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Application of algae as co-substrate to enhance the processability of willow wood for continuous hydrothermal liquefaction

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Abstract

This work proposes a novel strategy to improve the continuous processing of wood slurries in hydrothermal liquefaction systems by co-processing with algae. Of all algae tested, brown seaweeds and microalgae perform best in preventing slurries dewatering, the main reason for pumpability issues with wood slurries. Rheological tests (viscosity-shear rate profile) indicate that the addition of these two algae to the wood slurry causes the highest increase in viscosity, which coincides with improved wood slurries stability and pumpability. Hydrothermal liquefaction of wood-algae slurries at 400 °C and 15 minutes in 10 mL tubular batch reactors shows that macroalgae slightly decrease the biocrude yield from 28.5 wt% to 21.6-25.5 wt% while microalgae increase the biocrude yield with more than 40 % relative to pure wood liquefaction. Another benefit of microalgae addition is that the total biomass loading and the organic mass fraction of the slurry can be increased by 100 % and 90 % respectively. Therefore, when co-processed with wood, microalgae can improve the wood feedstock pumpability, biomass loading, organic matter and the biocrude yield.

Keywords: HTL, algae, lignocellulosic biomass, co-processing, biocrude

1. Introduction

Macroalgae have been used for centuries for the extraction of polysaccharides with thickening and gelling properties. Today, brown- and red seaweed extracts together represent about 18 % of the total market value for food hydrocolloids[1]. Algae are also considered as an important resource for bioenergy production. The high growth rate, high CO_2 absorption capacity, cultivation on non-arable land and versatility in terms of chemical composition, represent important advantages of marine biomass over

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terrestrial biomass [2,3]. For these reasons, algal biomass was intensively investigated for the suitability to produce a new generation of biofuels, known as third generation biofuels [4].

Second generation biofuels are those obtained from lignocellulosic biomass like wood, straw and other plant biomass. These materials are challenging for conventional biomass-to-biofuel conversion technologies (fermentation, digestion) due to their recalcitrance to biological treatments [5,6]. The chemical structure of lignocellulosic materials can be more easily disrupted under thermochemical treatments such as hydrothermal liquefaction (HTL)[7]. In this case, a combination of high pressure (20 MPa to 30 MPa), high temperature (300 °C to 400 °C) and water catalytic properties leads to fast conversion of biomass into biocrude oil compounds. However, in case of HTL processing another challenge arises from to the low density of lignocellulosic matter that limits the dry matter content of the feedstock and promotes phase separation between the solid biomass and the liquid water during pressurization. The phase separation represents a major obstacle to pump aqueous slurries at pressures of 20 MPa to 30 MPa. Previous works show that fine milling, chemical pretreatment or slurry make-up with various additives is compulsory for continuous processing of wood in HTL systems where slurries with maximum wood concentration of 17 wt% were processed [8,9,10]. While wood and other lignocellulosic materials require special treatment to obtain pumpable aqueous slurries, continuous liquefaction of algae pastes can be implemented quite easily [11,12,13]. As described by Elliott et al., algae form ‘puree-like’ feedstocks either simply after mixing of dried algae with water, or dewatering and wet milling of the raw algae [11,12].

To improve the processability of lignocellulosic aqueous slurries, this work proposes co-processing wood with materials that have thickening and water binding properties, in this case algae. Microalgae were previously used as co-stream in HTL of rice husk [14], manure [15], coal [16], macroalgae [17] or synthetic polymers [18]. These studies, except the case of algae-manure co-processing, showed that the addition of microalgae into the feedstock has a positive effect on the biocrude yield due to lower thermal resistance and higher conversion into biocrude of microalgae compounds. Co-processing of wood with macro- and microalgae has not yet been reported. Moreover, the co-processing of algae and lignocellulosics with the purpose to improve the feedstock texture and flow behavior is a novel approach in HTL feedstock pretreatment and also an unexplored topic in literature.

Microalgae are the most investigated marine biomass for hydrothermal liquefaction, probably due to the fact that microalgae contain higher mass fractions of lipids and proteins and have lower ash content compared to macroalgae. Higher biocrude yields from microalgae compared to macroalgae are in general obtained though large variations are noticed in both cases. For microalgae the biocrude yields reported in literature range between 18 wt% [19] and 83 wt% [20] (on dry ash free basis) and for seaweeds between 4 wt% [21] and 36 wt% [22] (on dry ash free basis). The higher biocrude yields from microalgae liquefaction is in general explained by the higher fractions of lipids and proteins in microalgae compared to seaweeds but the hydrothermal liquefaction conditions (temperature, reaction time, catalyst) also plays an important role. Temperatures around the water critical conditions [23,24,25] and short reaction times (up to 15 minutes) [26,27] were found to be the most advantageous with respect to biocrude yield. Alkaline catalysts are advantageous for algae with high content of carbohydrates like macroalgae because it can reduce the char formation and increase the biocrude yield [19]. The most frequent solvent used for the extraction of algae-derived biocrude is dichloromethane but acetone, chloroform or diethyl ether were also reported.

This work investigates the technical feasibility of using seaweeds (green, brown and red) and microalgae to improve the processability of wood aqueous slurries. The main reason for using algae as wood slurries stabilizers is that macro- and microalgae contain polysaccharides with thickening and water binding properties. These properties could prevent feedstock dewatering and solids settling. Four different algae species are compared in terms of thickening properties, water holding capacity and the ability to improve wood slurries pumpability as well as the variation of these properties in alkaline conditions. The impact of wood and algae co-processing on the biocrude yield, elemental composition and boiling point distribution is also studied.

2. Materials and methods

2.1. Raw Material

Brown seaweeds, *L. Digitata* (cultivated in open ocean) and red seaweed *P. Palmata* (wild harvested), were provided by Ocean Rainforest, Faroe Islands. The algae were collected in March 2016. Green seaweed *Ulva spp*. and microalgae *Chlorella Vulgaris* were obtained from commercial sources (Porto-Muiños S.L. and Algomed®). Fresh algae were dried at room temperature for three days and then in oven at 60 °C. Willow (genus *Salix*) was collected at Ny Vraa Bioenergi I/S, Tylstrup, Denmark. Trees were harvested at two years old, in winter 2014. The chemical composition of the algae is given in Table 1. Willow consists of 53.3 wt% cellulose, 14.8 wt% hemicellulose, 20.3 wt%

lignin and 1.9 wt% ash, on dry basis [28].

The seaweed and the willow were milled using a laboratory scale cyclone mill to obtain a powder that passed through a 60 mesh (250 µm). The size distribution of the willow and the seaweed powders is given in Table 2. For the analysis of lipid content, microalgae and seaweed powders were further milled with a Retsch CryoMill to a particle size below 100 µm to facilitate the extraction (the extraction procedure is described in Section 2.2.).

