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Pyrolysis of Seaweeds for Bio-oil and Bio-char Production

Jae Hyung Choi[a,b], Hee Chul Woo[b] and Dong Jin Suh[a,*]

[a]Clean Energy Research Center, Korea Institute of Science and Technology, 5, Hwarang-ro 14-gil, Seongbuk-gu, Seoul, 136-791, Korea
[b]Department of Chemical Engineering, Pukyong National University, 365 Sinseon-ro, Nam-gu, Busan, 608-739, Korea
*djsuh@kist.re.kr

A pyrolysis study on a species of brown algae *Saccharina japonica* was carried out in a fixed-bed reactor. The yields of bio-oil and bio-char obtained at 450 °C were 47 % and 33 %, respectively. The raw *S, japonica*, ethanol and acid pretreated samples and the resulting pyrolysis products were also characterized with respect to proximate and ultimate analysis, and higher heating value. The crude bio-oil fractionation by distillation under reduced pressure followed by catalytic hydrodeoxygenation (HDO) over Pd/C could be employed to upgrade the bio-oil. The higher heating value (HHV) of HDO bio-oil product was close to those of conventional gasoline and diesel.

1. Introduction

Biomass-derived fuels have received increasing attention to give a solution to the problems of fossil fuel depletion and global warming. Biofuels are considered to be carbon cycle neutral because CO_2 released into the atmosphere when burnt is fixed in the biomass by photosynthesis. In recent years, there has been considerable interest in producing biofuel from algae, a so-called third generation biofuel. Macroalgae (seaweeds) have a huge potential to be used as a source for the production of biofuels due to their high photosynthetic efficiency, fast growth rate, high carbohydrate content, no requirement of cultivation land area and no competition with food crops. The aquaculture production of macroalgae in the world has been increased continuously to 15 million wet-metric-ton with an annual growth rate of 10.5 % in 2010 (FAO yearbook, 2012). Various types and species of macroalgae have traditionally been cultivated for food in the coastal regions of East Asia. Among them, brown algae are the most suitable type for mass production in Korea because they grow more than red and green algae in the temperate regions.

Macroalgae can be converted to biofuels through biological and thermochemical routes. Pyrolysis is considered to be one of the most plausible conversion processes to produce biofuels by heating biomass in absence of oxygen. In literature, compared to pyrolysis of lignocellulosic biomass, there are limited studies on macroalgae pyrolysis. The yields of bio-oil from brown algae pyrolysis was not generally high, mostly lower than those of bio-char since the high ash content of the algae brought low bio-oil yield by secondary tar reaction. It is reported that the maximum yield of bio-oil depends on several parameters such as water and ash contents, biomass composition, pyrolysis temperature and vapor residence time (Fahmi et al., 2008). The pyrolysis products can also be affected by the morphology of biomass primarily due to heat transfer effects. Although fluidized-bed fast pyrolysis processes are known for the production of high yields of bio-oil, several other pyrolysis modes have been introduced to overcome their inherent disadvantages of a high level of carrier gas flow and the corresponding excessive energy requirements (Oyedun et al., 2012).

Crude bio-oil produced by pyrolysis cannot be used as fuel due to its high water and oxygen contents, and the presence of unsaturated and phenolic moieties (Bae et al., 2011). As a result, bio-oils need to be upgraded or treated to improve their quality before used for most applications.

The aim of this study was to investigate the feasibility of bio-oil and bio-char production from brown algae via a fixed-bed pyrolysis, fractionation by vacuum distillation, and catalytic hydrodeoxygenation.

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2. Materials and methods

2.1 Feedstock

Saccharina japonica, a brown alga, as a feedstock was supplied from Wando Island, Republic of Korea and used after drying. The feedstock was ground with a knife mill and sieved to obtain particles in the ranges of 3- 5 mm.

2.2 Fixed-bed pyrolysis

Pyrolysis was carried out in a cylindrical fixed-bed reactor (33 cm in length and 2.5 cm in diameter) filled with a screen mesh holder containing biomass particles. Nitrogen carrier gas was fed at a flow of 0.6 L/min for 10 min to remove air in the reactor before reaction. The pyrolysis vapour leaving the reactor was condensed in three condensers in series (room temperature, ice water and liquid nitrogen cooled). The condensed liquid (bio-oil) was collected in flask while the solid residue (bio-char) remained in the reactor. Pyrolysis conditions were as follows: temperature, 450 °C; holding time, 8 min.; Carrier gas flow rate, 0.6 L/min (2.0 cm/sec). The bio-char yield, defined as (solid dry weight) × 100 / (feed dry weight), was obtained by weighing the biomass holder before and after pyrolysis while the liquid yield was defined as (dry weight of collected liquids) × 100 / (feed dry weight). The gas yield was calculated from the balance.

