

Catalytic activity of palladium and copper based catalysts for macroalgal bio-oil hydrotreatment

Jae Hyung Choi¹, Dong-Ha Lim¹, Hee-Chul Woo^{2*}

1 Green Materials and Processes R&D Group, Korea Institute of Industrial Technology, 55 Jongga-ro, Jung-gu, Ulsan, 44413, Korea

2 Department of Chemical Engineering, Pukyong National University, 365 Sinseon-ro, Nam-gu, Busan 48547, Korea
(woohc@pknu.ac.kr)

ABSTRACT

Catalytic hydrotreatment of macroalgal bio-oil using supported palladium and copper chromite catalysts was systematically studied. The aqueous fraction of brown algal bio-oil (BABO) produced by fast pyrolysis was used as feedstock and was hydrotreated in temperature range of 250-400 °C at LHSV 0.48 h⁻¹ and 10 MPa H₂ using a trickle bed reactor. The yields of the organic phase products over the 5wt% Pd/Al₂O₃ and CuCr₂O₄ catalysts were maximal 42.33 wt% and 39.73 wt% at 350 °C, respectively. When the reaction temperature increased, the H/C ratio of the organic products increased with decreasing the O/C ratio. The carbon double bonds along with proof of unsaturated compounds were saturated by catalytic hydrotreatment. The supported palladium catalysts produced more furans and esters with increasing carboxylic acids in aqueous phases, whereas the copper chromite increased the heterocyclics and phenolics.

Keywords: Macroalgae, Brown algae, Bio-oil, Catalytic upgrading, Hydrotreatment

NONMENCLATURE

Abbreviations

HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HDN	Hydrodenitrication
BABO	Brown algal bio-oil
DOD	Degree of deoxygenation

1. INTRODUCTION

Biomass-derived fuels are renewable carbon source as petroleum replacement for climate change and fossil fuel depletion. Macroalgae (i.e., seaweeds) biomass have attracted a potential feedstock of renewable energy because of their fast growth rate, high productivity, high photosynthetic efficiency, and great potential for carbon dioxide fixation [1]. Among them, brown algae (e.g., *Saccharina japonica*) are naturally abundant in coastal waters and can be the most promising species for bioenergy and biorefinery resource because they contained various polysaccharides of alginate, mannitol, laminaran and fucoidan [2].

Liquid biofuels can be easily produced from brown algae via pyrolysis and catalytic upgrading processes. The liquid biofuels have a higher energy density and lower transportation cost than gaseous biofuels [3]. Biomass pyrolysis is a technique of chemical decomposition from organic matter in absence of oxygen for bio-oil production. The Bio-oils are highly polar, containing about 35-40 wt% oxygen on dry basis, while petroleum oils contain oxygen at ppm levels [4]. Especially, the bio-oil derived from *Saccharina japonica* as brown algae is a very complex mixture of water, carboxylic acids, aldehydes, ketones, alcohols, esters, and anhydrosugars [5]. The organic fraction in bio-oil is characterized by the wide distribution of polarity and molecular weight, which poses challenges to the efficient separation. Even worse, bio-oil is produced under thermodynamically non-equilibrium conditions, thus some oxygenated components in bio-oil tend to react with each other (e.g., polymerization, condensation, esterification, and etherification) at room or higher temperatures, leading

to storage instability of bio-oil [6]. For overcoming this problem, the catalytic hydrotreatment process for hydrodeoxygenation can convert the bio-oil or its fractions into specific fuels and chemicals. The HDO catalysts of bio-oil have been investigated for noble metal-based catalysts (Ru/Al₂O₃, Ru/C, Ru/TiO₂, Pd/C and Pt/C) [7] and non-noble metal-based catalysts (CoMo, NiMo, NiW, Ni, Co, and CuCrO [8].