Table 1 Chemical composition and ash content of algae samples (wt%, dry basis)

	Willow (genus *Salix*)	Green seaweed *Ulva spp.*	Brown seaweed *L. Digitata*	Red seaweed *P. Palmata*	Microalgae *C. Vulgaris*
Proteins	-	7.8±0.0	10.5±0.0	20.4±0.0	40.3±0.0
Lipids	-	6.8±0.0	10.1±1.2	9.1±0.8	16.3±0.2
Carbohydrates	68.1[a]	54.8[b]	44.4[b]	47.6[b]	35.4[b]
C	47.9±0.0	41.7±0.8	36.5±1.6	37.1±0.7	50.1±0.2
H	6.1±0.0	6.3±0.2	5.1±0.1	5.5±0.3	7.1±0.4
N	0.01±0.0	1.7±0.0	2.3±0.0	4.5±0.0	8.8±0.0
S	n.d.	1.2±1.7	2.2±0.5	1.2±0.1	1.1±1.1
O[c]	44.1	18.6	18.9	28.8	24.9
Ash	1.9±0.1	30.5±0.5	35.0±0.4	22.9±0.1	8.0±0.5

[a]represents the sum of cellulose and hemicellulose; [b]by difference (100-ash-proteins-lipids); [c]by difference (100-C-H-N-S-ash); n.d.= not detected

Table 2 The size distribution of willow and algae powders

	d_{50} (mm)	Size distribution (wt%)		
		0.250 mm-0.125 mm	0.125 mm-0.050 mm	< 0.050 mm
Willow	0.130	38.0	23.0	25.2
Seaweeds	0.115	38.7	34.7	20.3

2.2. Analytical methods

Proximate analysis

The ash content of biomass was measured at 575 °C according to the standard procedure ASTM E1755-01 [29].

Elemental and chemical analysis

The carbon, hydrogen, nitrogen and sulfur content of the biomass and the biocrude oils were measured with a vario MACRO cube Elementar analyzer. Measurements were performed in duplicates and the average values are reported. The oxygen content was determined by difference. The content of protein in algal biomass was derived from the elemental analysis using the nitrogen-protein conversion factor (N-factor) 4.58 [30]. The N-factor was determined as an average of 10 marine microalgae species with a standard deviation of 0.11. The content of lipid in algal biomass was determined by extraction with a chloroform-methanol mixture in a Soxhlet extractor [31, 32]. Approximately 2 g of algae were weighed into a 37 mm x 130 mm single thickness cellulose thimble. The lipids were extracted with 350 mL of solvent (chloroform-methanol 2:1 v/v) for 5 h to 6 h until a total of 16-18 cycles were completed. The solvent was removed in a rotary evaporator at 35 °C and afterwards the samples were dried for 1 h at 105 °C. The content of lipid was determined gravimetrically. Lipid content was performed in duplicates and mean values are reported. The carbohydrates were determined by difference. The results presented in Table 1 are similar to the values reported in literature; the seaweeds are rich in carbohydrates (between 44 wt% and 55 wt% and less abundant in proteins (between 8 wt% and 22 wt%) and lipids (between 7 wt% and 10 wt%) [22,33]. Microalgae have higher fractions of proteins (40 wt%) and lipids (16 wt%) and lower fraction of carbohydrates (35 wt%) compared to seaweeds [19,23].

Thermogravimetric analysis (TGA) was performed with a PerkinElmer STA6000 TG/DSC instrument in nitrogen atmosphere. The samples were heated from 50 °C to 1000 °C with a heating rate of 10 °C/min. The gas flow rate was 20 mL/min.

Functional properties of biomass

The water holding capacity (WHC) of biomass was determined by the centrifugation method as described by Sosulski [34] and Yaich et al.[35]. Wood and algae solutions with 12 wt% biomass loading were prepared in pre-weighed centrifuge tubes. The samples were left to rest at room temperature for 60 minutes followed by centrifugation at 3000 g for 25 min at 25 °C. The supernatant liquid was removed and the tubes were placed mouth down at an angle of 15˚ to 20˚ in a drying oven at 50 °C for 25 min. The percentage of water absorbed was determined gravimetrically and was expressed as the amount of water retained by 1 g of dry solid sample.

The viscosity of the algal slurries was measured with a rotational viscometer Brook RV-DV II-Pro, according to the standard procedure ASTM D2196-86 [36], at 20 °C. Appropriate spindles were used according to the viscosity range measured.

2.3. Slurry preparation

The wood-algae mixtures were prepared by first mixing the algae powder with the liquid agent (water or NaOH 1M) followed by the addition of wood. The mixtures were left to rest for 60 minutes before any test.

2.4. Slurry stability tests

The stability of the wood, algae and wood-algae slurries was evaluated according to the syringe test[37] and the centrifugation test. The syringe test evaluates if dewatering occurs when the slurry is passed through an orifice. The test sample is loaded into 12 cm^3 syringe with outlet diameter of 3.38 mm and inlet to outlet diameter ratio of 4.7. Dewatering of the slurry is visually monitored while the slurry is discharged. Mixtures that pass through the syringe homogeneously, are considered stable and those that separate in two phases, i.e. a liquid phase that is discharged and a solid cake that remains into the syringe tube, are considered unstable. Examples of stable and unstable slurry evaluated with the syringe test are illustrated in Figure 1. The centrifugation test reproduces the conditions used to determine the water holding capacity of biomass (3000 g, 10 minute). Stable and unstable slurries according to the centrifugation test are illustrated in Figure 2. Comparative studies showed that there is a high probability for successful feedstock pumpability if both the syringe and the centrifugation tests are passed. The comparison between the laboratory scale pumpability tests and the performance of a high pressure piston pump is based on the experience gained from operating the continuous bench scale HTL plant installed at Aalborg University, described elsewhere[10]. The continuous HTL system includes a high pressure piston pump that delivers the feedstock at 30 MPa.

