Hydrothermal liquefaction of wet biomass in batch reactors: critical assessment of the role of operating parameters as a function of the nature of the feedstock

Claudia Prestigiacomo[a], Onofrio Scialdone[a], Alessandro Galia[a,*]

[a]Dipartimento di Ingegneria, Sezione Chimica Ambientale Biomedica Idraulica e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy.

Corresponding author

E-mail address: alessandro.galia@unipa.it (A. Galia)

Abstract

A scientometric analysis of articles published from 1986 to 2021 on batch hydrothermal liquefaction of microalgae, macroalgae, lignocellulosic biomass, sewage sludge (SS) and organic wastes was performed. We found that biocrude (BC) yield can be correlated with the kinetic severity factor (KSF) and the level of correlation strongly increased when heating rates of the reactor higher than 25°C/min were adopted. H/C and O/C of BC obtained from microalgae decreased with KSF while ER exhibited a maximum at about 8-10 of KSF. Also with fast heated SS the ER and H/C improved and O/C decreased with KSF but values over 10 were not studied. For other biomasses elemental composition and ER data are more limited, obtained with slow heating rate and with uncertain correlation with KSF. From this analysis it seems interesting to assess more systematically the role of KSF and heating rate with not algal biomass.

Keywords

Hydrothermal liquefaction, biofeedstocks, biomass, kinetic severity factor, biocrude, critical review

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1. Introduction

The hydrothermal treatments of wet organic matrices (biofeedstocks) are part of a larger cluster of biorefinery processes. If water is used as the solvent, these processes could represent an innovative method for converting the entire wet biofeedstock (no need for fractionation) into solid, liquid and/or gaseous fuels or fuel precursors. Furthermore, to carry out these processes, it is not necessary the energy intensive drying of the biofeedstock since water constitutes the solvent and so, wet matrixes are treated in their native state. The main scope of the hydrothermal process technologies is to generate a product with a higher energy density than the starting organic matrix mainly by increasing the H/C ratio and by removal of oxygen. The products of the process depend on the adopted temperature: below 200°C char is mainly produced and the process is called hydrothermal carbonization (HTC); between 200°C and 400°C the HTL takes place to produce as target product a fuel precursor called biocrude (BC). Above 400°C instead, hydrothermal gasification (HTG) occurs, which predominantly produces syngas [1]. The char produced from HTC can be co-fired with coal or used as a biochar for soil amendment [2], the BC from HTL can be upgraded to a variety of fuels while the syngas from HTG can be used for combustion or converted to hydrocarbons by either biological or catalytic processing e.g. Fisher Tropsch synthesis. Many reviews in the last years reported about sustainable routes for biofuel and bioenergy production [3–15]. These reviews were focused on the description of the applicative feasibility of several technologies and provided knowledge of the current status and perspectives on the field of biofuels production. The publications on HTL of wet biofeedstocks are complex to analyze and synthesize owing to the multiphasic nature of the reaction system, the variability of the biofeedstock, of the adopted experimental apparatuses, of the operative conditions and of the separation procedures [16]. Dimitriadis et al. [16] published in 2017 a critical review with the purpose to summarize the main published research findings on HTL of different biofeedstocks. They concluded that the variation in different type and composition of the feed, of the reaction conditions and of the catalysts studied to improve the BC quality, result in a wide and fragmentary spectrum of knowledge. From 2017 to 2020, HTL has undergone an unexpected increase in the number of publications that further contributed to the fragmentation of knowledge on the subject. Many efforts were done to synthesize results obtained in the study of hydrothermal processes [17–19] and most of the reviews recently published on HTL were focused on the analysis of specific portions of the research field, i.e., for example, the analysis of influence of the feedstock in the integration of HTL with biological processing [20], the review on the potential application of HTL to micro- and macro-algae [21–25] or to lignocellulosic biomass [26], the analysis of hydrothermal co-liquefaction of the feedstock bioconstituents [27], a review on the comparison between HTL and pyrolysis of waste tire [28] or to analyze the accumulation of nitrogen in the BC produced from HTL of protein rich-feedstock [29]. Only few reviews were focused on the systematic analysis of the influence of operative parameters on yields and quality of the products. Yang et al. [30] provided a summary of the current developments on HTL in term of reaction mechanism and influencing factors analyzing the literature through a bibliometric analysis. Basar et al. [31]studied the effect of operative parameters on productivity and quality of BC with special emphasis on continuous reaction system. Gao et al.[32], performed this study but limited their analysis to the literature on HTL assisted by microwaves. Lu et al. [33] grouped the existing biomass into six lumps to analyze the correlation between the biochemical composition and the product distribution. Their analysis involved the elemental distribution in the products and the transformation of organic and inorganic elements. Sharma et al. [34], covered the field of HTL of microalgae at different reaction temperatures and with different catalysts to highlight their effect on the BC yield and quality.

In the work herein we considered the relevant publications in HTL of different biofeedstocks from 1986 to 2020 to extract from the variegated cluster of published results some general rules that can be a reference to design new research activities on HTL in the perspective of its industrial application. Reported yields were critically analyzed as a function of the kinetic severity factor of the process focusing attention on the HTL of biomasses in pure water solvent to find correlation between operative parameters and performances of the process.

1.1. Hydrothermal liquefaction (HTL) of wet biofeedstock

HTL is considered an interesting process to produce a liquid fuel precursor [16,35] by hydrolytic cleavage of the bio-constituents of a wet biofeedstock and by the reforming of the depolymerization products to simple organic molecules. The heated and compressed liquid water, in conditions close to the critical point (T_c = 373.95°C, P_c = 220.64 bar) changes its chemical-physical properties. When water is heated along the liquid-vapor saturation curve, its dielectric constant decreases due to the decrease in the density of hydrogen bonds among its molecules [1]. The lower dielectric constant allows the hot and compressed water to solvate organic molecules in a single fluid phase. The ionic product of water, on the other hand, increases with the temperature up to about 280°C and then decreases around the critical point. The higher ionic product in hot and compressed liquid water, increases the concentration of H_3O^+ ions, catalyzing the hydrolytic reactions of organic macromolecules.

