co-digestate urban sludge and waste	79.5 %
OFMSW	Organic Fraction Municipal Solid Waste	88.5 %
CVx	Chlorella vulgaris	69-81 %

The focus of the resources is on low lipid resources especially in the cultivation of the algae. Two sludges from the meat industry have been included that contain significant amounts of lipids. The resources were supplied by the project partners. The University of Almeria, Spain, produced algae. A natural consortium dominated by *Scenedesmus almeriensis* grown in open raceways on fertiliser, pig waste and urban waste water. CEA Cadarache, France, cultivated *Chlorella sorokiniana* and *Chlorella vulgaris* in photo-bioreactors. Facsa, Spain, supplied sludges and food waste. The sludges vary from digested sludges, municipal sludges to slaughterhouse sludges. The food waste is the product of mechanical separation from municipal solid waste. Two experiments were performed with cellulose. Pruning waste was procured from CEA Grenoble, France. Some experiments were performed with pure cellulose.

2.2 Resource composition

The biochemical composition of the resources is estimated from simplified analyses. The inorganic content is approximated by the ash produced after combustion at 550 °C (ISO 18122). The lipid content follows the animal foodstuff norm (ISO 6492), hydrolysis and extraction with a nonpolar solvent (n-heptane in our case). Proteins are estimated by the nitrogen content from the elemental analysis multiplied by a factor. This factor is 5.04 for algae and 6.25 for other resources. Carbohydrate content is estimated by difference. This biochemical composition is a very simplified estimation but it has the advantage of being repeatable and can be performed on a great number of samples.

The dry ash free compositions of the resources are presented in ternary form in Figure 1.

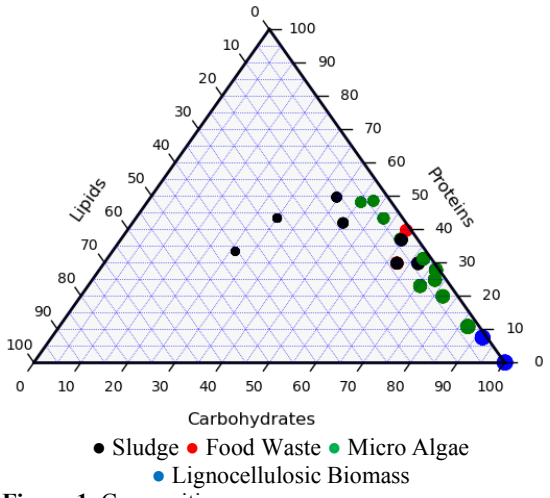

Figure 1: Composition resources

2.3 Hydrothermal Experiments

The resources have been converted in a 600 ml batch reactor (Parr Instrument Company, USA). For a typical experiment a mixture of 300 ml is prepared and placed in the reactor. After inerting and leak testing the reactor is heated to the desired temperature in 15 to 20 minutes. Experimental conditions vary from 200 to 300 °C and the holding times were between 30 minutes and 4 hours. After the holding time, the reactor is cooled in about 20 minutes.

After the experiment, the gas is recovered and analysed by micro chromatography (Inficon Fusion, Switserland). With the initial and final pressures and temperatures and the gas composition, the gas yield is calculated.

After opening of the reactor, the products are separated by filtering and are weighed. The total organic and inorganic carbon and nitrogen is quantified (Skalar Formacs TOC/TN analyser, the Netherlands).

The hydrochar is analysed by elemental analysis (Vario El Cube from Elementar, Germany), thermogravimetry (Setsys), ash content by combustion (550 °C and 815 °C) and by solvent extraction with ethyl-acetate and acetone. The fraction volatile matter and fixed carbon are calculated from the thermogravimetry results.

3 RESULTS AND DISCUSSION

The experiments on the 19 different resources yielded a lot of experimental results that are presented in this section. The results are mostly presented in a graphical form for all resources, all resources and conditions confounded. The temperature or holding times are true process parameters that can be varied, the composition is however an observed variable. Varying the fraction of carbohydrates means varying the resource, including other compositional and physical parameters. This means that the variable “carbohydrates” is somewhat artificial. While this way of presenting the data gives interesting insights to the importance of the composition and its role in the hydrothermal carbonisation process, it cannot be interpreted as the carbohydrate composition changes independently in one specific resource.

3.1 Hydrochar yields

The hydrochar yields are presented in Figure 2. The presented data include different hydrothermal conditions and resources. The objective is to generate data across all of this data to generate an accurate machine learning model. The constraints of the ARIANE fixed bed gasifier are: ash content under 10 wt%, fixed carbon content above 16 wt%, volatile matter content above 70 wt%, and the lower Heating Value (LHV) above 15 MJ/kg dry matter.