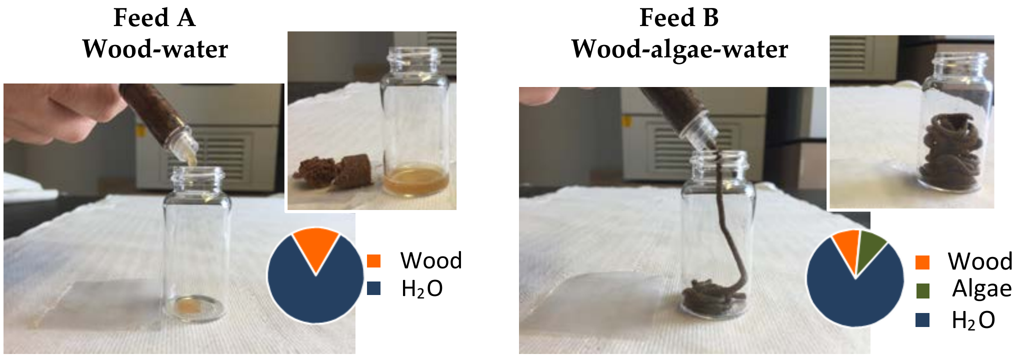


Figure 1 The syringe test applied to a mixture containing 15 wt% wood, 85 wt% water (Feed A) and a mixture containing 10 wt% wood, 10 wt% brown seaweed, 80 wt% water (Feed B)

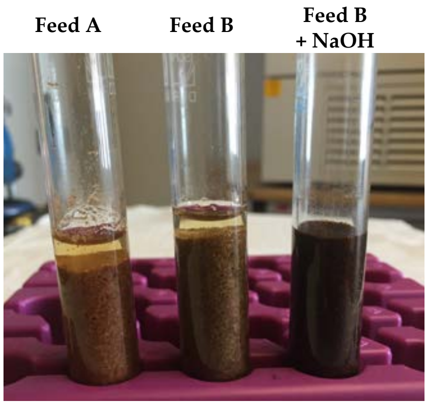


Figure 2 Samples after centrifugation at 3000 g for 10 minutes; Feed A contains 15 wt% wood, 85 wt% water, Feed B contains 10 wt% wood, 10 wt% brown seaweed, 80 wt% water and Feed B+NaOH contains 10 wt% wood, 10 wt% brown seaweed, 80 wt% solution NaOH 1M

2.5. Hydrothermal liquefaction experiments

HTL experiments were carried out in 10 mL stainless steel tubular batch reactors at 400 °C for 15 minutes. In a typical run, approximately 7 g of feedstock was loaded into the reactor. The biomass was mixed with NaOH 1M solution to obtain feeds containing 15 wt% wood-based slurries, 20 wt% wood-seaweed slurries and 30 wt% wood-microalgae mixture. Detailed composition of the feedstock used for the HTL experiments is given in Table 6. The reactor was purged with nitrogen for oxygen removal and pre-pressurized with 2 MPa of nitrogen. All experiments were performed in duplicates. Two reactors were inserted simultaneously into a pre-heated fluidized sand bath (model: Techne SBL-2D) and reached the final temperature in about 2 minutes. After 15 minutes, the reactors were removed from the sand bath and rapidly cooled in a water bath followed by products deparation according to

Figure 3. After cooling, the reactor content was poured into a vessel and thoroughly rinsed with acetone. The liquid poured from the reactor was mixed with the acetone used to wash the reactor and filtered for solids separation. The solids were further washed with distilled water to dissolve the water-soluble inorganics and dried over night at 105 °C. The acetone filtrate was evaporated under reduced pressure in a rotary evaporator to remove the acetone. The biocrude was re-dissolved with dichloromethane (DCM) and the mixture transferred into a separation funnel. A layer of water phase separated from the biocrude-DCM mixture, which was then removed, and the biocrude-DCM mixture was poured into a pre-weighed collection tube. The DCM was evaporated at atmospheric pressure until the sample reached a constant weight. The biocrude was analyzed for moisture content and elemental analysis. The biocrude yield was expressed as the ratio between the biocrude on dry basis and the biomass on dry ash free basis.

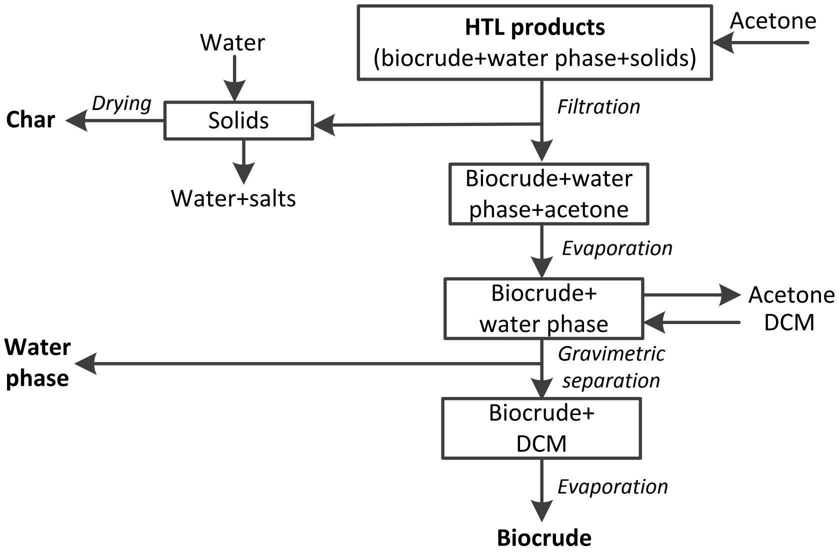
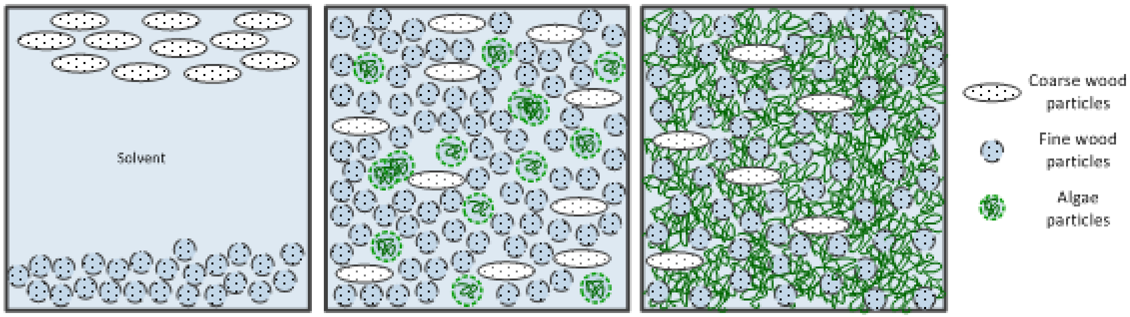


Figure 3Schematic representation of the HTL product separation procedure

3. Results and discussion

3.1. Utilization of algae as wood slurries stabilizers

The difference in density between wood and water is the main reason for wood slurries separation. Wood particles separate either by settling or by floating as shown in Figure 4 (left). Small wood particles (<100-200 µm) have a large number of open, accessible pores that are rapidly filled with liquid causing the wood particle density to increase and thereby settling. Coarse particles contain a larger number of internal inaccessible pores thus the density of these particles will not increase significantly when immersed in water. These particles will have a tendency to float. In order to avoid settling or floating of wood particles, the viscosity of the liquid phase can be increased. This will restrict the mobility of wood particles and will ensure a uniform distribution of the solids in the slurry. Slurry dewatering that occurs under high pressure conditions due to the low interactions between the biomass and the liquid phase can be avoided by adding materials with a high water binding capacity. Usually, materials with water binding capacity also have thickening properties. Examples of such materials are some carbohydrates contained in algae. Algae addition into wood slurries may cause both viscosity and water holding capacity increase, and consequently improving the wood slurries stability (see Figure 4, middle and right).



