

## Fast Hydrothermal Liquefaction of Macro-Alga: Characterization of Products

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In this work, as a continuation of our previous study on fast hydrothermal liquefaction of macro-alga, the chemical compositions of bio-oil and water soluble products were further studied by Gas Chromatography Mass Spectrometry (GC-MS) and High Performance Liquid Chromatography (HPLC) techniques, respectively. Bio-oil produced at different hydrothermal liquefaction (HTL) conditions including holding time (5, 10, 15, 20 min), heating rate (585 and 321 °C/min), with and without KOH catalyst addition, were used in this study. The results show that water soluble products consist of mainly C5-C6 sugars and C4-C2 organic acids. The formations of these compounds were resulted from the de-composition of carbohydrates and alginate in the kelp biomass. Moreover, increasing heating rate and adding catalyst have similar effect on the compositions of the HTL bio-oil.

### 1. Introduction

The use of macro-algae biomass as feedstock for biofuel production possesses some advantages compared with other plant biomass. For example, being cultivated in sea water, macro-algae do not compete with arable land for food crops. Macro-algae allow a 3-dimensional growth, which can significantly reduce the surface area, in comparison with the 2-dimensional growing of plant biomass. During the growth, macro-algae absorb more CO<sub>2</sub> than terrestrial biomass due to their higher photosynthetic activity (Aresta et al., 2005). In addition, growing macro-algae can contribute to cleaning of water contaminated with urea (Elliott, 2011) and/or heavy metals (Raize et al., 2004).

There are several conversion methods for macro-algae for bioenergy applications. They include the production of bio-ethanol via fermentation of the sugars present in seaweed biomass (mannitol and laminarin for brown macro-algae) (Borines et al., 2013). Moreover, pyrolysis (Wang et al., 2007, Anastasakis et al., 2011) and direct combustion (Wang et al., 2009) of seaweed biomass are also possible.

Among the thermochemical conversions, hydrothermal liquefaction (HTL) (Yang et al., 2014, Anastasakis and Ross, 2015, Elliott et al., 2013, Bach et al., 2014, López Barreiro et al., 2013, Faeth et al., 2013, Anastasakis and Ross, 2011) is capable of producing high energy density bio-oil from algal biomasses, which have high moisture and alkali metal contents. The main products obtained from the hydrothermal process include bio-oil, solid residues, and water-soluble products. The bio-oil has high potential to replace the crude oil, the solid residues can be utilized as solid fuel for combustion, and water-soluble products can be subjected to fermentation for bioethanol production. The distribution of products can be controlled by varying the reaction conditions, which allows focusing on either solid or liquid fractions. In general, less severe reaction conditions offer more solids, and oppositely, more severe conditions produce more liquids.

Our recent paper (Bach et al., 2014) has revealed a method to produce high bio-oil yields, up to 79% on wet basis, from kelps, a variety of brown macro-algae. High through-put technique with rapid heating (up to 585 °C/min) was employed for the HTL process. Although the yield and fuel properties of bio-oil were investigated, the chemical compositions of bio-oil as well as water soluble products were not included. Therefore, this study is a continuation aims at characterization of the bio-oil and water-soluble products obtained from HTL of kelp in previous work. The bio-oils were analyzed by a Gas Chromatography – Mass Spectrometry (GC-MS) to

investigate the effects of heating rate and catalyst addition on their compositions. The compositions of WSP were studied by a High Performance Liquid Chromatography (HPLC).

## 2. Material and methods

### 2.1 Material

The feedstock used for this study is sugar kelp (*Laminaria Saccharina*), a brown macro-alga, which was harvested in June 2011 in Trondheim, Norway. The fuel characteristics including proximate, ultimate analyses and heating value of the kelp biomass are given in Table 1. The collected sample of kelp was frozen and stored in plastic bags at -20°C within 8 hours after the harvesting. The frozen kelp was de-frozen and washed in plenty of water to remove the sea salts before drying, grinding, sieving and wetting again to produce slurry solutions suitable for HTL.