The main product of HTL is the BC obtained together with an aqueous phase (AP), a gaseous phase (GAS) and solid residues (SR) as co-products. The BC is a complex blend containing a large number of compounds of different molecular weight and, when no catalyst is used in the HTL, its quality in terms of viscosity and high heating value (HHV) is too poor to be considered a fuel. One of the main objectives of the studies on HTL was to change different operative parameters searching for maximum efficiency of conversion of the initial biofeedstock into BC. The type of biofeedstock, its initial concentration in water, the residence time and temperature were the main parameters studied for this purpose. The first outcome of the literature review is that the HTL process has been mainly investigated in batch reactors using hot and compressed water (200 − 400°C and 50 – 280 bar) as solvent and co-reagent also in the presence of inert gases (He, N_2, Ar) [1]. Several studies on HTL reported the use of organic solvents (for example, acetone[36], ethanol[37–39], methanol[36]) in the place of water: the BC yields of these processes are quite high, the quality of the BC is better and the optimal reaction temperature are even lower, especially in the presence of alcohols that promotes the conversion of the acids in the BC, into methyl and ethyl esters. Furthermore, if the organic solvent is used as water alternative, the preliminary drying of the biofeedstock of the HTL reactor strongly affect the economic sustainability of the process. Among the relevant literature considered in this work, also in the most recent years, fewer investigations were focused on the continuous HTL. This lack can be due to the fact that the implementation of a continuously operated plant has a lot of complications such as plugging occurring in the pipes or difficulties of pressurization and/or pumping. Castello et al.[40] performed a critical analysis on the relevant literature on continuous HTL in 2018, finding that even some collected results suggest the feasibility of HTL due to energy densification versus BC yield, some global issues hinder the development of the process to the industrial scale.

1.2.Biofeedstock description

1.2.1. Microalgae

A wet biofeedstock as microalgae is produced through the photosynthesis, which, using solar energy, ensures the synthesis of organic compounds from simple molecules such as water and carbon dioxide. Energy production from microalgae is environmentally sustainable. Many species show fast growth, high productivity and can accumulate large quantities of lipids, that is considered a positive factor for a high BC yield [41]. *Chlorella v.* in particular, appears to be a good option for BC production, having lipid content of 25-63 %w/w dry biomass [41]. However, several techno-economic analysis of HTL processes of microalgae, showed that one of the main drawback to the economic sustainability of the process is the high cost of the raw material [42,43].

1.2.2. Macroalgae

Macroalgae, also called seaweed, are macroscopic, multicellular organisms that grow and live in seawater. They have been evaluated as an economic alternative to microalgae because they growth using nutrients already present in seawater. The macroalgae, to date, are positively evaluated because they have the potential to couple the biofuel production with the bio-fixation of atmospheric CO_2. For these reasons the number of publications on HTL of macroalgae quickly grew in recent years.

1.2.3. Lignocellulosic biomass

Lignocellulosic biomass is an abundant raw material made of plant matter that is not useful for food and feed. The attention on lignocellulosic biomass increased because of the food vs. fuel debate that promoted the transition from the first to the second generation of biofuels in the bioethanol route that can be fed by lignocellulosic biomass instead of dedicated crops. However, the composition and the structural morphology of these matrixes make the process of recovery and fermentation of the sugar components economically unsustainable. In this context, HTL could represent a way to convert all the bioconstituents of the lignocellulosic biomass, and not just polysaccharides, into products of greater added value.

1.2.4. Sewage sludge

Generally, sewage sludge (SS) are waste materials very expensive to be disposed; their potential use as feedstock for biorefinery processes could have two main advantages: they are constituted by organic materials as microalgae, macroalgae or lignocellulosic biomass; they represent a zero-cost or even negative-cost organic matrix and so an income for the process economy. However, according to what was reported by ISPRA in 2017, in Italy only the 0.8% of sewage sludge were energetically valorized. Depending on the treatment stage from which they are recovered, different types of sludge are produced [44]:

- Primary sludge: produced by primary treatment of wastewater, they contain entrained solid particles, deposited by sedimentation, and oil, grease and light solids float removed before the remaining liquid can be addressed to a secondary treatment.
- Secondary sludge: produced by secondary treatment of wastewater. They contain all the dissolved and suspended biological matter that microorganisms metabolize.
- Mixed sludge: are constituted by primary and secondary sludge mixed together, downstream to the wastewater treatment plant.

Most of the time, SS used for HTL application were recovered after digestion process; in this case they are mixed sludge termed "digested sludge". It must be underlined that SS contain different environmentally hazardous and toxic substances, among which heavy metals and plastics, that enhance problems for their disposal or utilization. Also in the case of HTL process the effect of these non biogenic components on the performances of the process must be carefully investigated. The main organic compounds in sewage sludge are lipids, carbohydrates, proteins and nucleic acids and the exact ratio of these organic substances can vary in a wide range according to their origin. Approximately, the 60 wt% of the SS are constituted by a relatively energy dense organic matter [44] constituted by aforementioned biochemical compounds (lipids, carbohydrates, and proteins, as already said) [44,45]Huang et al. [46], showed that sewage sludge have a lower N content than microalgae and this evidence was also confirmed by Lemoine et al. [47].

1.2.5. Organic wastes

The organic waste category includes the human wastes that are produced by the municipality, like plastics, food and animal residues. The thermo-chemical valorization of these matrices by HTL is acquiring more interest in recent years as, due to the growth of the world population, the total amount of organic waste materials will increase, thus offering a cheap feed that in more industrialized countries is already object of a well-organized collection. Relevant publications in which real organic waste material has been studied are few and recent.

2. Analytical methodologies for scientometric analysis and critical review

In this study we analyzed the state of the art of HTL technology to detect general rules that can constitute a sound base for the design of new research activities on HTL in the perspective of its industrial application.

To reach this goal we conducted a bibliographic analysis of articles dealing with HTL of biofeedstocks published on Scopus database from 1986 to 2021. The relevant outcomes of the papers were critically analyzed as a function of the kinetic severity factor of the process focusing the attention on the HTL of biofeedstocks using just water as solvent.

A number of 146 papers were taken into account, with a total of 699 data obtained from HTL experiments.

To overcome the first source of fragmentation, i.e. the large variability in studied biofeedstocks and then in their composition and microstructure, the literature review was performed grouping them into five clusters i.e. microalgae, macroalgae, lignocellulosic biomass, sewage sludge and organic waste, as follows:

- **Microalgae:** it includes HTL experiments performed with *Chlorella vulgaris, Chlorella pyrenoidosa, Chlorella sp., Spirulina, Botriococcus Braunii, Cyanidioschyzon merolae, Desmodesmus sp., Dunaliella Salina, Nannochloropsis gaditana, Nannochloropsis oculata,* *Nannochloropsis salina, Neochloris oleabundus, Nostoc ellipsorum, Picochlorum* and *Scenedesmus almeriensis*.