2.3 Bio-oil distillation

The produced bio-oil was fractionated using a vacuum distillation apparatus. 1 L of the crude bio-oil was put in a round bottom flask with two necks; one neck for distillation temperature measurement and control and the other neck for connecting the distillation column with 10-theoretical plates. The temperature was monitored at the top of the distillation column while the system pressure was maintained by vacuum pump (N840 Diaphragm Pump, KNF, Germany).

2.4 Hydrodeoxgenation

The aqueous and non-aqueous fractions of bio-oil obtained by the vacuum distillation were further upgraded by catalytic hydrodeoxygenation (HDO). The catalytic reaction was performed in a bench-scale trickle-bed reactor with concurrent downflow of bio-oil and hydrogen. The reactor was a stainless steel tube of 475 mm in length and an inside diameter of 11 mm, which was placed in an electric furnace controlled by a temperature and a thermocouple located below the catalyst bed. The reaction pressure was maintained by a Tescom back pressure regulator. Hydrogen was introduced into the reactor via a mass flow controller (Brooks Instruments) from a gas cylinder manifold system. The bio-oil was fed into the reactor by HPLC pump (Shimadzu, Japan). The liquid products were cooled and collected using a chiller placed at the outlet of the back pressure regulator.

In a typical experiment, 25 mL of catalyst pellets were loaded on the supporting bed consisting of glass wool and glass beads. The reaction conditions were as follows: temperature, 300-400 °C; pressure, 100 bar; Liquid hourly space velocity (LHSV), 0.24-0.72 h^{-1}. The upgraded product yield was evaluated on the basis of the production of non-aqueous or organic phase oil from a feed bio-oil. The upgraded bio-oil was characterized by measuring elemental compositions (C, H, O, N and S), water, density, pH, and higher heating value (HHV).

2.5 Analytical methods

The proximate analysis of *S. japonica* determined the moisture and ash contents according to the ASTM standard methods E 1756 and E 1755. The content of volatile matter was determined using a non-isothermal thermogravimetric (TG) method by following the ASTM E 872-82 method. The content of fixed carbon was calculated by difference. The contents of volatile matter and thermal characteristics of *S. japonica* and bio-char were also obtained by the TG method. In the TG method, 20 mg of sample were heated in a thermogravimetric analyzer (TGA 2000, TA Co., USA) at the atmosphere of 30 mL/min of N_2. The temperature was programmed from room temperature to 1000 ^oC at a rate of 20.0 ^oC/min.

The elemental compositions (C, H, N and S) of the *S. japonica* and bio-oils were determined on an elemental analyzer (Thermo Fisher Scientific, FlashEA 1112). The moisture content of the bio-oils was determined through Karl-Fischer titration according to KS M 2115.

The organic components of bio-oils were qualitatively identified with a GC-MS (7890A, Agilent Technologies, HP-5 capillary column, 60 m × 0.25 mm × 0.25 μm). The GC oven temperature was held at 40 °C for 5 min, and programmed to ramp at 5 °C/min to 300 °C. And then the oven was kept at the final temperature for 10 min. The injector temperature was 280 °C, and an injection volume of 1 μL was adopted with the split ratio set as 50:1. The mass spectrometer was operated in full scan mode, and its mass range was 30–300 atomic mass units. The identification of the chromatographic peaks was based on an automatic library search (NIST library version 2.0).

3. Results and discussion

3.1 Feedstock characterization

The characteristics of the raw *S. japonica*, ethanol and acid pretreated samples for fixed-bed pyrolysis were summarized in Table 1. Since pyrolysis transforms any type of biomass into bio-oil and bio-char, residual biomass after extraction of value-added compounds (ethanol pretreatment) or pretreatment for further biological conversion (acid pretreatment) can be used for pyrolysis feedstock. The ash content of *S. japonica* was much higher than that of most lignocellulosic biomass while the carbon content was lower accordingly (Kim et al., 2012). The high ash content may inhibit the pyrolysis oil production, while leading to improved quality of bio-char as a soil amendment because inorganic nutrient contents remained high. A decrease of carbon and increase of oxygen contents after the ethanol pretreatment may be involved in mild oxidation of organic carbon constituents in *S. japonica* with hot ethanol. The ash content decreased drastically from 23 % to 1.46 % after the acid pretreatment.