The hydrochar yield strongly depends on the biochemical composition as well as the temperature. Other parameters such as the holding time and the dry matter content of the solution also play a role, but to a minor extend. We observe a general trend that the hydrochar yield strongly depends on the carbohydrate yield and that it goes through a global minimum. The high values are at the extreme of the graph, low carbohydrate and high carbohydrate content.

Hydrochar is formed by various mechanisms. Primary char is formed by dehydration and decarboxylation of the biopolymers in the resources. Secondary char is formed by polymerisation reactions [4], Maillard reactions and others. Lipids that are present in the resources are only marginally converted under these conditions. Two of the sludges have a very high lipid content. After cooling they are fixed to the formed char and recovered as hydrochar [5]. This last phenomenon explains that for low carbohydrate, high lipids, resources, the hydrochar yield is high.

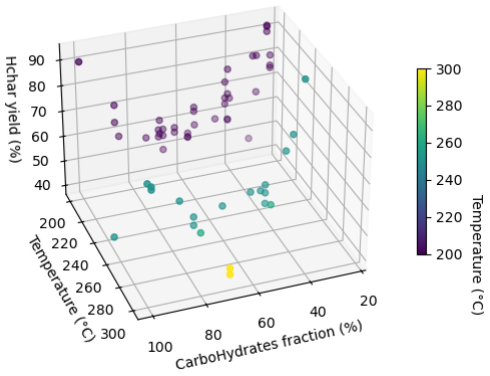

Figure 2: Hydrochar yields

It is normal that the trend in figure 2 displays some dispersion. This graph includes all resources and two parameters are too few to completely describe the experimental variables and characterise the resources. There is some compositional variation with the *Chlorella vulgaris* samples, grown in different reactors over a long period of time. Figure 3 presents the same data for different *Chlorella vulgaris* samples, all experiments with holding times of 30 minutes.

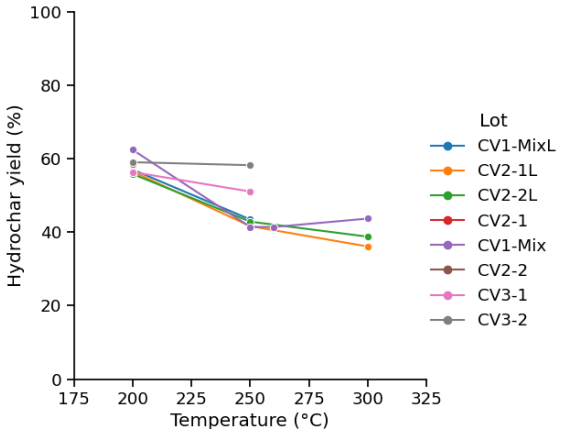

Figure 3: Hydrochar yields with Chlorella vulgaris

Increasing the temperature generally lowers the hydrochar yield favouring the transfer to the aqueous phase.

3.1 Aqueous phases

Most resources are slightly acidic (food waste in particular due to some natural fermentation), or nearly neutral (digestate and algae) with a reaction mixture pH in the 4-6 range. The pH of the aqueous phase after the transformation depends on the carbohydrate content of the resources varying from 8 to 6 for protein rich resources to 3 for carbohydrate rich resources. Protein rich resources often produce basic aqueous phases due to ammonia that is produced during the deamination of amino acids. Figure 4 gives the acidity of the aqueous phase for all experiments as a function of the carbohydrate content only. There is a fair amount of scatter as more than one parameter intervenes, but the global trend is clear. For other parameters such as protein and lipid content, or reaction temperature do not produce a clear trend.

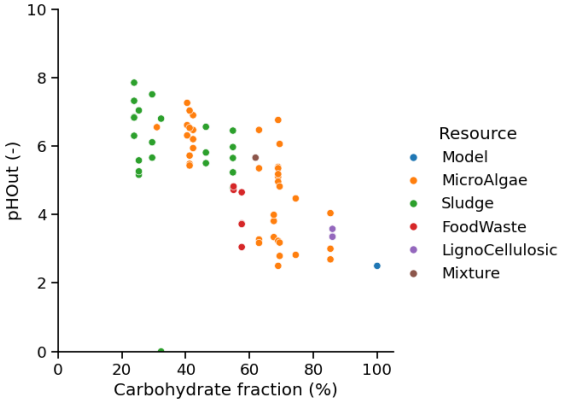

Figure 4: pH aqueous phase after reaction

Protein rich resources such as algae and sludges produce relatively high pH aqueous phases. Cellulose and pruning waste produce very acidic aqueous phases.