- **Macroalgae:** it includes HTL experiments performed with *Alaria esculenta, Amphirosa fragilissima, Chetomorpha, Cladophora,Derbesia, Entheromorpha, Euglena, Fucus serratus, Galdiera sulphuraria, Laminaria digitata, Laminaria hyperborea, Laminaria saccharina, Laminaria digitata, Oedogonium, Salicornia, Sargassum muticum, Sargassum tenerissimus, Ulva lactuca, Ulva prolifera.*

- **Lignocellulosic biomass:** it includes HTL experiments performed with corn straw, eucaliptus, glycyrrhiza, kenaf, lactuca scariola, larch, lignin, miscanthus, mongolian oak, peanut straw, pistachio hull, potato starch, red grape seeds, rice bran, saccharina, sawdust (pine), soybean straw, sweet potatoes residues, waste newspaper, secondary pulp/paper-mill sludge, wheat stalk, wheat straw.

- **Sewage sludge:** it includes HTL experiments performed with cow manure, fish sludge, swine manure, domestic sewage sludge, activated sewage sludge, digested sewage sludge, primary sludge, secondary sludge.

- **Organic waste:** it includes HTL experiments performed with animal carcass, municipal solid waste, food waste.

A cumulative growth rate (CGR) of publications was calculated according to equation (1). Through this factor, it was possible to compare the cumulative annual increase of publications and get knowledge about the interest of the researchers in investigating HTL of different types of biofeedstock:

$$CGR = \frac{\sum_{i=0}^{t} P_i}{P_{i=0}} \tag{1}$$

where i represent the year of publication, i = 0 means the year of publication of the first paper for each category, $P_{i=0}$ is the number of paper published the first year and P_i is the number of paper published at the year i. Experimental details (listed in Table 1) and obtained results were collected and/or estimated from each paper and they were synoptically organized in order to identify the parameters which play an important role in the HTL process. Quantitative estimation of the combined effect of reaction temperature, time and of the heating rate was made using the concept of kinetic severity factor of the process (KSF=log(R^0)) defined by eq. (1) that was used as a first tentative quantitative criterion to organize published experimental results :

$$KSF = Log\ (R^0) = Log\ (\int_{t0}^{tf} e^{\frac{Tr-100}{14.75}} dt\ ) \qquad (1)$$

Where T_r and t_f are the reactor temperature and the heating time. Dry biofeedstock basis yield were taken into account to conduct the critical review. The following equation (2) was used to convert dry ash free into dry biofeedstock basis yield of biomass.

$$Yield_{db}(\%) = \frac{Yield_{daf}(\%)}{(1 - {}^{Ash\%}/_{100})} \qquad (2)$$

3. Discussion

3.1. Scientometric analysis of paper published on HTL

In Fig.1 it is possible to see the trend of CGR per year of all publications on HTL process technology while in Fig. 2 the same plot is reported for each class of biomass considered in this study.

As reported in Table 2, microalgae were the most investigated feed and papers dealing with them are homogeneously distributed over a longer period of time (Table 3) moreover it can be observed a steep increase in the number of papers published per year in the 2018-2021 period, also driven by the will of filling the gap of knowledge preventing the transfer of the process from the laboratory to the industrial scale. It is possible to see that, even if the greater number of publications are on microalgae in the last three years the attention shifted towards other types of organic matrices, such as SS, lignocellulosic biomass and organic waste materials. In the diagram it is possible to note that this change starts in 2017 in the same period in which first conceptual analyses of possible biorefinery processes based on HTL of microalgae [42,43] clearly indicated that the cost of this biomass negatively affects the economic sustainability of the process. This awareness, coupled with the need to dispose increasing quantity of waste biomass generated by anthropic activities, could explain the growing interest of researchers in investigating HTL of residual feedstocks.

3.2. Effect of kinetic severity factor (KSF) on HTL of different biofeedstocks

An important evidence of the literature review is that the reaction temperature and time are the operative parameters that mostly affect the BC yield and in the evaluation of experimental data performed in this study their effect was combined using the concept of kinetic severity factor (KSF) defined by Overend et al. [51].

The first screening was made taking the results obtained from batch non-catalyzed HTL of the five classes of biofeedstocks and estimating the nominal KSF considering the reaction temperature and time without any consideration of the possible role of the heating transient.

Using KSF to organize the data we observed that, even if the number of published articles changes significantly with the nature of the biofeedstock, with all tested matrixes it was possible to obtain yields of BC higher than 40 %, provided that proper values of KSF are adopted.

From the data analysis, higher BC yields are reached with aqueous feed slurry that contains biomass concentration from 10 to 30% by weight [48].

In Fig. 3 the percentage distribution of experimental data obtained at different values of KSF is reported. HTL of biofeedstocks was conducted in a wide interval of severities ranging roughly from 3 to 16 and the most abundant amount of data was concentrated at KSF from 9 to 10.

If we focus the analysis on the biofeedstocks studied in this range of KSF (Figure 4), it is possible to observe that the distribution of experiments per each value of severity factor reproduce the percentage distributions of investigated biofeedstocks without evidence of any adaptation of KSF to a specific feed.

A critical analysis was then carried out plotting the BC yield as a function of the KSF for each type of biofeedstock (Fig. 5) to search for a correlation between these parameters for each kind of biofeedstock at similar KSF the BC yield variation is not negligible. This fragmentation could depend on uncertainty in the biofeedstock characterization and concentration in water but also on differences among the used experimental apparatuses whose technological features in terms of stirring efficiency and heating rate are difficult to characterize.

HTL of microalgae, the most investigated biofeedstock, was performed in the wider range of KSF and, even if a large data spreading is observed, published results clearly indicate that the higher BC yields were mainly located in the interval 8-10 of KSF.

Faeth et al. [49] and Qian et al.[50] investigated the fast HTL, i.e. liquefaction with heating rate higher than 200°C/s and one minute of reaction time, of *Nannochloropsis sp.* and SS, and their results clearly indicate that another possible cause of the fragmentation of experimental results of HTL studies could be the heating transient. In fact it has been highlighted that different outcomes from batch experiments can be obtained if the heating rate is rapid (sand bath or molten salts bath utilization) or if this rate is slow (electric heaters) and not controlled.

To this regard it must be underlined that the most common heating apparatus used for batch experiments is composed of an electric heater that imparts to thick wall high pressure stainless steel reactors heating rate in the range 3-20 °C/min. This observation could be important to filter the outcomes of several studies carried out with similar nominal conditions and to investigate its role we splitted experiments in two large classes depending on the rapidity of the heating rate: one grouping experiments performed with rate lower than 20°C/min (slow heating HTL) and the other including HTL with rate higher than 25°C/min (fast heating HTL) In Fig. 6 is depicted the plot of biocrude yield as a function of the KSF in fast heating HTL experiments with micro and macroalgae, SS, lignocellulosic biomass and organic waste. It can be observed that the spreading of data decreases and the vast majority of them can be fitted by a single master curve with a maximum independently on the nature and composition of the adopted feedstock. This result suggests the importance of heating rapidly the feed to reaction temperature to force reaction network to develop at isothermal condition. Further considerations have been done considering the data acquired from HTL of microalgae in which the heating of the reactor was conducted through the utilization of a sand bath or molten salt bath (Fig. 7). Quite interestingly, analyzing the trends of the product yields in this case it was possible to observe complementary effects which can allow to tune the HTL of microalgae. At KSF below 9, the high solid residues yield can be due to a low conversion and the preferred reaction pathway is the decomposition of microalgae into water soluble products. At values of KSF from 9 to 10, the selectivity in BC increases, then, above 10, water soluble products and BC itself are gasified suggesting that consecutive reaction sequence interconnects these classes of products. Figure 8 reports that most of the experiments with microalgae were conducted with *Chlorella*, *Nannochloropsis* and *Desmodesmus species*, which are characterized by a composition of lipids, proteins and carbohydrates in the range 10-28, 38-59 and 12-30% respectively. The previously described analysis of the trends of yields of solid residue, water soluble products and gas phase cannot be extended to HTL of biofeedstocks different from microalgae for the limited number of available experimental data.