In this study, the catalytic hydrotreatment efficiency of brown algal bio-oil (BABO) were investigated to overcome low heating value, high oxygen and moisture contents and high viscosity. The influence of hydrotreating parameters over alumina supported palladium (5 wt% Pd/Al₂O₃) and copper chromite (CuCr₂O₄) catalysts in a trickle bed reactor was investigated, and then their products on physical and chemical properties were analyzed by elemental analyzer, GC/MS, FT-IR, ¹H NMR.

2. EXPERIMENTAL

2.1 Brown algal bio-oil feedstock

Crude bio-oil used in this study was obtained by the fast pyrolysis of brown alga *S. japonica* in a fixed-bed pyrolysis at 450 °C, details of which are reported elsewhere [9]. The aqueous fraction of crude bio-oil was used as the bio-oil feedstock for catalytic hydrotreatment. To calculate mass balance, it was analyzed for carbon, hydrogen, nitrogen, sulfur, oxygen, and water content, as presented in Table 1.

Table 1. Properties of aqueous bio-oil fraction as a feedstock.

Elemental analysis (wt%)					HHV ^a (MJ/kg)	Moisture content (wt%)	Apparent density (g/mL)
C	H	N	S	O			
40.55	8.45	1.47	0.03	44.90	17.77	25.90	1.150

^a Estimated by the correlation of Demirbas et al. [10].

2.2 Catalytic hydrotreatment

The catalytic hydrotreatment was performed at a pressure of 10 MPa H₂ in a bench-scale trickle bed reactor with cocurrent downflow of bio-oil and hydrogen. The reaction pressure was maintained by a Tescom back pressure regulator. Hydrogen was introduced into the reactor via a mass flow controller (5850S, Brooks Instruments) from a gas cylinder manifold system. The bio-oil was fed into the reactor by HPLC pump (515 HPLC Pump, Waters). 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 consisted of glass wool and glass beads. The reaction conditions were controlled as follows: temperatures of 250-400 °C and liquid hourly space velocities (LHSV) of 0.48-1.20 h⁻¹.

In practice it is not possible to evaluate the conversion of each individual component in the bio-oil. The products yield of aqueous-phase hydrotreating was evaluated on the weight basis of the production of oil and aqueous phases from a feed bio-oil. Several important gross parameters were used for evaluation the carbon mass balance and the degree of deoxygenation (DOD) as:

$$\text{Organic phase (wt\% C)} = \frac{\text{wt\% yield}_{\text{organicphase}} \times \text{wt\% C}_{\text{organicphase}}}{\text{wt\% C}_{\text{feed}}}$$

$$\text{Aqueous phase (wt\% C)} = \frac{\text{wt\% yield}_{\text{aqueousphase}} \times \text{wt\% C}_{\text{aqueousphase}}}{\text{wt\% C}_{\text{feed}}}$$

$$\text{Gases (wt\% C)} = 100 - \text{organic phase (wt\% C)} - \text{aqueous phase (wt\% C)}$$

$$\text{DOD} = \left(1 - \frac{\text{wt\% O}_{\text{organicphase}} + \text{wt\% O}_{\text{aqueousphase}}}{\text{wt\% O}_{\text{feed}}} \right)$$

where wt% C_{organic phase}, wt% C_{aqueous phase} and wt% C_{feed} are the percentage of carbon in products and feedstock, respectively. wt% O_{organic phase}, wt% O_{aqueous phase} and wt% O_{feed} are the percentage of oxygen in products and feedstock, respectively.