Typical behavior of wood particles in water: settling and floating

Wood-algae slurries with low content of algae $C_{algae} < C_{wood}$

Wood-algae slurries with high content of algae $C_{algae} \geq C_{wood}$

Figure 4 Schematic representation of phase separation in wood aqueous slurries and stabilisation with algae hydrocolloids; high concentration of algae in the slurry is needed to ensure the contact and the entanglement of hydrocolloids

The ability of algae to develop viscosity, change the slurry texture and prevent dewatering might be related to the presence of hydrocolloids in algae. Hydrocolloids are long chain hydrophilic polysaccharides that form dispersions and have a common property: thickening. Some hydrocolloids are also able to provide stickiness or to form gels[44]. Polysaccharides such as ulvans (green seaweeds), alginates (brown seaweeds), fucoidans (brown seaweeds), carrageenan (red seaweeds) or agar (red seaweeds) are common thickeners and gelling agents used in the food industry and other sectors. In some seaweed species, these hydrocolloids represent the main fraction of polysaccharides, which makes the algae a good source of natural thickeners and gelling agents[45]. For example alginates may constitute between 10 wt% and 47 wt% of the dry weight of brown algae [45], carrageenan up to 50 wt% and agar between 20 wt% and 30 wt% of the dry weight of some red seaweeds species [45,46] and ulvans between 8 wt% and 29 wt% of the green seaweeds [39]. The thickening mechanism is based predominantly on nonspecific entanglement of polymer chains. This requires that the polymers are in contact and hence their concentration in solution needs to be sufficiently high [44]. Other factors that affect the thickening effect are the polymer chain length, molecular weight, type of solvent, temperature and time [41].

In Table 3, wood slurry containing 15 wt% dry matter is compared with algae slurries of identical solid loading in terms of texture, stability under the syringe and the centrifugation test and viscosity. With respect to the slurry texture, seaweeds and microalgae form with water pastes with homogeneous aspect, unlike wood that forms two-phase, non-cohesive mixtures with water. The type of algae also affects the slurry aspect; green seaweeds form yield stress fluids (that flow only when stress is applied), thicker than brown- or red seaweeds slurries that form with water free flowing, thin pastes. Microalgae slurries with 15 wt% dry matter content even have a lower viscosity than those obtained with brown- or red seaweeds. The transition of microalgae from a liquid-like to a paste-like consistency occurs at around 30 wt% dry matter content. At this concentration the microalgae slurry is a thin instead of a free-flowing paste. With respect to slurry stability (solids dewatering), there is a clear distinction between wood and algae slurries. With water, all algae form stable mixtures (according to the syringe test) while the wood slurry separates when passed through the syringe, as shown in Figure 1. Under centrifugal forces, 15 wt% wood-, 15 wt% seaweed- and 15 wt% microalgae slurries undergo dewatering while the 30 wt% microalgae slurry resists dewatering, as shown in Table 3. The presence of NaOH prevents brown seaweed slurries dewatering under centrifugation despite the fact that for both brown- and red seaweeds slurries the viscosity increases in presence of NaOH. A thickening effect is also noticed for the 30 wt% microalgae slurry in presence of NaOH. For the green seaweeds, alkaline conditions have negative impact on the slurry stability and also a thinning effect. The results in Table 3 show that unlike wood, algae form cohesive mixtures (stick together) and are less prone to dewatering. In general, alkaline conditions determined an increase of algae slurries viscosity and improved the stability of the brown seaweeds slurry. The results in Table 3 can be summarized by two main observations: 1) algae slurries have better stability than wood slurries, and 2) the most stable feeds are the 30 wt% microalgae and the 15 wt% alkaline brown seaweed slurries.

The viscosity-shear rate profiles of the 15 wt% seaweed slurries and the 30 wt% microalgae slurry are shown in Figure 5. All algae slurries showed a shear thinning (pseudoplastic) flow behaviour, typical for most thickeners above the critical overlap concentration [38]. Figure 5 (left hand side) shows that the 30 wt% microalgae slurry has the highest viscosity followed by the brown seaweed, green seaweed and red seaweed slurries. From Figure 5 (right hand side) and Table 3 it can be noticed that NaOH increased the viscosity of all algae pastes, except the green seaweed. For brown seaweed and microalgae the slurry viscosity in alkaline conditions increases more than ten-fold compared to neutral conditions while for the red seaweed the slurry viscosity increases about six-fold. Green seaweed *Ulva spp*. shows a significant decrease in viscosity in presence of alkalis, 12 to 14 - fold lower than in neutral conditions. The variation of slurries viscosity with the algae type may be related to the chemical structure, molecular weight, chain length and linearity of the algae polysaccharides. Ulvans, the main polysaccharides of green seaweeds, are water-soluble and develop low viscosity due to the branched structure and short chain length [39]. The decrease of green seaweed slurry viscosity in 1M NaOH solution may be related to the formation of the sodium form of ulvans that are not able to form gels [39]. Brown seaweeds are rich in alginates (gelling agent) and fucoidan (viscosifier). Fucoidan is soluble in both water and alkaline solutions [40] but for alginates only the sodium salt is water-soluble [41]. The addition of alkalis to an algae aqueous solution generates sodium-alginates[42] which may explain the increase of brown seaweed viscosity in NaOH solution. Red seaweeds are abundant in agar and carrageenans, well known and exploited gelling agents. Agar is not soluble in cold water while of the three types of carageenans (kappa, iota and lambda) only the lambda carrageenan and the sodium salts of kappa and iota are soluble in cold water[43]. Like brown seaweed, the formation of sodium salts of carrageenan may explain the increase of viscosity of red algae slurries in NaOH solution. The thickeners in microalgae are not well described in literature thus is not clear which are the compounds that develop viscosity in *Chlorella Vulgaris* slurries.