4. Biocrude (BC) as fuel precursor

4.1. Considerations about the quality of the biocrude (BC)

As previously mentioned, the BC is the fuel precursor obtained through the HTL of several types of biofeedstocks and, in certain situations, it can be obtained with an high heating value (HHV) similar to that of crude oil; in most cases, the value of this parameter is around 30-38 MJ/kg [48] and can be correlated to the elemental composition of the BC by the Dulong formula:

$$\text{HHV (MJ/kg)} = 0.338\text{C} + 1.44(\text{H} - 0/8) + 0.094\text{S} \qquad (3)$$

Quite interestingly, most of the studies reported the energy recovery (ER) as a figure of merit of the HTL process to measure the energetic content of the organic fractions that are produced by the process. In this case, if the biofeedstock is a waste, the ER has a broader meaning since represents an indication of the amount of energy that is recovered from wastes and stored in the products. It was reported a cumulative ER of the products obtained from HTL of sewage sludge are higher than 100% demonstrating that the energy used to drive the process can be stored in the products of HTL[51]. This is very interesting for the evaluation of the process in a biorefinery context in which solar heat can be used to drive the process[52].

4.2. Analysis of the effect of KSF on the quality of the biocrude (BC)

The physical-chemical properties of BC largely depend on the quality of the biofeedstock treated and on the operating conditions of HTL. As we reported in the previous section, from the bibliography analyses it was possible to observe that a maximum in the BC yield can be obtained at intermediate values of KSF. It has been observed that the BC produced by fast HTL (from a few seconds to one minute) [49,50,53,54] has a higher carbon content and calorific value than BC derived from the traditional isothermal HTL process, which is usually carried out at lower temperatures for tens of minutes. This marked reduction of the reaction time significantly reduces the reactor volume necessary for the continuous production of BC, and then the costs of the process. However, these researches have always been carried out at the laboratory level and it is not certain that similar results can also be found at higher plant scales.

The BC obtained in HTL of organic matrices without added catalysts is typically very viscous at room temperature and has too high oxygen, nitrogen and sulfur content to be used directly as fuel [55]. The presence of these heteroatoms poses great challenges for the use of BC for the production of biofuels since they can cause corrosion and formation of SO_X and NO_X during combustion. In this regard, research has recently been carried out on possible catalysts active in reducing heteroatom content of synthesized BC. All these hydrotreating processes are more expensive the higher the average molecular weight and the heteroatom content of the BC are [56]. We can use as a reference the European legislation EN 14214 that fixes specifications of biofuels on the market setting a cumulative heteroatom content (N, O, S) lower than 24 mg/kg; sulphur content below 10 mg/kg; viscosity (40°C) 3.5-5 mm^2/s and HHV of 40 MJ/kg. The BC is a complex blend that contains a large number of compounds of different molecular weights. The oxygenated compounds typically detected and identified in BC through gas-chromatography coupled to mass spectrometry (GC-MS) analyses are fatty acids, heterocyclic compounds and ketones. Instead elemental analyses on selected samples were mostly conducted in order to evaluate carbon content, H/C and O/C molar ratio. The outcomes, reported in Fig. 9, consist in the plot of H/C, O/C and ER % from the literature at different values of KSF for each type of biofeedstock. From the analysis of experimental data obtained with algal biofeedstock (Fig. 9, A), it seems that ER % reaches a maximum and then decreases while H/C and O/C both decrease with KSF. This trend is more clearly detected in experimental points that are obtained in HTL of microalgae with fast heating rate. In the case of SS, an appealing residual biomass to valorize by HTL, published data suggest that increasing KSF in the range 6-10 it is possible to obtain BC with higher ER, higher hydrogen content and lower residual amount of oxygen (Fig. 9B). Also with SS these trends are more clearly recognized in data obtained with fast heating rates. In the case of other residual biomass the data available prevents any sound correlation of ER with KSF probably also because these feedstocks were not investigated in systems heated by molten salt or sand bath (Fig. 9C). In general the highest values of ER, higher than 70%, were obtained from microalgae, sewage sludge and organic waste while ER with macroalgae, lignocellulosic biomass hardly overcomes 50%.

4.3. Catalytic HTL

Given the great variety of molecules present, the BC derived from the liquefaction of organic matrices must be subsequently treated to reduce the quantity of heteroatoms and to synthesize the hydrocarbons of the target fuel by hydrodeoxygenation (HDO), hydrodeazotation (HDN) and hydrodesulfurization (HDS) in the presence of suitable catalysts [35,57,58,60]. The study of catalysts for the improvement of the process in terms of yield and quality of the BC (reduction of the heteroatom content and increase of the calorific value) is instead a crucial issue to make the process more attractive and suitable for the transition to industrial scale.