3.2 Fixed carbon

The fixed carbon and volatile matter content of the resources and the hydrochar were evaluated by thermogravimetry. The fixed carbon content (of the resource and its hydrochar) is globally proportional to the carbohydrate content of the resource. The gasifier needs a minimum of 16 % fixed carbon. The results show that only few resources satisfy this constraint as shown in Figure 5.

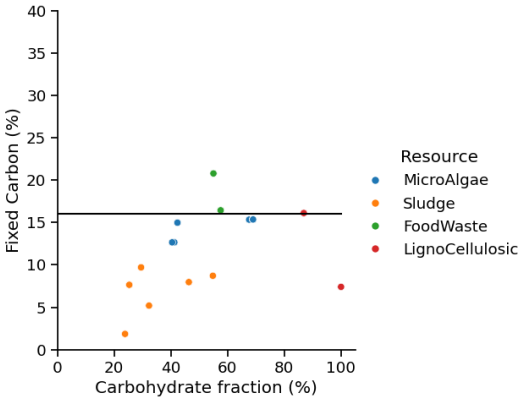

Figure 5: Fixed carbon in the resources

After hydrothermal carbonisation, most samples, except for those from sludges, have a sufficiently high fixed carbon content. The sludges have a low fixed carbon content due to the high ash content and the high lipid content for some.

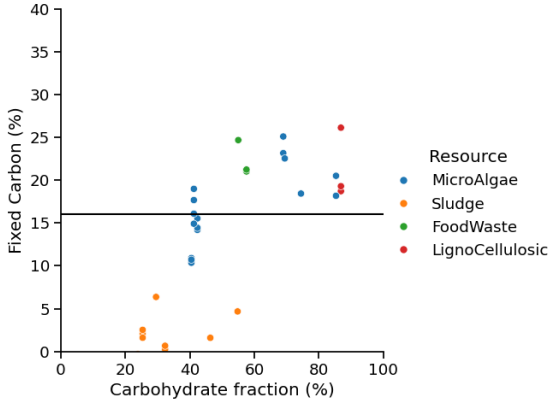

Figure 6: Fixed carbon in the hydrochar

The volatile fraction in the resources is generally compliant to the requirements of the gasifier. HTC lowers the volatile matter content of the resources. With some exceptions, most hydrochars remain suitable for gasification, even though the volatile matter content is sometimes low.

3.3 Elemental Analysis

The elemental analysis shows generally an increase in carbon content of the hydrochar. Many deoxygenation reactions take place during carbonisation. Dehydration reactions remove oxygen with hydrogen to form water. Decarboxylation reactions remove oxygen in carboxyl groups to form CO_2. The van Krevelen diagram in Figure 7 shows the evolution of three of the project resources with increasingly severe conditions. Each resource takes a different pathway in the van Krevelen diagram. In this diagram, the black symbols represent the raw resource, blue symbols represent experiments at 200 °C and 30 minutes. Magenta symbols represent 200 °C and 240 minutes. Red symbols 250 °C and 30 minutes. The arrows are freely drawn to indicate trends.

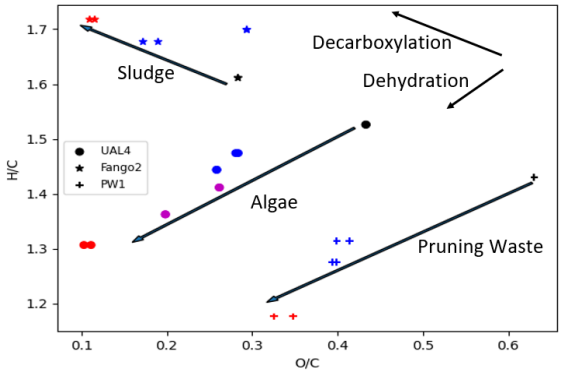

Figure 7: Van Krevelen diagram for three resources

From the van Krevelen diagram we observe that the algae UAL4 (*Scenedesmus almeriensis* grown on pig slurry) and the pruning waste reduce the O/C and the H/C ratios at the same time. Both dehydration and decarboxylation reactions take place. The Fango2 (sludge from a slaughterhouse) resource is rich in lipids and shows a very different behaviour. Decarboxylation reactions dominate and the little hydrogen is withdrawn from the resource via dehydration reactions, the H/C ratio actually increases. The explanation probably resides in the fatty acids that lose their carboxylic acid groups but the aliphatic chains are relatively stable under these conditions.