Table 3 Characterization of wood and algae slurries in water and NaOH 1M solution; the effect biomass type, biomass loading and solution pH on the slurries stability, viscosity and texture

Biomass type	Dry matter content (wt%)	Slurry texture		Dewatering *syringe test*		Dewatering *centrifugation test*		Viscosity[a] (Pa s)	
		H_2O	NaOH	H_2O	NaOH	H_2O	NaOH	H_2O	NaOH
Wood	15	Two-phases material, non-cohesive	Non-flowing, thick paste, non-cohesive	x	x	x	x	-	-
Green seaweed	15	Non-flowing, thick paste, cohesive	Flowing, thin paste, cohesive	✓	x	x	x	22	1.7
Brown seaweed	15	Flowing, thin paste, cohesive	Non-flowing, thick paste, cohesive	✓	✓	x	✓	29	~300[b]
Red seaweed	15	Flowing, thin paste, non-cohesive	Flowing, thin paste, cohesive	✓	✓	x	x	5	30
Microalgae	15	Flowing, liquid	Flowing, liquid	-	-	x	x	~0.09[b]	~0.16[b]
Microalgae	30	Non-flowing, thin paste, cohesive	Non-flowing, very thick paste, cohesive	✓	✓	✓	✓	65	-

[a] dynamic viscosity measured at shear rate of 2 s^{-1} at 20 °C [b] values predicted by extrapolation of the viscosity measurements performed at shear rate values below or above 2 s^{-1}.

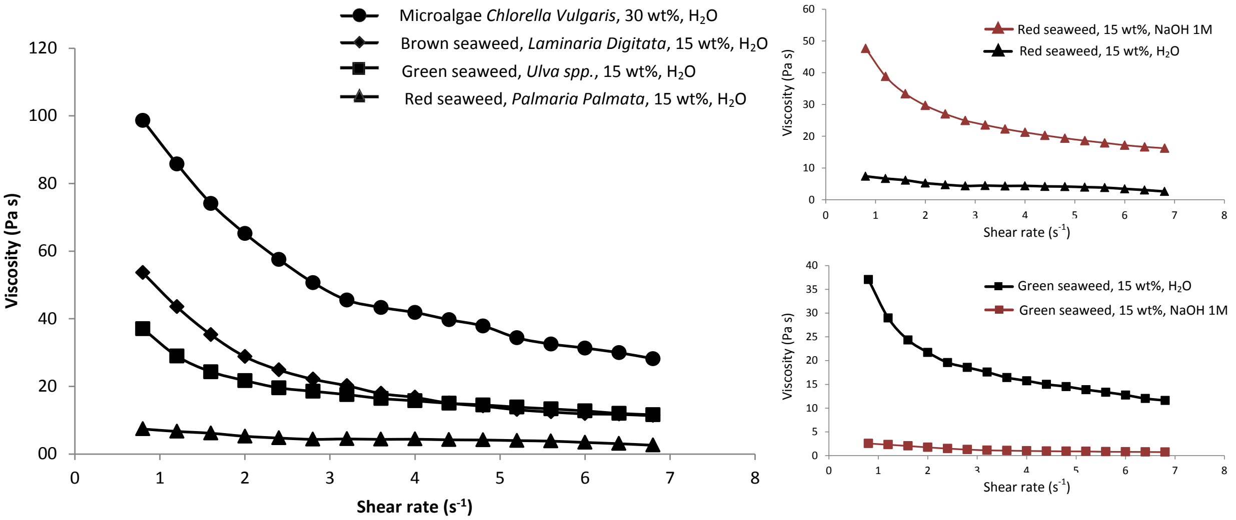


Figure 5 The viscosity of the algae pastes in water and sodium hydroxide solution against the shear rate

The next question of this study was how much wood can be co-processed with algae without affecting the algae slurry stability. For this purpose, brown seaweeds were mixed with wood in different ratios, to prepare mixtures with 20 wt% dry matter content. The slurries stability was evaluated according to the syringe test. As shown in Figure 6, the minimum ratio at which wood-brown seaweed slurries are stable is 1/1 which was defined as the critical algae-to-wood ratio (R*). Below this point the mixtures undergo separation and above the critical ratio the slurries stability and consistency do not change. Using the algae-to-wood ratio of 1/1, mixtures of wood and other algae types, in both water and NaOH solution were prepared.

The results in Table 4 show similar trends like those observed for the pure algae pastes (Table 3): all wood-algae mixtures are stable according to the syringe test, except the wood-green seaweed mixture. There are also important differences between the single-component and the two-component wood-algae slurries. One of them is the observed instability of the wood-microalgae slurry in water, when subjected to the centrifugation test. Apparently, the presence of wood particles in microalgae pastes reduces the ability of microalgae to bind the water. However, in presence of NaOH the stability of the wood - microalgae slurry is regained. Another difference is the improved stability of red seaweed slurry in NaOH solution when co-processed with wood. This might be related to the fact that wood absorbs the liquid in the system. Therefore the concentration of the algae in the solvent increases, enabling the hydrocolloids entanglement.

Table 4 The effect of algae type and solution pH on the stability of wood-algae slurries according to the syringe and the centrifugation test

Biomass	R	Dry matter content (wt%)	Dewatering *syringe test*		Dewatering *centrifugation test*	
			H_2O	NaOH 1M	H_2O	NaOH 1M
Wood-green seaweed	1/1	15	x	x	x	x
Wood-brown seaweed	1/1	20	✓	✓	x	✓
Wood-red seaweed	1/1	20	✓	✓	x	✓
Wood-microalgae	1/1	30	✓	✓	x	✓