Catalysts can be used to improve the quality of the BC in terms of its elemental composition. A lot of investigations were made on catalytic HTL of wet biofeedstocks. However, even if homogeneous and heterogeneous catalysts were widely investigated to produce a better quality BC, many aspects hindered their long term applicability in HTL technology and further investigations are required. In general, ethanol, methanol, formic acid, acetic acid, Na_2CO_3, KOH, NaOH, K_2CO_3 were the most investigated sacrificial homogeneous additives. Although it was found that the addition of organic compounds to the hydrothermal process, as with sacrificial organic acids, improves the quality of the BC, factors such as their cost or origin should be carefully considered. In the biorefinery concept these additives should not be of fossil origin. On the other hand, the heterogeneous catalysts, more interesting because potentially more easily separable from the products, are more sensitive to poisoning by the heteroatoms contained in the feedstock or because of the water used as a solvent. The analytical study of the existing data on catalytic HTL resulted in a variety of outcomes that if analyzed alone could increase the complexity of the entire spectra of knowledge on HTL. In Table 4, $\mathrm{HHV} \geq 39\ MJ/kg$, $\mathrm{H/C} \geq 1.9$ and $\mathrm{O/C} \leq 0.09$ were used as reference thresholds to evaluate and filter the performances of the catalytic systems found in the literature. The threshold values of the target parameters were selected to be representative of a high quality BC. In this framework, all the collected data were analyzed and classified. The performed screening suggests that, even if the stability of the catalytic systems has to be deeply investigated, there are some of them that could improve the quality of the BC that is produced from microalgae, sewage sludge and organic wastes. Results obtained from catalytic HTL of macroalgae and lignocellulosic biomass were not reported in the Table 4 because they do not meet the target values in the screening here conducted. Ma et al. [61] reported a positive effect of ZSM-5 on the HHV of the BC produced from macroalgae (34.8 MJ/kg), instead Seehar et al.[62] reached a HHV of 35.5 MJ/kg studying the HTL of lignocellulosic biomass in the presence of K_2CO_3. From the outcomes of this screening (Table 4) it was possible to point out that, catalytic HTL has to be performed at a reaction temperature higher than 300°C in order to register a significant effect of the catalytic system. Furthermore, it was found that some of the catalytic systems resulted more active in improving the BC yield only in the cases of microalgae confirming that the performances of the catalysts strongly depend on the nature of the biofeedstock (this is the case of Na_2CO_3, KOH, CH_3COOH and Pt/C) while HCOOH and $CoMo/Al_2O_3$ are both active in improving the HHV of BC obtained from HTL of microalgae and sewage sludge. Quite interestingly, the only catalysts that allowed simultaneous improvement of HHV, H/C and O/C of BC, is the KOH. This effect can be due to its activity in promoting water gas shift reaction that can lead to the production of native hydrogen inside the HTL reactor.

5. Conclusions

The development of scalable and sustainable HTL plants, as well as environmental and technical-economic analysis of the system, still represents a challenge. In this framework, this critical review on batch HTL of five clusters of biofeedstocks (microalgae, macroalgae, lignocellulosic biomass, sewage sludge and organic wastes) was conducted to extrapolate general rules governing the effect of operating parameters on the yield and quality of the biocrude (BC). For the first time, to the best of our knowledge, the KSF was used to analyze the entire spectra of the literature, and the following guideline can be proposed:

- The optimal KFS value that allows to maximizing the yield of BC is between 9 and 10;
- The heating transient of the reactor significantly affects the performance of the process and fast heating rate strongly decrease the variance of collected experimental BC yields with KSF ;
- With microalgae, tuning the KSF value in fast heating rate experiments it is possible to obtain a BC with high yields and ER, and this result suggest to study more systematically the role of the kinetic parameter with not algal biomass using fast heating of the reaction mixture.
- Values of ER greater than 70 % were obtained from microalgae, sewage sludge and organic waste;
- Collected results on catalytic HTL suggest that a stable catalytic system is not yet available. However, since not catalyzed HTL under optimized KSF allow to produce a BC with high yield and quality not far from that reached using catalytic systems, it seems reasonable to perform non-catalytic HTL followed by a successive hydrothermal catalytic up-grading of the biocrude not necessarily separated from the aqueous phase.

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Figure Captions:

- **Figure 1:** Cumulative Grow Rate (CGR) of the publication on HTL from 2000 to 2021.
- **Figure 2:** Cumulative Grow Rate (CGR) of the publication on HTL of microalgae, macroalgae, sewage sludge, lignocellulosic biomass, organic waste from 2000 to 2021.
- **Figure 3:** Distribution of percentages of experimental data obtained using several values of KSF
- **Figure 4:** Distribution of experimental data obtained at the KSF most investigated with the examined biofeedstocks.
- **Figure 5:** BC yield variations with KSF. a) microalgae; b) macroalgae; c)lignocellulosic biomass; d)sewage sludge; e)organic waste.
- **Figure 6:** BC yield as a function of the KSF. HTL experiments assisted by fast heating of microalgae, organic waste, macroalgae, lignocellulosic biomass, sewage sludge
- **Figure 7:** Product yields obtained from HTL of microalgae at different KSF values and fast heating (sand bath used to heat the reactor). A)BC yield; b) solid residues and gas phase yields; c)water soluble products yield. All the reported yield are daf % (dry ash free)
- **Figure 8**: Biocrude (BC) yields obtained from HTL of microalga *Chlorella p.*, *Nannochloropsis sp*. and *Desmodesmus sp.* at different KSF values and fast heating (sand bath used to heat the reactor).
- **Figure 9:** H/C, O/C and ER (%) of BC from the HTL of A) microalgae and macroalgae; B1) sewage sludge; B2) organic waste and lignocellulosic biomass. HTL experiments were conducted at different KSF without catalysts, and water as solvent.

Table 1: list of data extrapolated from publications

Category	**Extrapolated data**
Experimental set up	biofeedstock category biofeedstock name solvent catalyst or additive T (°C) t (min) P reactor configuration heating rate (°C/min) biomass conc. (% w/w)
Biofeedstock characterization	C (% w/w) H (% w/w) N (% w/w) S (% w/w) Lipids (% w/w) Protein (% w/w) Carbohydrate (% w/w) Ash (% w/w)
Product yields	Biocrude Solid residues Gas Aq. Phase Volatiles
Biocrude characterization	HHV (MJ/kg) H/C O/C N/C ER (%)

Table 2: Distribution of published papers. Percentages calculated with respect the total number of publications considered in this study.

Biofeedstock	% of papers published on HTL of different biofeedstock
Microalgae	42
Macroalgae	15
Lignocellulosic biomass	18
Sewage sludge	22
Organic waste	3

Table 3: Published papers per year on HTL of different biofeedstocks.

Biofeedstock	**Years**														
	1986	**1987**	**2006**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**
Microalgae	_	_	_	[63,64]	[65–72]	[73]	[44,45,49,74,75]	[76–79]	[35]	[80–83]	[84–87]	[88–93]	[59,94–104]	[38,103–109]	[110–113]
Macroalgae	_	_	_	[114]	_	_	[115,116]	_	[117]	_	_	_	[118–120]	[61,106,107,110,123–125]	[37,124,125
Lignocellulosic biomass	_	_	[126]	_	[127]	_	[46]	_	[128,129]	_	_	[93,132,133]	[100,134–139]	[62,105,140–144]	[143–153]
Sewage sludge	[154]	[45]	_	[39]	[68]	_	[46,155,156]	[36,157]	[158]	_	[54,159]	[93,162–166]	[59,103,167]	[50,51,107,166–168]	[143,169–173
Organic waste	_	_	_	_	_	_	[155]	_	_	_	_	_	[174–176]	[177]	[178–182]