This partially explains why the fixed carbon content of sludges does not increase significantly during HTC as shown in Figure 6. It is likely that this trend does not continue at high temperatures and that at some point the H/C ratio also decreases for these lipid rich sludges.

3.4 Heating value of the hydrochars

An important parameter of the feed to a gasifier is the heating value of the resource. Figure 8 presents the higher heating value of all hydrochars as a function of the higher heating value (HHV) of the initial resource. Mostly, the HHV of the hydrochar is higher than that of the original resource. There are a few exceptions. High ash resources, digestate and one batch of algae, actually lower the HHV value during the hydrothermal carbonisation process. This is due to the fact that the ash remains preferentially in the hydrochar and there is some loss of organic material to the aqueous phase.

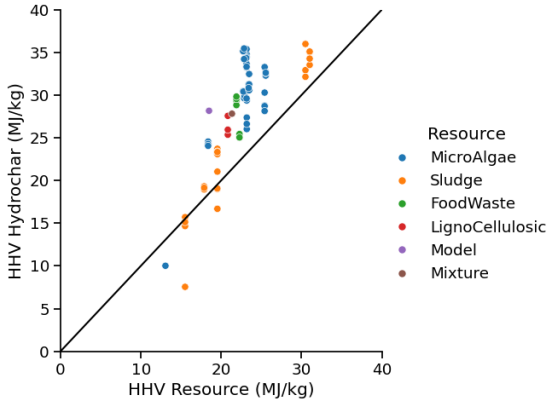

Figure 8: HHV hydrochars and resources

In Figure 8, we observe clusters of datapoints, vertically aligned data points, corresponding to different experiments on a same resource. Figure 9 presents the same data with the coloration of the points proportional to the temperature in the hydrothermal experiment. The highest datapoint for each vertical line generally corresponds to the highest temperature. Showing that the temperature is an important process parameter to improve the heating value of the hydrochar.

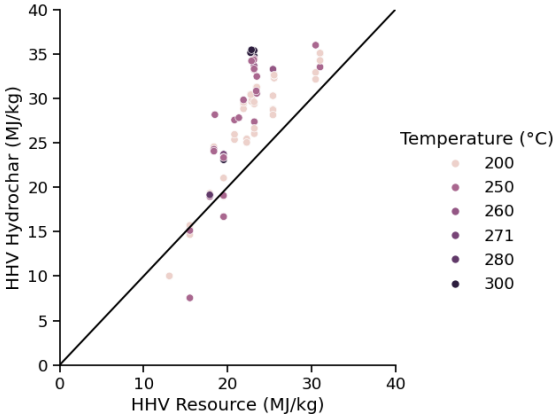

Figure 9: HHV hydrochars and resources with temperatures

3.5 Discussion

The biochemical composition, and in particular the carbohydrate and lipid contents of a resource, is an important parameter in hydrothermal carbonisation. The hydrochar yield and quality are strongly affected by the composition, even more than by the temperature.

The presented experimental data clearly indicate that the chemistry of the hydrothermal carbonisation process is complex but has a lot in common with other hydrothermal processes. Protein rich resources produce high pH aqueous phases indicating the release of basic ammonia [6]. Carbohydrates and proteins both produce carboxylic acids in their thermal degradation.

The results show that low carbohydrate content resources with a high lipid content produce hydrochar with little fixed carbon, confirming that the volatile lipids are condensed in the hydrochar. Lipids are not very reactive at low temperatures and tend to stay on the hydrochar. The

ash concentrates in the hydrochar making hydrothermal carbonisation unfavourable for high ash resources.

4 CONCLUSIONS

Hydrothermal carbonisation is an interesting option to increase the heating value and fixed carbon content to improve the suitability of resource for fixed bed gasification. Most hydrochars satisfy the quality requirements imposed by fixed bed gasifiers, even though this remains problematic for sludges.

Resource analysis is vital for the understanding of the results of hydrothermal processes. The advantage of a simplified resource analysis is that it can be applied rapidly on a large number of resources. This type of analysis is sufficient to understand and predict the hydrochar properties.

The hydrochar yield goes through a minimum at intermediate carbohydrate and protein content. Proteins are easily dissolved in water in hydrothermal conditions and carbohydrates produce small organics, often acid, molecules under these conditions. Condensation reactions do not seem to produce sufficient hydrochar to compensate for the losses to the aqueous phase.

Lipids are volatile and the requirement of a minimum fixed carbon content makes high lipid content resources problematic. It is therefore important to evaluate all the properties of the hydrochar and take these into account in optimising hydrothermal conditions. Other properties to be taken into account are higher heating value and ash content.

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