2.3 Analytical methods

The moisture content of the bio-oil feedstock and hydrotreated products was determined by Karl-Fischer (CA-200, Mitsubishi) titration according to the ASTM E203 method. Elemental compositions (C, H, O, N, and S) of the samples were determined with the following elemental analyzers: the content of carbon, hydrogen, and nitrogen (FLASH 2000, Thermo Scientific, ASTM D5291), the sulfur content (NSX-2100V, Mitsubishi Chemical Analytech, ASTM D4294), and the oxygen content (FLASH 1112 series, Thermo Finnigan, ASTM D5622). The average value of three replicate measurements of the samples was reported according to ASTM test methods in Korea Petroleum Quality and Distribution Authority (KPetro). The higher heating value (HHV) of the samples was calculated based on the modified Dulong's formula [10] as follows:

$$\text{HHV (MJ/kg)} = 0.338 \times C + 1.428 \times [H - (O/8)] + 0.095 \times S$$

where C, H, O, and S are the mass percentages of carbon (C), hydrogen (H), oxygen (O), and sulfur (S), respectively, obtained from ultimate analysis.

The organic components of the samples were qualitatively identified with gas chromatography-mass spectrometry (GC-MS 7890A, Agilent Technologies, HP-5ms capillary column, 60 m × 0.25 mm × 0.25 μm). The GC oven temperature was held at 40 °C for 5 min, and was programmed to ramp at 5 °C/min to 300 °C. Then, the oven temperature was kept at 300 °C 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). The functional groups of the samples were measured by Fourier Transform Infrared Spectroscopy (Nicolet iS50R, Thermo Scientific) with the attenuated total reflectance (ATR) method. The ¹H Fourier Transform Nuclear Magnetic Resonance Spectrometer (FT-NMR) spectra were determined using a JEOL JMS ECP-400 spectrometer at 400 MHz in deuterated solvents (i.e., CCl₃D-d for organic phase and DMSO-d₆ for aqueous phase).

3. RESULTS AND DISCUSSION

The noble-metal catalysts (5 wt% Pd/Al₂O₃) and transition-metal catalyst (CuCr₂O₄) were selected for catalytic hydrotreatment of the BABO. The bio-oil hydrotreatment was performed at 250–400 °C to investigate effects of reaction temperature at LHSV 0.48 h⁻¹ and 100 bar H₂ for 9 h. Fig. 1 showed the results of bio-oil hydrotreatment over 5 wt% Pd/Al₂O₃ and CuCr₂O₄ catalysts. Almost all of the hydrotreatment experiments resulted in two liquid phases: an orange aqueous phase and a brown oil phase with a lower density than that of the water phase. However, the hydrotreated product obtained at up to 250 °C was difficult to distinguish for a phase separation, and this result was also reported in the literature [11] for the mild hydrotreatment of bio-oil derived wood. The highest yield of oil phase from the BABO over 5 wt% Pd/Al₂O₃ and CuCr₂O₄ catalysts at 350–400 °C was 43.8 wt% and 40.0 wt%, respectively. This results were compared with

carbon and water content in hydrotreated products changed during bio-oil hydrotreatment. The decrease of the oxygen content in the oil phase with increasing hydrotreatment temperature contributed to the increase of its carbon content (Fig. 2). This results implies that hydrophobic (i.e., non-polar) components were produced by HDO, HDS, HDN, hydrocracking, etc. [12]. In degree of deoxygenation, the 44.9 wt% of oxygen content in the oil phase using 5 wt% Pd/Al₂O₃ and CuCr₂O₄ catalysts at 350–400 °C was decreased to 11.8 wt% and 6.1 wt%, respectively. The remaining oxygen of incomplete HDO may be caused by the presence of less reactive aromatic oxygen components (e.g., phenolics) where C-O bonding in aromatics is more durable (422–468 kJ/mol) than one in aliphatics. The remained oxygen in oil phase were mainly phenolics. In addition, the presence of nitrogen components and water cause lower HDO efficiency [12,13]. When the reaction temperature increases, the degree of desulfurization increased with decreasing up to 0.03 wt% of sulfur content in oil phases.