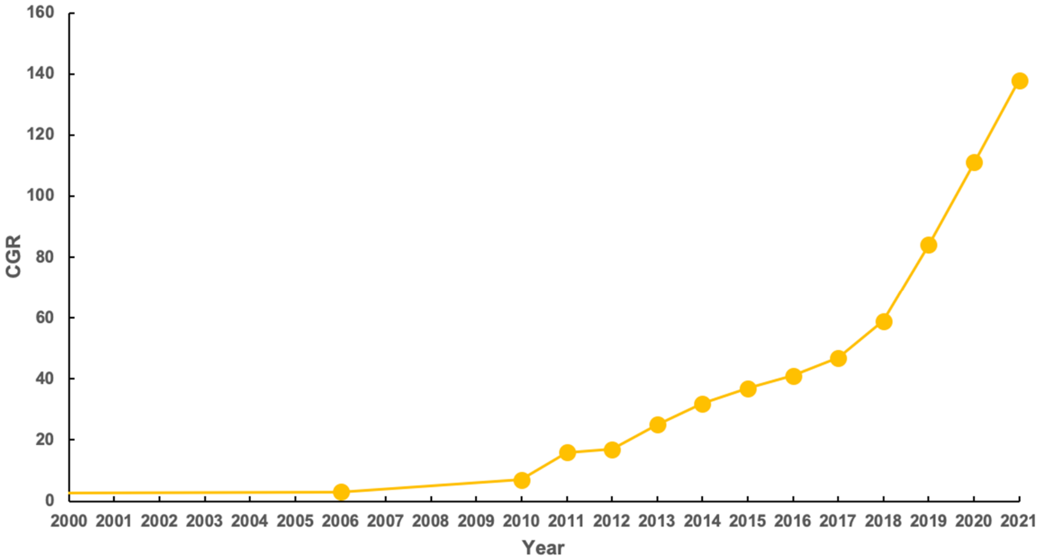


Figure 1

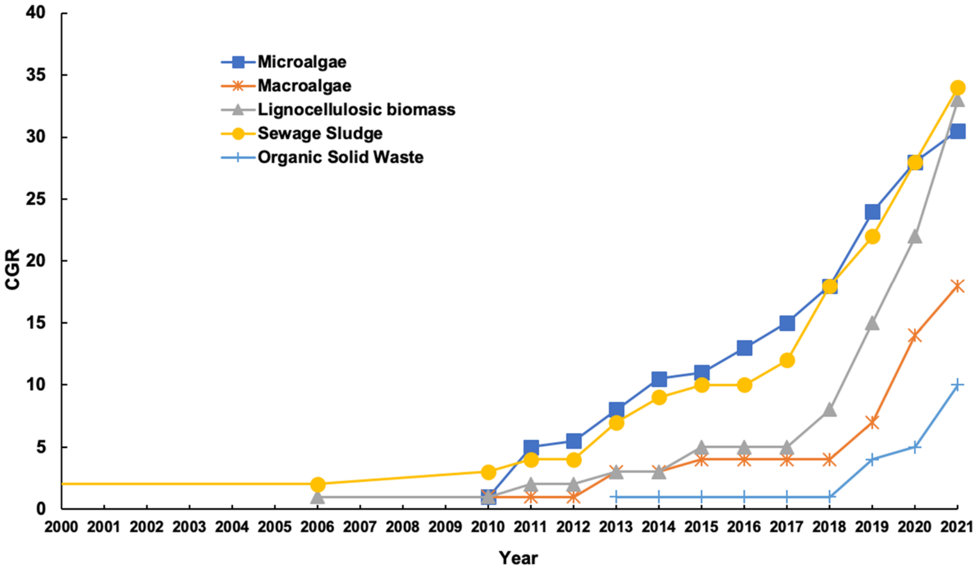
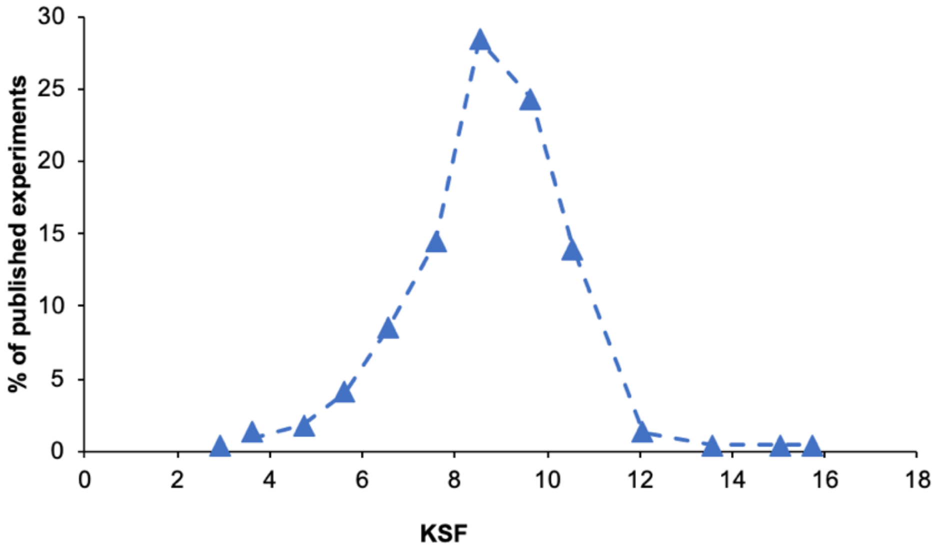


Figure 2



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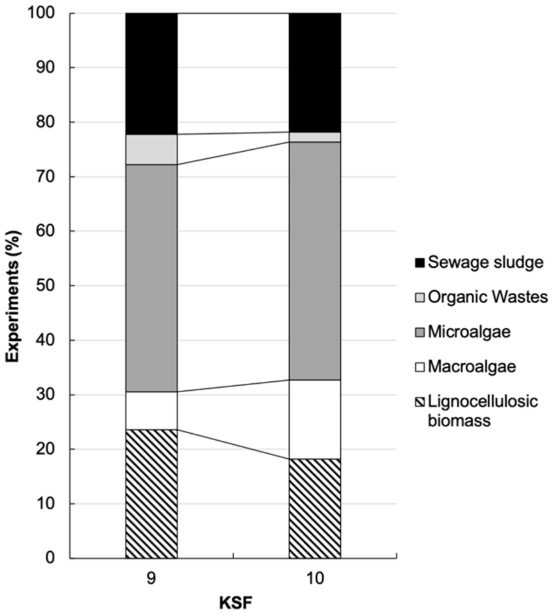