Table 1. Characterization of the feedstock

Feedstock	Proximate analysis			Ultimate analysis					HHV
	Ash	VM	FC	C	H	O	N	S	
Sugar kelp ( <i>Laminaria Saccharina</i> )	16.58	69.32	14.10	47.27	6.16	42.27	3.59	0.72	16.10

### 2.2 Hydrothermal liquefaction

HTL experiments were carried out using quartz capillary reactors with a length of 200mm, and an inner diameter of 2 mm. Two different wall thicknesses of 1 and 2 mm were employed to investigate HTL at different heating rates (585 and 321 °C/min or high and low). Before loading, quartz reactors were cleaned with distilled water, dried, and then sealed at one end by an acetylene torch. After that, feed solutions (with or without KOH catalyst) were loaded into the reactor, which was purged with nitrogen (99.99%) and sealed at the other end. A cylindrical sand bath made of stainless steel (height of 25cm, diameter of 20cm), locating in a muffle furnace (Thermoconcept KC 64/13), was used as heating media of the reactors. The sand bath was pre-heated to a pre-set temperature and held for one hour to allow a thermal stability condition throughout the bath. Then, loaded and sealed reactors were quickly placed into the sand bath for HTL process. After a given reaction (holding) time, the reactors were quickly taken out and immersed in a water bath at room temperature to quench further relations. The reactors were then opened by cutting one end for products collection. Due to practical limitation and considerations, the gaseous products were not collected in this study, but calculated by mass balancing. For collecting the solid and liquid products, a long stainless steel syringe (Sigma Aldrich Z261297) was used to inject a mixture of dichloromethane and water into the reactors. The final products including solid residue (SR), bio-oil and water soluble products (WSP) were separated by centrifugal method. A more detailed procedure can be found in our previous paper (Bach et al., 2014).

### 2.3 Products characterization

The yield and fuel properties of HTL products have been reported in our previous paper (Bach et al., 2014). Information for the distribution of the main products is summarized and presented in Table 2. In this work, the chemical composition of the bio-oil is explored using Gas Chromatography Mass Spectrometry (GC-MS) technique. GC-MS apparatus consists of a Hewlett-Packard HP6890 Gas Chromatograph interfaced to a HP5973 Mass Selective Detector (Agilent, Denmark). Helium was used as carrier gas at a flow rate of 1.2 ml/min. In addition, the composition of the WSP was identified by a High Performance Liquid Chromatography (HPLC, Shimadzu, Japan). The system was equipped with an auto-injector (SIL-9A, Shimadzu, Japan) and an RI-detector, Shimadzu RID-6A.

Table 2. Distribution of HTL products

HTL conditions	350°C high heating rate and no catalyst				350°C and 15 min		
	5 min	10 min	15 min	20 min	High HR, no catalyst	Mid HR, no catalyst	Mid HR, catalyst
<b>Bio-oil</b>	59.9	70.3	79.3	74.5	79.3	64.8	66.9
<b>Solid residue</b>	23.0	18.8	15.1	19.7	15.1	17.7	16.8
<b>WSP</b>	19.1	15.3	11.1	10.2	11.1	15.3	18.6
<b>Gases</b>	8.0	7.2	7.6	8.0	7.6	12.9	8.8

### 3. Results and discussion

#### 3.1 Chemical composition of water soluble products

Figure 1 shows the concentration of main chemical compounds in the WSP obtained from HTL at 350°C and varied holding time (high heating rate and no catalyst). Dominant compounds include glucose (C6 sugar), arabinose (C5 sugar), succinic acid (C4 acid), lactic acid (C3 acid) and acetic acid (C2 acid). The formation of these sugars and organic acids is resulted from the de-composition of carbohydrates and alginate in the kelp biomass. It can be seen from the figure that the concentrations of arabinose, succinic acid, lactic acid show decreasing trends with increasing holding time, which can be explained by the degradation of these components over time. However, trends for glucose and acetic acid are unclear.