Table 1: Proximate and ultimate analysis and heating value of S. japonica samples

Parameter	Types of biomass		
	Raw biomass	Ethanol pretreated[a]	Acid pretreated[b]
Proximate analysis (wt.%)			
Moisture[c]	2.79	2.14	1.51
Volatile matter[d]	70.90	74.96	74.58
Fixed carbon[e]	3.32	4.99	22.45
Ash[f]	22.99	17.93	1.46
Ultimate analysis(wt.%, dry basis)			
Carbon	42.09	30.10	38.46
Hydrogen	4.38	4.73	4.57
Nitrogen	1.53	1.10	0.68
Sulfur	0.40	0.46	0.48
Oxygen[e]	51.60	63.61	55.81
HHV[g] (MJ/kg)	14.05	9.16	13.05

[a] Pretreated in a 98 wt.% bioethanol solution with reflux for 180 min.
[b] Pretreated in a 5 wt.% H_2SO_4 solution at 100 ^oC for 500 min.
[c] Determined according to the ASTM E 1756 standard method.
[d] Determined by thermogravimetric analysis.
[e] By difference.
[f] Determined according to the ASTM E 1755 standard method.
[g] The higher heating value (HHV) was estimated by the correlation of Channiwala and Parikh (2002).

3.2 Fixed-bed pyrolysis

The results of fixed-bed pyrolysis of the raw and pretreated *S. Japonica* were summarized in Table 2. Compared with traditional fast pyrolysis, fixed-bed pyrolysis produced more char and less oil. The product distribution was found to be quite dependent on pretreatment. Pretreatment decreased bio-oil yield and increased that of non-condensable gases without any noticeable change in bio-char yield. These results may be associated with the loss of condensable carbon sources by the pretreatment, as evidenced by changes in carbon and oxygen content as shown in Table 1. It was reported that the ash such as alkali and alkaline earth metals in biomass served as catalysts in degrading condensed bio-oil to gas, leading to reduced bio-oil yield (Fahmi et al., 2008). Therefore, the dominant factor for determining the yield of bio-oil from fixed-bed pyrolysis of acid pretreated *S. japonica* was the loss of condensable carbon sources rather than ash removal. As expected, bio-char produced from the acid pretreated *S. japonica* had an increased carbon content and HHV with only a small ash content. This kind of bio-char can be used as a solid fuel source.

It was observed from TGA results that thermal decomposition of *S. japonica* into bio-oil, bio-char, and gases occurred over the temperature range 200-500 ^oC, mostly 200-350 ^oC, which can be divided into three stages (Figure 1). The first stage at temperatures up to 190 ^oC corresponded to dehydration. The second stage between 200 and 270 ^oC was associated with the decomposition of carbohydrates such as alginic acid, laminarin, fucoidan and mannitol. The third stage up to 350 ^oC was a result of the decomposition of proteins. TGA curves of the feedstocks and their corresponding bio-chars at

temperatures higher than 350 ^{o}C were quite similar, indicative of further decomposition of bio-char into solid residues.

Table 2: Results of fixed-bed pyrolysis of S. japonica samples

Parameter	Types of biomass		
	Raw biomass	Ethanol pretreated	Acid pretreated
Product Yields (wt.%)			
Bio-oil	47.0	44.4	37.3
Biochar	33.2	32.6	32.0
Gas	19.8	23.0	30.7
Proximate analysis of bio-char (wt.%)			
Moisture[a]	1.90	2.58	3.64
Volatile matter[b]	29.75	35.41	26.97
Fixed carbon [c]	7.46	13.15	68.00
Ash[d]	60.89	48.86	1.39
Ultimate analysis of bio-char (wt.%, dry basis)			
Carbon	47.57	31.95	66.06
Hydrogen	2.35	2.18	2.79
Nitrogen	1.75	1.11	1.44
Sulfur	2.32	0.80	0.30
Oxygen[c]	46.01	63.96	29.41
HHV[e] (MJ/kg)	13.54	6.14	23.28

[a] Determined according to the ASTM E 1756 standard method.
[b] Determined by thermogravimetric analysis.
[c] By difference.
[d] Determined according to the ASTM E 1755 standard method.
[e] The higher heating value (HHV) of bio-char was estimated by the correlation of Channiwala and Parikh (2002).