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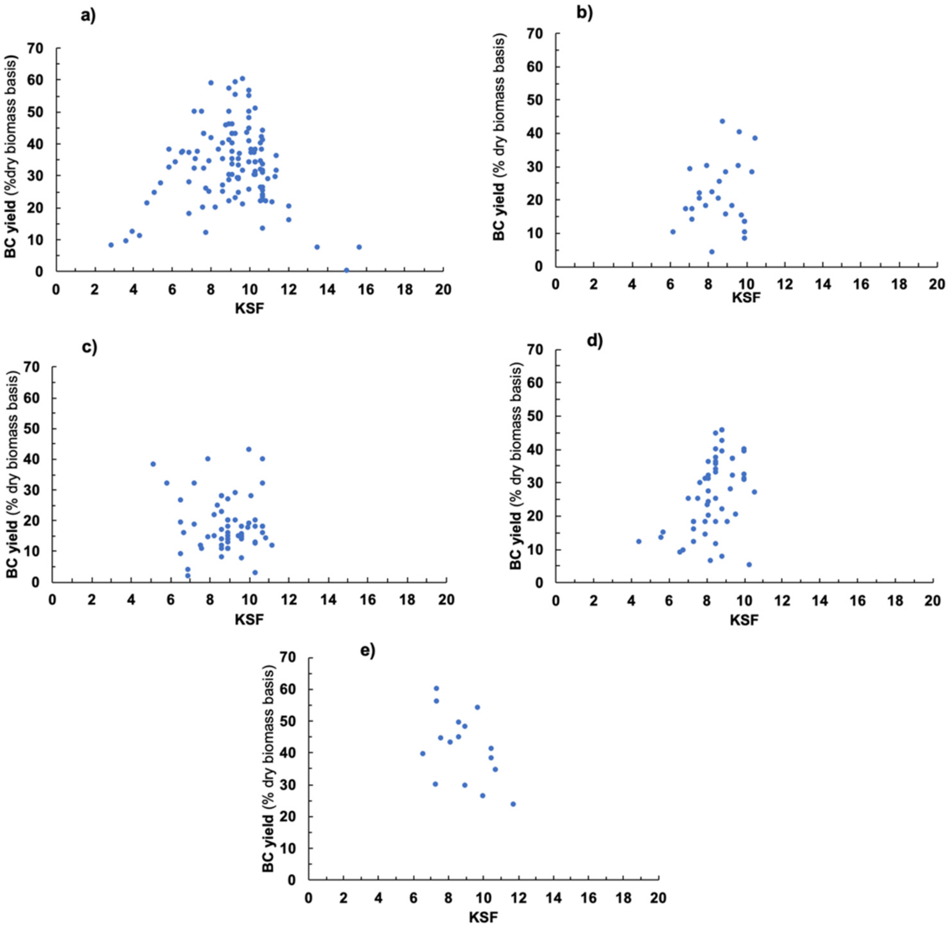

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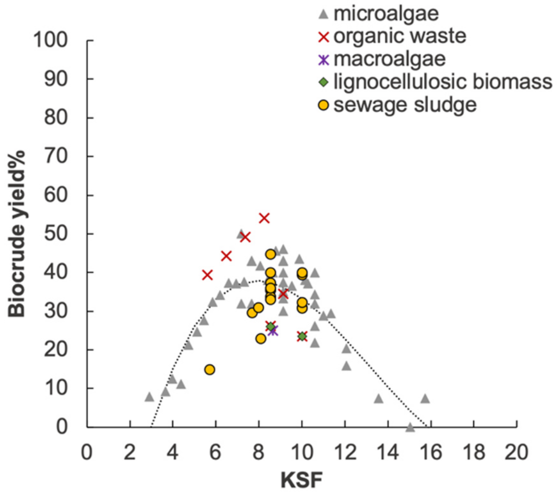

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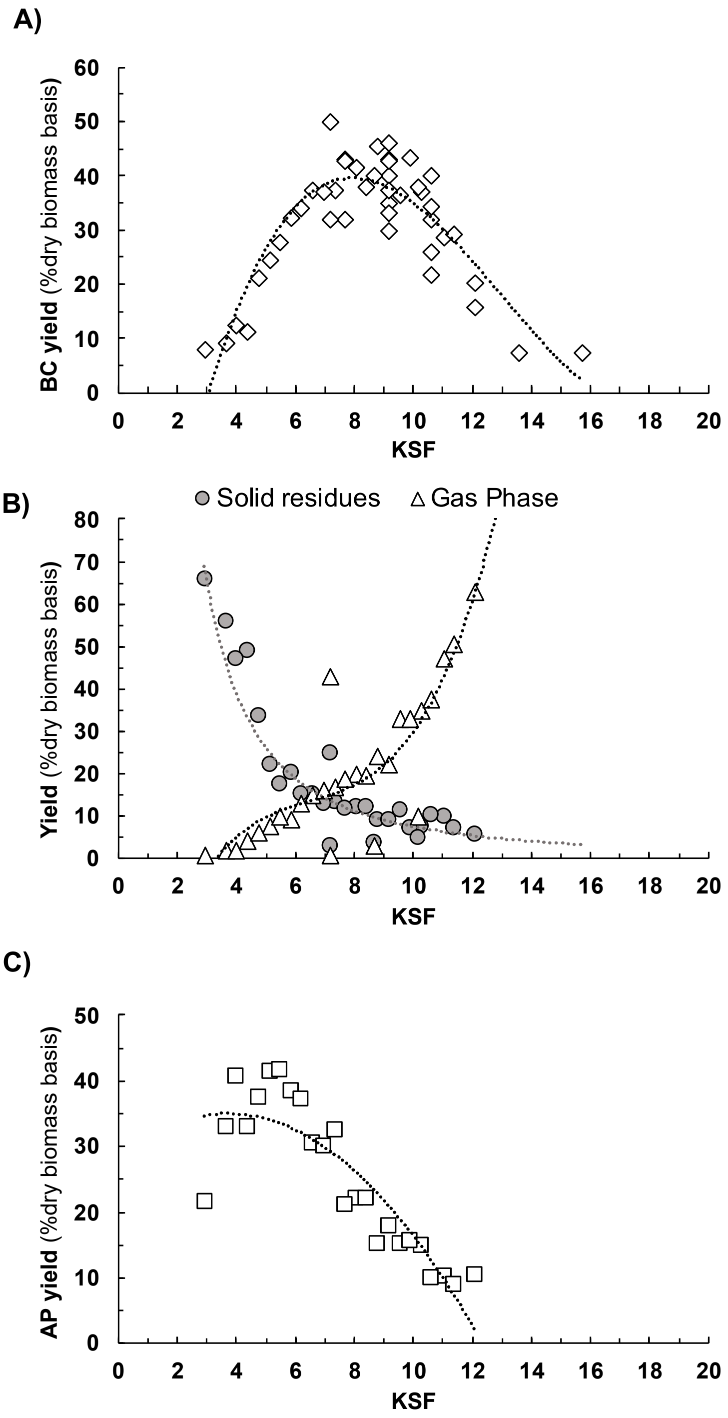
A)
BC yield (%dry biomass basis)
0
10
20
30
40
50
60
KSF
0
2
4
6
8
10
12
14
16
18
20
B)
● Solid residues
△ Gas Phase
Yield (%dry biomass basis)
0
10
20
30
40
50
60
70
80
KSF
0
2
4
6
8
10
12
14
16
18
20
C)
AP yield (%dry biomass basis)
0
10
20
30
40
50
KSF
0
2
4
6
8
10
12
14
16
18
20