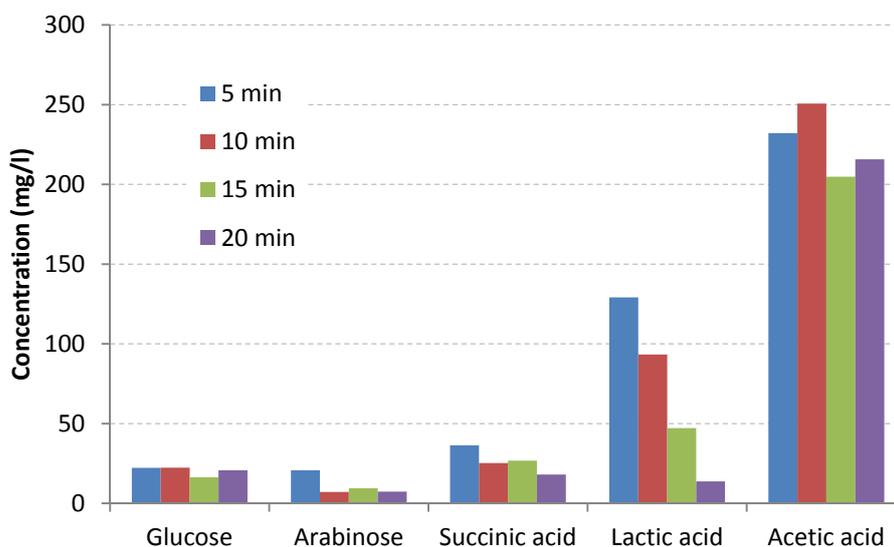


Figure 1. Effect of holding time on the composition of water soluble products

The effects of heating rate (HR) and catalyst on the yield and fuel properties of the bio-oil were found to be similar in our previous work. These effects (at 350°C and 15 min) on the composition of the WSP are presented in Figure 2. The figure shows that concentrations of main compounds in the WSP are reduced when high heating rate was applied, compared with the low one. Moreover, the trend is in good agreement with the yield of WSP, which shows a lower WSP yield when higher heating rate was applied for HTL. In addition, catalyst addition at low heating rate further enhances the concentrations of glucose, lactic acid and acetic acid but reduces those of arabinose and succinic acid.

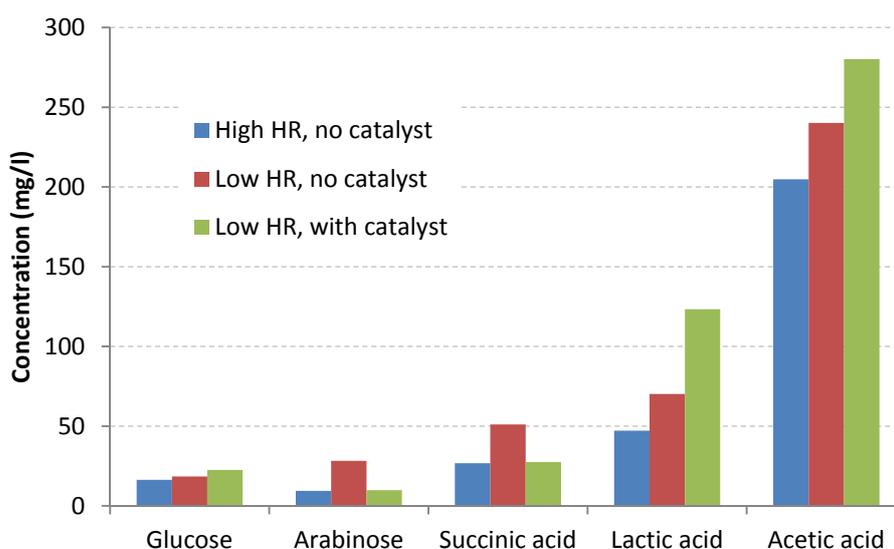


Figure 2. Effect of heating rate and catalyst addition on the composition of water soluble products

### 3.2 Chemical composition of bio-oil

GC-MS spectra for bio-oil samples (produced at high and low heating rates, with and without catalyst addition) are demonstrated in Figure 3. Chemical compounds in the bio-oil were identified using NIST library version 2.0 f. (Agilent, Denmark) and presented in Table 3. These bio-oil samples were produced at 350°C, 15 min and selected for GC-MS analysis as they showed relative higher yield compared with the others. The table shows that HTL bio-oil from kelp biomass consists of high fractions of dodecyl acrylate, phenol, 2,2-methylenebis(6-1,1-dimethyl)-4-methyl) and oleamide. Other compounds however have much lower fractions. Moreover, there are some compounds which are present only in the bio-oil produced at high heating rate or at low heating rate with catalyst such as furfurals, 2-cyclopenten-1-one, 3-ethyl-, pyrrolidine, 1-acetyl-, 2,5-pyrrolidinedione-1-ethyl. This again confirms similar effect of heating rate and catalyst addition in HTL with regarding to yield, fuel properties and chemical composition of the bio-oil.