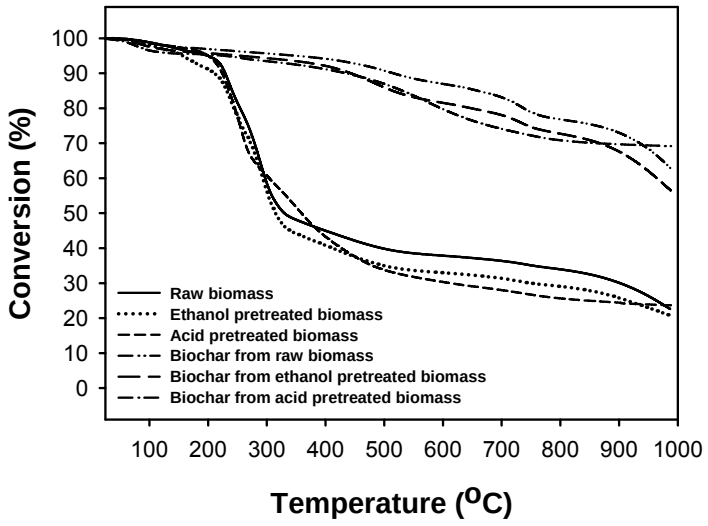

Figure 1. TGA profiles of S. japonica samples and their corresponding bio-chars

3.3 Bio-oil distillation

Bio-oil is a thermally unstable mixture of hundreds of oxygenated organic compounds. Atmospheric distillation at high temperatures is thus not considered to be a suitable technique for the crude bio-oil separation (Brown, 2011). Distillation under reduced pressure allows thermally unstable compounds to be distilled at lower temperatures. As shown in Table 3, the three distilled fractions of the crude bio-oil were obtained at temperature 25-160 ^{o}C with a reduced pressure of 40 mmHg: the fraction I (first distillate, boiling point (bp) < 40 ^{o}C), the fraction II (second distillate, 40 ^{o}C < bp < 160 ^{o}C), and the residue (third

distillate, bp > 160 °C). The lightest fraction (fraction I) containing mostly water was more than 50 % of the crude bio-oil, but not used for further catalytic upgrading. The fraction II could be separated into two liquid phases: the upper non-aqueous portion and the lower aqueous portion. The H/C ratio of fraction II was in the range of 1.58-1.65, which is closer to the value for aromatics rather than for alkanes. Bio-oil is composed of heterocyclic aromatic compounds such as 1-(2-furanyl)-ethanone, dianhydromannitol, isosorbide and cyclopentene etc (Kim et al., 2012). Bio-oil is known to be a complex mixture of oxygenated organic compounds. The aqueous phase oil (O/C = 0.40) contained more quantities of oxygenated compounds than the non-aqueous phase oil (O/C = 0.12). The distilled bio-oil was upgraded by catalytic hydrogenation to remove oxygen and saturate double bonds, leading to an increased H/C and decreased O/C. The lower H/C ratio of solid coke implies a high degree of unsaturated structures like aromatic compounds.

Table 3: Results of reduced pressure distillation of S. japonica bio-oil

	Distillation Temp. (°C)	Yield (wt.%, wet basis)	Water content (wt.%)	Ultimate analysis (wt.%)					Appearance
				C	H	O	H/C	O/C	
Fraction Ⅰ	<40	58.3	96.2	-	-	-	-	-	Bright yellow
Fraction Ⅱ	40-160	24.7	-	-	-	-	-	-	Phase separation
Non-aqueous phase		5.9	2.0	71.81	9.48	11.71	1.58	0.12	Dark brown
Aqueous phase		18.8	25.9	40.55	5.58	21.88	1.65	0.40	Orange
Residue (solid coke)	>160	15.4	-	68.63	5.54	20.50	0.96	0.22	Black
Loss	-	1.6	-	-	-	-	-	-	-