R:wood/algae mass ratio

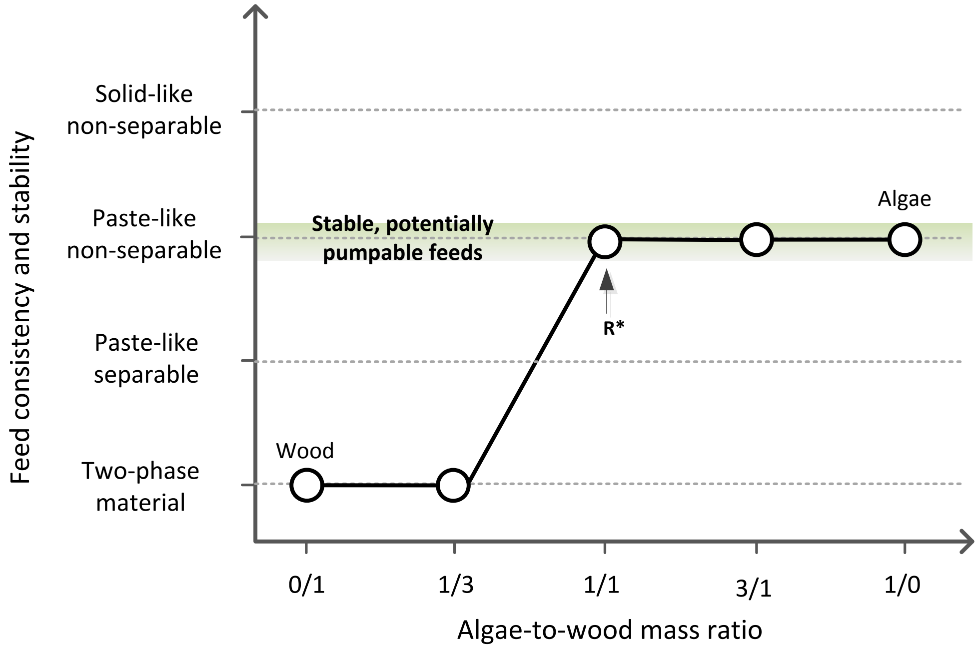


Figure 6 The variation of feed stability (according to the syringe test) with the increase of algae mass fraction; a study case for mixtures of willow and brown seaweed *Laminaria Digitata*; total dry matter of wood-algae slurries is 20 wt% and wood slurry 15 wt%

Figure 7 shows the water holding capacity (WHC) of the algae measured in neutral and alkaline conditions. The amount of water held by 1 g of algae represents the sum of capillary water, water bound to the polysaccharides and water trapped in the fiber matrix [47]. Wood and green seaweed *Ulva* *spp*. show similar WHC. Also, for both of them the WHC decreases in alkaline conditions. Brown and red seaweed species have similar WHC in neutral conditions and lower compared to green seaweed and wood. In alkaline conditions the WHC of brown seaweed increases with 28 % and with 8 % for red seaweed, relative to the values in neutral conditions. The microalgae show the lowest WHC capacity that increases with 32 % in alkaline conditions. Because microalgae have unicellular structure and no porosity, it can be assumed that all water held by microalgae is chemically bound. This is in contrast to wood which has a highly porous structure and establishes mainly weak interactions with water [48]. Therefore, seaweeds fall between these two extremes and it can be considered that their WHC is a combination of water absorbed by physical means and water bound chemically.

From the above it can be concluded that the water holding capacity of biomass is not a good parameter to predict the slurries stability. However, the water holding capacity can be used to approximate the maximum biomass loading of the slurry. Considering that the WHC of the biomass represents the maximum amount of water or solution that can be absorbed by 1 g of biomass, the amount of biomass that can absorb 100 g of water can be derived (equals to 100/WHC). From here, the theoretical maximum dry matter content in slurry (C*) prepared with 100 g of water can be calculated according to Equation (1):

$$C^{*}(wt\%) = \frac{m_{biomass}}{m_{biomass} + m_{H2O}} \times 100 = \frac{100/\mathrm{WHC}}{100/\mathrm{WHC} + 100} \times 100 \qquad (1)$$

According to this definition, a slurry with the maximum dry matter concentration C*, contains no free water (all the water being absorbed by the solid phase). This determines a change of the slurry aspect from paste-like to very thick paste or solid-like consistency. Slurries with dry matter content bellow the critical C* values are more likely to be pumpable. In Table 5, the calculated C* values are compared with the experimental C* values determined by visual observation of the slurry aspect.

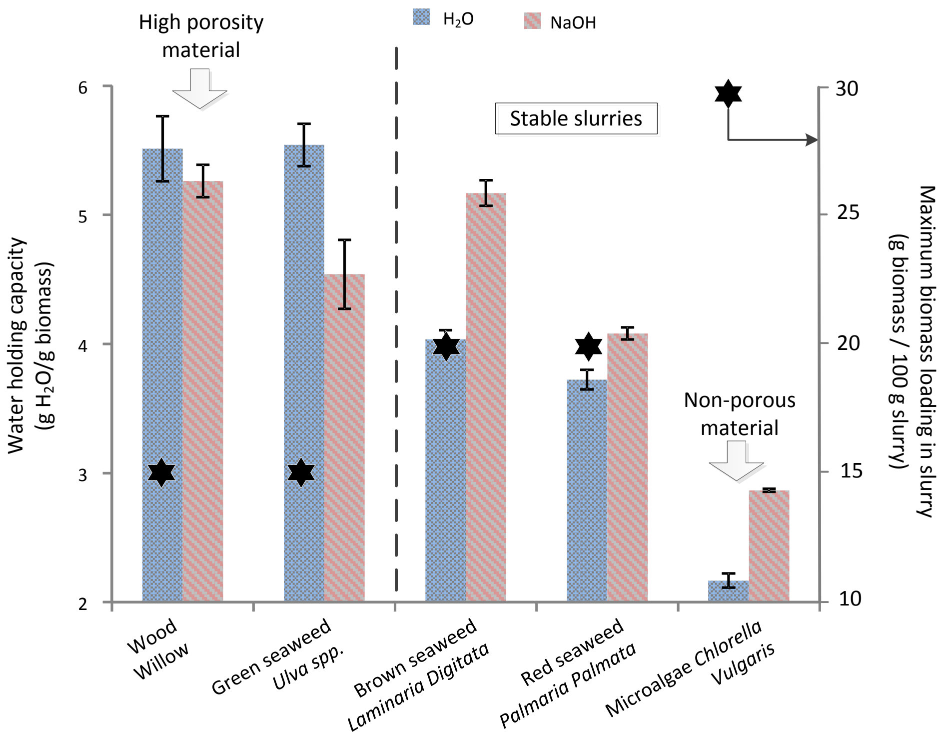


Figure 7 The water holding capacity of wood and algae measured by the centrifugation method and the maximum biomass loading of the wood-algae-water slurries with the composition given in Table 5; materials with high WHC yield slurries with low solids content

Table 5 Theoretical and experimental maximum biomass loading of single component wood and algae slurries prepared with water; the experimental values were obtained by visual observation of the point where mixtures consistency changes from paste-like to solid-like aspect

	WHC ($g_{H2O}/g_{biomass}$)	C* (wt%)	
		Calculated with Equation 1	Experimental
Willow	5.5±0.3	15.4	15.0
Green seaweed	5.5±0.2	15.4	15.0
Brown seaweed	4.0±0.1	20.0	20.0
Red seaweed	3.7±0.1	21.3	20.0
Microalgae	2.2±0.1	31.3	35.0

3.2. Hydrothermal liquefaction of wood-algae slurries

Alkaline wood-algae slurries were converted under supercritical water conditions. A reference feed containing wood only was also converted. In Table 6, the chemical composition of the feeds, the product distribution and the biocrude elemental composition are given. With respect to feed composition, the wood slurry biomass loading was increased with 5 % by co-processing with seaweed and with 15 % by co-processing with microalgae. However, the organic fraction of the wood-seaweed slurries is only slightly increased compared to the wood slurries while in the microalgae-wood feed the organic matter fraction is 63 % to 75 % higher than the wood-seaweed slurries. This clearly underlines the advantage of utilizing microalgae as co-stream for wood over macroalgae. The microalgae are advantageous due to the low ash content and the lack of a porous structure which contributes to the increase of the organic matter fraction and the biomass loading in the feedstock.