Figure 7

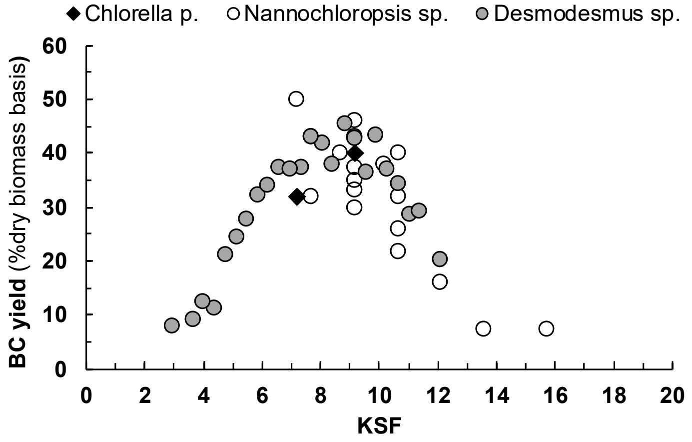

Figure 8

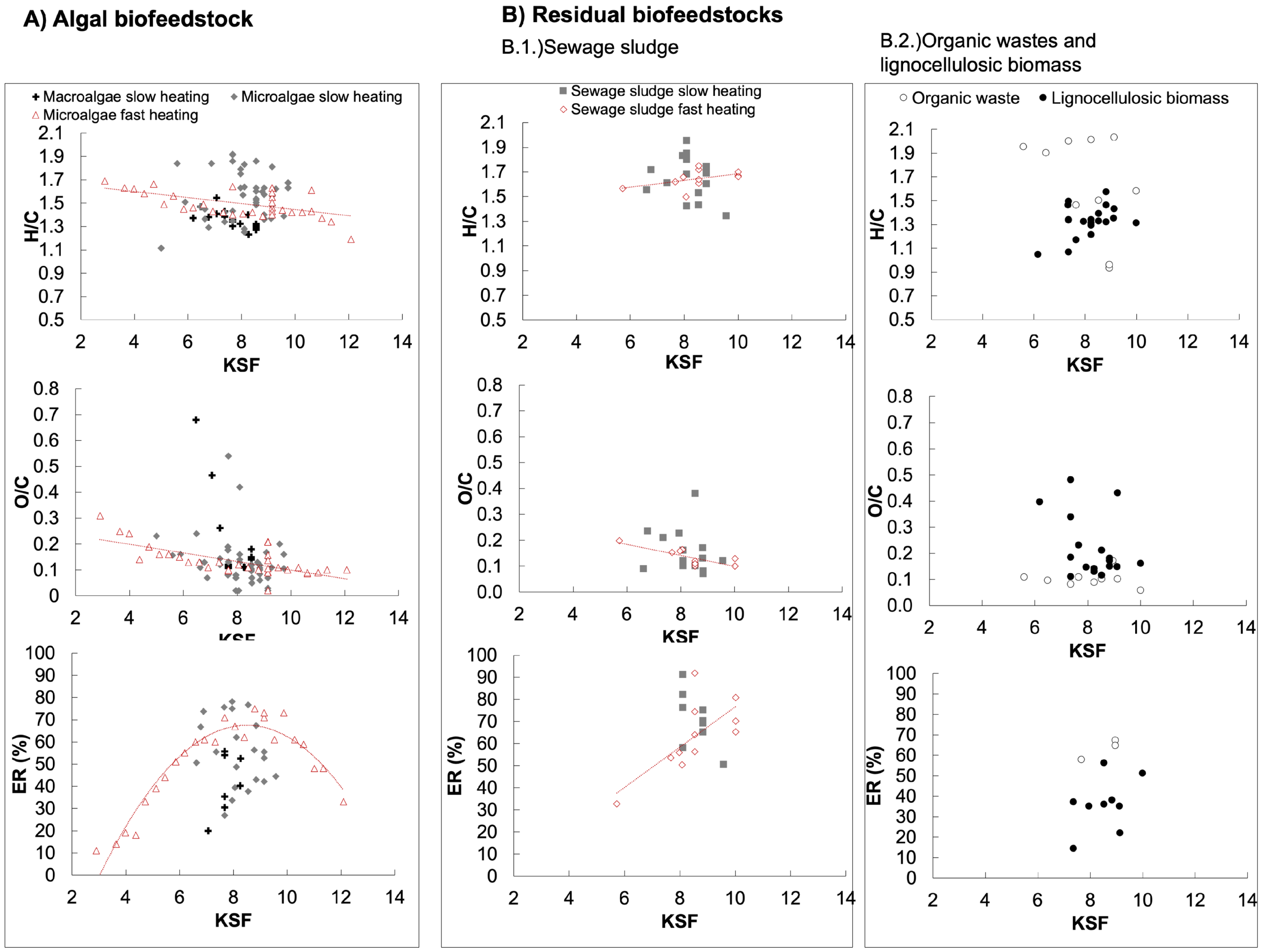

Figure 9

Table 4: Performances of catalytic systems used for HTL of the selected biofeedstocks (microalgae, macroalgae, lignocellulosic biomass, sewage sludge and organic wastes), in the presence of water as solvent

	Ref.	**Catalyst**	**T (°C)**	**t (min)**	**HHV $\geq 39\ MJ/kg$**	**$H/C \geq 1.9$**	**$O/C \leq 0.09$**
Microalgae	[183]	Na_2CO_3	300	60	x	x	
		KOH	350	60	x	x	x
		CH_3COOH	300	60	x		
	[65]	HCOOH	350	60	x		
	[70]	Pt/C	350	60	x		x
		$CoMo/Al_2O_3$	350	60	x		x
Sewage sludge	[167]	K_2CO_3	350	15			x
	[166]	K_2CO_3	400	15			x
	[170]	HCOOH	325	30	x		x
	[59,172]	Activated Carbon felt	325	30	x	x	
	[170]	$CoMo/Al_2O_3$	325	30			x
	[164]	Ni- raney, Ru/C	350	120	x		x
Organic waste	[180]	K_2CO_3	350, 400	15	x		x