3.4 Hydrodeoxygenation

Most studies on catalytic upgrading to date have been done using model compounds of bio-oil rather than real bio-oil. In this work the distillate fraction II was used as feedstock for catalytic upgrading by hydrodeoxygenation. A commercial carbon supported palladium (1 wt/% Pd/C, Aldrich) was chosen as catalyst. The maximum yield of HDO product oil was 0.37 g/g feed under the reaction conditions of 400 °C, 0.48 h^{-1} LHSV and 100 bar H_2 pressure. The fuel properties of HDO bio-oil product were compared with those of gasoline and diesel (Table 4 and Figure 2). The HHV of HDO bio-oil product with decrease of its oxygen content from 21.9 % to 8.7 % was increased to 37.5 MJ/kg compared with 18.9 MJ/kg of macroalgae bio-oil (Trinh et al., 2013), approached to 45 MJ/kg of conventional gasoline and diesel. As expected, the H/C ratio of the HDO product increased with decreasing the O/C ratio. The double bonds of unsaturated compounds were saturated by hydrodeoxygeation. Particularly in the aqueous phase of the distillate fraction II, heterocyclic aromatic compounds such as dianhydromannitol and isosorbide could also be deoxygenated. According to total ion chromatograms, the HDO product comprising 16.2% aliphatics, 18.2% aromatics, 29.4% cyclopentanes, 5.1% cyclohexanes, 20.7% heterocyclics, and 10.4% furanes showed a somewhat similar pattern to gasoline (Figure 2).

Table 4: Fuel properties of HDO bio-oil produced from S. japonica compared with typical properties of gasoline and diesel

Properties	This work	Gasoline[a]	Diesel[a]
Moisture content (wt.%)	1.23	0.0035	0.0042
Density (@ 15 °C, kg/m^3)	955.5	700.4	822.8
pH	5.4	-	-
Ultimate analysis (wt.%)			
Carbon	75.10	82.68	86.58
Hydrogen	9.6	15.13	13.41
Nitrogen	3.20	0.0016	0.0005
Sulfur	0.11	0.0006	0.0005
Oxygen	8.68	2.09	0.01
HHV (MJ/kg)	37.54	45.80	45.96

[a] Summer gasoline and diesel in Republic of Korea

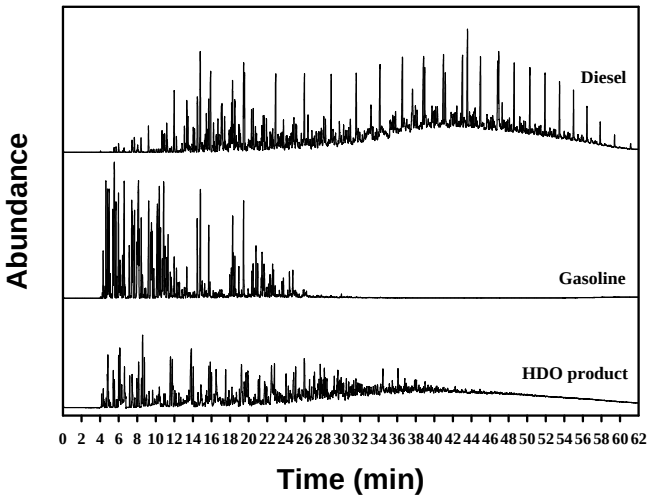

Figure 2. Total ion chromatograms of the HDO product, gasoline and diesel

4. Conclusion

Bio-oil and bio-char were produced by pyrolysis of a species of brown algae *Saccharina japonica* in a fixed-bed reactor at 450 ^{o}C. The yields of bio-oil, bio-char and non-condensable gases were 47 %, 33 % and 20%, respectively. Pretreatment of *S japonica* with ethanol or acid decreased bio-oil yield due to loss of condensable carbon sources. The crude bio-oil was fractionated into three fractions by distillation with a reduced pressure 40 mm Hg. The second fraction under boiling point range of 40-160 ^{o}C was upgraded by catalytic hydrodeoxygenation (HDO). The maximum yield of HDO product over 1 wt.% Pd/C was 0.37 g/g feed under the reaction conditions of 400 ^{o}C, 0.48 h^{-1} LHSV and 100 bar H_2 pressure. The H/C ratio of the HDO product increased with decreasing the O/C ratio. The higher heating value (HHV) of HDO bio-oil product was increased to 37.5 MJ/kg from 18.9 MJ/kg for macroalgae bio-oil, close to those of conventional gasoline and diesel (45 MJ/kg).

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