Table 6 Feed composition, average yields of the biocrude, water soluble organics and solids (wt%) and biocrude characterization; HTL conditions: 400 °C, 15 min reaction time, solvent NaOH 1M solution

	Willow	**Willow+ green seaweed**	**Willow + brown seaweed**	**Willow + red seaweed**	**Willow + microalgae**
Feed composition					
Total biomass (wt%, db)	15.3	20.0	20.0	20.0	30.0
Organic matter (wt%, daf)	15.0	16.8	16.3	17.5	28.5
NaOH (wt% of total feed)	3.4	3.2	3.2	3.2	2.8
Water/biomass ratio	5.7	4.0	4.0	4.0	2.3
Algae /wood ratio	0.0	1.0	1.0	1.0	1.0
Product yields (wt%, db)					
Biocrude	28.5±1.0	24.3±1.0	25.5±0.9	21.6±2.1	41.8±0.1
Char	6.6±1.3	16.2±1.7	10.5±0.7	12.5±0.4	9.2±0.5
WSO + gas (by diff.)	64.9	59.5	64.0	65.9	49.0
Biocrude					
C (wt%, db)	81.0±1.0	71.3±5.3	79.5±1.0	79.8±1.9	74.0±1.5
H (wt%, db)	7.8±1.6	6.7±0.9	7.6±0.6	7.8±0.4	8.0±0.1
N (wt%, db)	1.2±0.0	2.1±0.2	2.0±0.0	3.1±0.3	4.8±0.0
S (wt%, db)	0.06±0.0	0.18±0.0	0.23±0.0	0.31±0.0	0.26±0.0
O*	9.9	19.7	10.7	9.0	12.9
Carbon recovery (%)	48.2	38.7	48.0	40.6	63.1

*by difference (100-C-H-N-S); WSO = water soluble organics

Co-processing of wood with macroalgae is detrimental for biocrude yield. As shown in Table 6, the lowest biocrude yields were obtained from wood-seaweed mixtures with the lowest value for the willow-red seaweed, 22 wt% oil yield compared to 29 wt% from willow alone. The highest biocrude yield was obtained from the willow-microalgae feed, 42 wt%. Also the carbon recovery in biocrude has lower values for willow-green seaweed and willow-red seaweed derived oils compared to willow based oil. Despite the decrease of the biocrude yield for the case of willow-brown seaweed mixture, the carbon recovery value is similar to that of the pure willow case. The highest carbon recovery corresponds to the willow-microalgae mixture due to the higher biocrude yield obtained from this mixture. The low biocrude yields from seaweeds can be explained by the fact that they contain high fractions of carbohydrates that are converted into water soluble compounds, solid and gaseous products. Studies on model compounds showed that in general the carbohydrates have low conversion into biocrude: 5 wt% from algae carbohydrates (280 °C, no catalyst) [49], 15 wt% from corn starch (350 °C, no catalyst) [50] or between 8 wt% and 20 wt% from glucose (350 °C, without and with Na_2CO_3) [19]. Higher conversion of glucose and xylose into biocrude was obtained at supercritical conditions, between 28 wt% to 30 wt% (400 °C, with Na_2CO_3) [51]. Most of the polysaccharides are converted into water soluble compounds (61 wt%), gas phase (25 wt%) and solids (9 wt%) [49]. During HTL conversion, the polysaccharides are broken into various polar soluble compounds such as carboxylic acids, ketones or alcohols. These will remain in the water phase product or will be further converted into gaseous product. The presence of alkalis may reduce the formation water soluble compounds probably due to decarboxylation reactions that are promoted in alkaline conditions. In the same time, a reduction of solid products formation and an increase of the biocrude yield from carbohydrates is noticed when alkalis are used [19]. Proteins, a major constituent of microalgae, generate slightly higher biocrude yields, between 16 wt% and 30 wt% [49,50]. A large fraction of the proteins, between 35 wt% and 80 wt%, will form water soluble compounds and only small amounts will be converted into gases or solids [52,50]. The highest conversion into biocrude corresponds to lipids, 80 wt%. The oil yield from lipids may decrease in presence of alkalis due to formation of soluble compounds[52]. Thus the high biocrude yield from microalgae containing feedstock can be explained by the higher protein and lipid content in microalgae and lower carbohydrates fraction (see Table 1). Temperature also impacts the conversion of algae into biocrude. A study showed that the biocrude yield from various streams of microalgae can increase from 18 - 45 wt% to 46 – 58 wt% by increasing the liquefaction temperature from 250 °C to 375 °C [23]. In the current study, even higher temperature of 400 °C was used to benefit from the special properties of water at supercritical conditions such as high dielectric constant and high ionic product. These properties enhance the dissolution of biocrude molecules into the liquid phase and suppress the radical reactions that favor char formation [53].

The elemental distribution of biocrude oils is given in Table 6. Willow-based oil shows the highest carbon content and relative low oxygen. The highest oxygen content was identified in the willow-green seaweed biocrude which in consequence leads to the lowest carbon content. Relative high content of oxygen was also measured in the willow-microalgae mixture which also showed the highest nitrogen fraction 4.8 wt% compared to 1.1 wt% in the wood based biocrude. Sulfur and nitrogen were found in all algae derived biocrude oils. Sulfur is mainly originating from sulfated carbohydrates specific for algae and the nitrogen from proteins. The presence of sulfur and nitrogen heteroatoms is a common drawback in using algae for biocrude production.