Table 3. Chemical composition of bio-oil

Retention time	CAS number	Name of compound	Area (%)		
			High HR, no catalyst	Low HR, no catalyst	Low HR, catalyst
8.72	10504-04-8	furan-trimethyl	0.6	0.6	1.3
9.32	1121-05-7	2-cyclopenten-1-one-2,3-dimethyl	2.8	2.1	5.3
9.72	28790-86-5	2-cyclopenten-1-one-2,3,4-trimethyl	0.8	0.7	1.0
10.04	98-01-1	furfural	0.3		0.7
10.58	4466-24-4	5-ethyl-2-furfural	0.7		1.3
10.86	5682-69-9	2-cyclopenten-1-one, 3-ethyl-	0.6		1.6
11.87	872-50-4	2-pyrrolidinone, 1-methyl-	0.8	1.1	1.2
12.26	2687-91-4	1-ethyl-2-pyrrolidinone	1.3	1.5	1.0
12.34	60-12-8	phenylethyl alcohol	0.4	0.5	1.1
12.79	54-54-19-3	decyl propionate	2.5	5.7	2.7
12.99	57472-68-1	dodecyl acrylate	23.4	38.4	28.6
13.39	106-44-5	phenol, 4-methyl		3.0	4.2
13.66	4030-18-6	pyrrolidine, 1-acetyl-	0.7		0.9
13.97	2314-78-5	2,5-pyrrolidinedione-1-ethyl-	1.5		1.0
14.2	105-67-9	phenol, 4-ethyl	2.8	2.3	4.7
14.25	1121-07-9	2,5-pyrrolidinedione-1-methyl	1.9		
16.95	120-72-9	indole	3.2	6.6	3.3
17.23	83-34-1	skatol	1.9	1.7	2.3
22.15	119-47-1	phenol, 2,2-methylenebis(6-1,1-dimethyl)-4-methyl)	35.3	10.9	22.7
23.03	301-02-0	oleamide	18.5	24.8	15.1

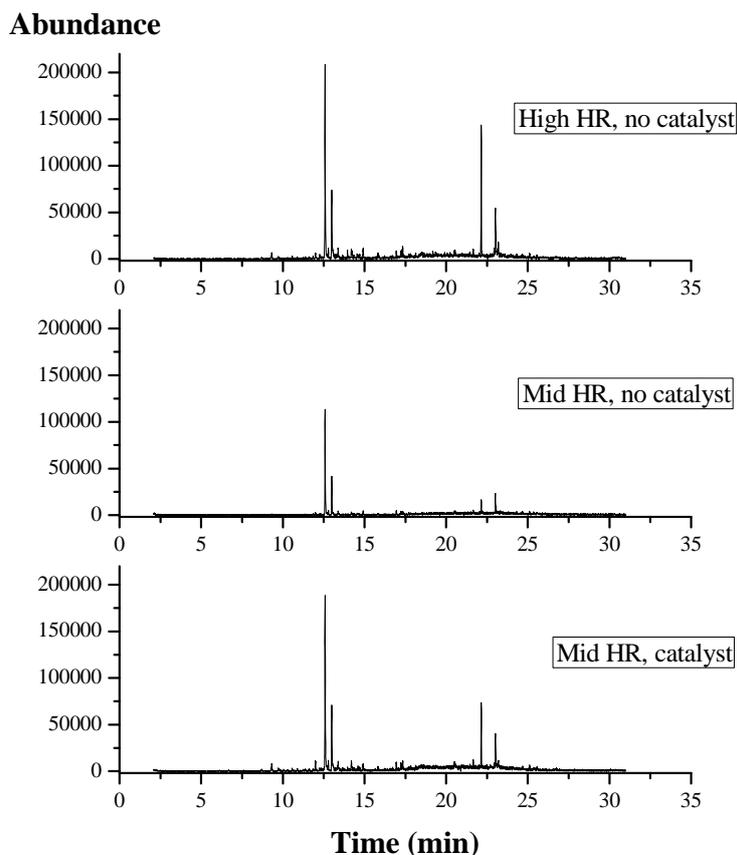


Figure 3. GC-MS spectra for bio-oil samples

#### 4. Conclusion

The chemical compositions of bio-oil and water soluble products obtained from fast HTL of kelp were studied by GC-MS and HPLC techniques. C5-6 sugars and C2-4 organic acids, products of carbohydrates and alginate de-composition, were found as the main compounds in the WSP. Arabinose, succinic acid, and lactic acid show reduced concentrations in WSP with increasing holding time. In addition, concentrations of main compounds in the WSP are reduced when high heating rate was applied.

On the other hand, dodecyl acrylate, phenol, 2,2-methylenebis(6-1,1-dimethyl)-4-methyl) and oleamide are the dominant compounds in bio-oil. Moreover, the results also reveal that increasing heating rate and adding catalyst have similar effect on the compositions of the HTL bio-oil.

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