Figure 8 shows the mass loss of the oil samples with temperature and Table 7 the mass fraction of the distillate ranges. As can be noticed from Figure 8, the degradation of the oils occurs in one step, beginning around 100 °C. Until 550 °C, between 78 wt% and 84 wt% of the biocrude is volatilized. The remaining non-volatile fraction, between 16 wt% and 22 wt%, represents the coke and the inorganic matter. About half of the biocrude was evaporated between 180 °C and 360 °C. This distillate range corresponds to the jet and diesel fuels suggesting the potential use of the biocrude oils in transportation sector. However, this would require the removal of oxygen, sulfur and nitrogen heteroatoms that can be achieved by intermediate hydrotreating of the biocrude [54]. Despite the differences in the chemical composition of willow and seaweeds, the biocrude oils derived from these feedstocks have very similar distillation curves. This suggests that carbohydrates and proteins generate compounds with similar boiling properties. Previous studies showed that carbohydrates and proteins generate various types of cyclic ketones and phenols with boiling point below or around 180 °C [19,51]. Lipids are converted in compounds like hexadecane or heptadecane which have the boiling point around 300 °C [19]. High boiling point compounds are also derived from lignin. The biocrude derived from the willow-microalgae mixture has a slightly higher fraction of volatiles with boiling point below 180 °C and between 360 °C and 550 °C compared to the oils derived from willow and willow-seaweed slurries. The reason for this deviation is unclear but one explanation could be the higher content of lipids that favor the formation of oil compounds with high boiling point and probably different structure of carbohydrates in microalgae that favor the formation of oil compounds with low boiling point. A detailed analysis of the composition of biocrude oils and the distillate fractions is necessary for better understanding the differences between microalgae and seaweeds derived biocrudes.

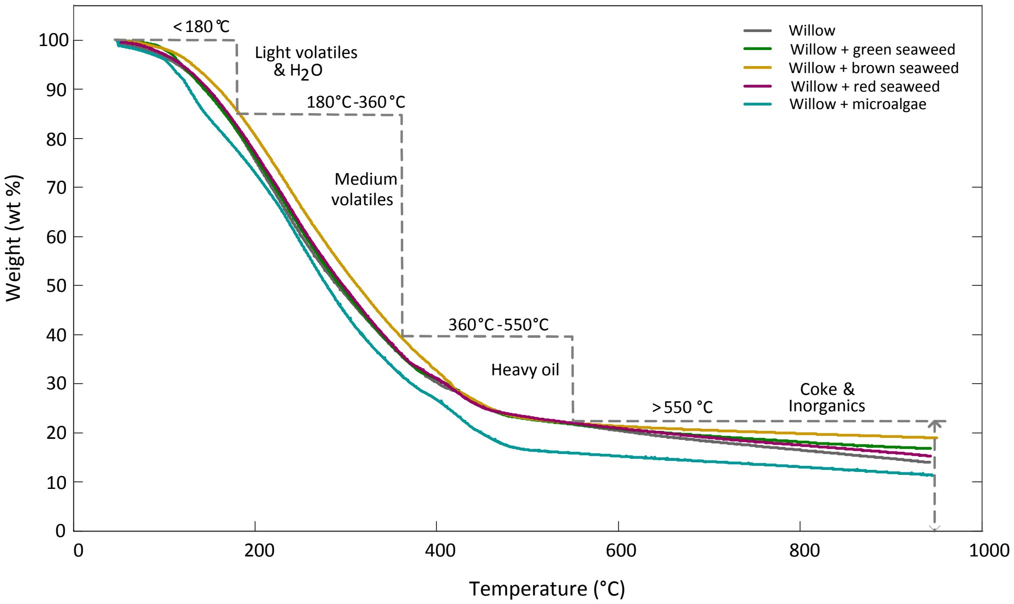


Figure 8 TGA curves of HTL biocrude oils obtained from willow and willow-algae liquefaction (TGA performed in nitrogen atmosphere, gas flow rate 20 mL/min, heating rate 10 °C/min)

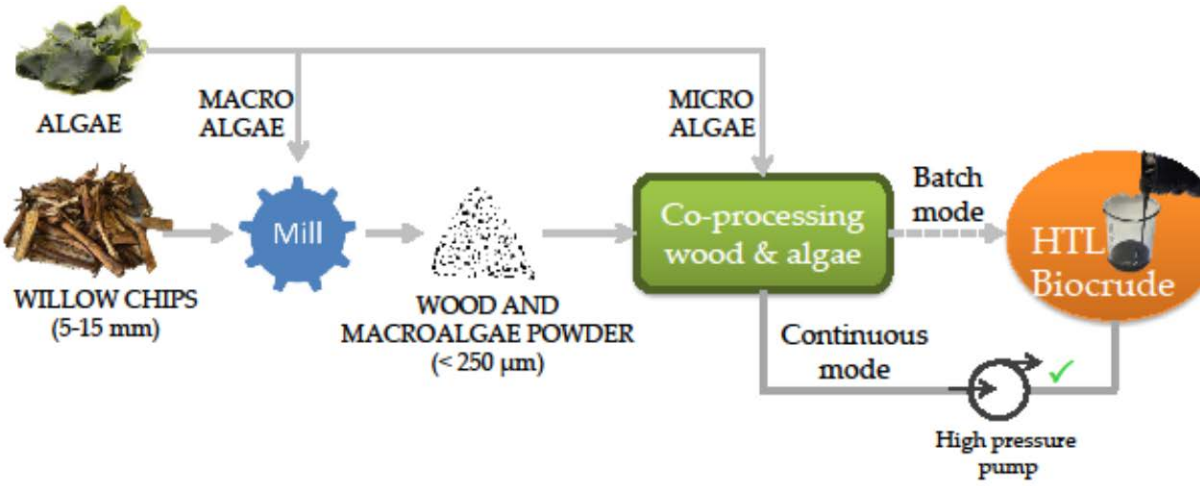
Table 7 The boiling point distribution of the biocrude oils obtained from willow and willow-algae liquefaction (wt%)

Distillate range		**Willow**	**Willow+ green seaweed**	**Willow + brown seaweed**	**Willow + red seaweed**	**Willow + microalgae**
Gasoline	<180 °C	18.4	18.3	14.3	17.4	22.4
Jet & diesel fuel	180 °C – 360 °C	45.6	45.8	46.0	46.3	45.6
Fuel oil	360 °C – 550 °C	14.2	14.2	17.7	14.3	16.2
Coke & ash	>550 °C	21.8	21.7	22	22	15.8

Conclusions

Wood slurries are one of the most difficult feedstocks to handle in continuous HTL. Solids dewatering, particles settling and low biomass loadings are the main disadvantages of woody biomass. These challenges can be tackled by co-processing wood with algae. The most suitable algae to improve wood slurries pumpability are brown seaweeds and microalgae mixed with wood in an algae-to-wood ratio of 1/1 or higher. The results indicate that wood-brown seaweeds mixtures with 20 wt% biomass loading and wood-microalgae mixtures with 30 wt% biomass loading could be suitable for continuous processing in HTL systems. Added benefits of co-processing wood and microalgae are increased biomass loading and increased biocrude yield. The main disadvantage of using algae as co-substrate is the introduction of sulfur and nitrogen heteroatoms into the biocrude. The high ash content of seaweeds is also a major drawback because reduces the fraction of organic matter in the feedstock. Co-processing of wood and algae is a novel approach in lignocellulosic biomass pretreatment for continuous HTL.

Graphical abstract



Acknowledgements

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