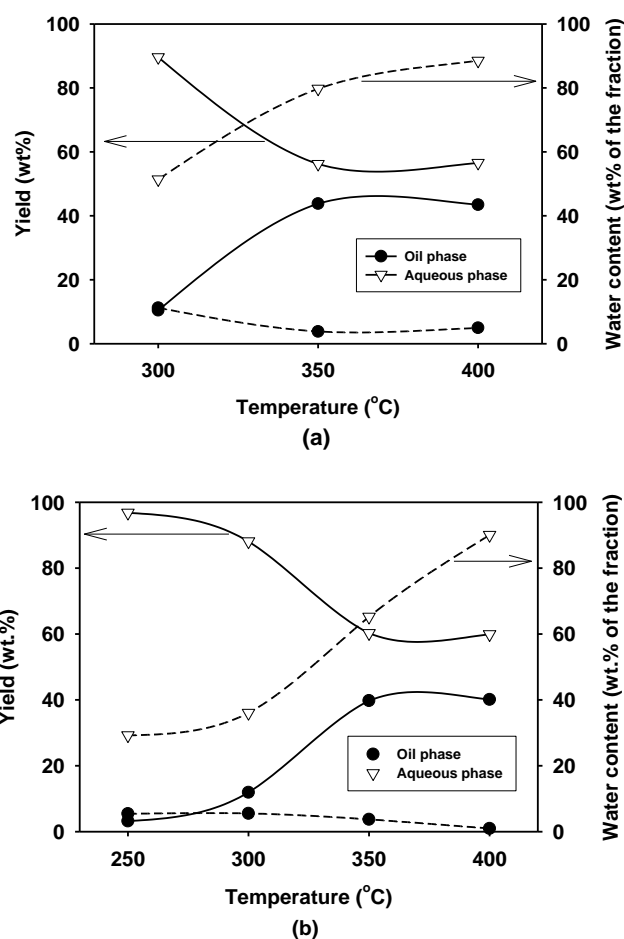


Fig. 1. Effect of reaction temperature on the product yields and water content over (a) 5 wt% Pd/Al₂O₃ and (b) CuCr₂O₄ catalysts.

However, the used catalysts and process parameters could not achieve satisfactorily HDN process because the reaction rate of HDN was generally lower than the one of HDS [12,13].

The $^1\text{H-NMR}$ spectra showed signal characteristics related to aliphatic, aromatic and carbohydrate groups of oil and aqueous phases in hydrotreated products over 5 wt% $\text{Pd/Al}_2\text{O}_3$ and CuCr_2O_4 catalyst (Fig. 3). With increasing the reaction temperature, the main difference of $^1\text{H-NMR}$ spectra between oil and aqueous phases was a strong reduction in the intensity of peaks in δ 5.0-3.0 ppm, simultaneously and an increase in intensity of peaks in δ 3.0-0.5 ppm range. The spectra region in δ 1.5-0.5 ppm represents the alkyl protons that attached to carbon atoms, and the next spectra in δ 3.0-1.5 ppm indicate the protons bonded to the carbon atoms of α -aliphatics to unsaturated or heteroatom. The intensity of

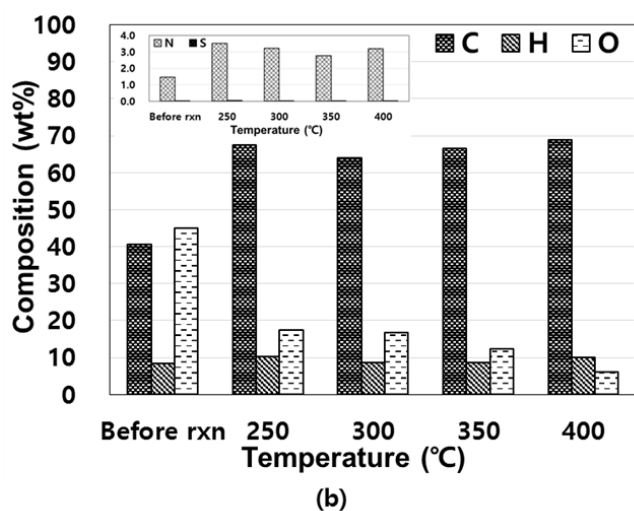
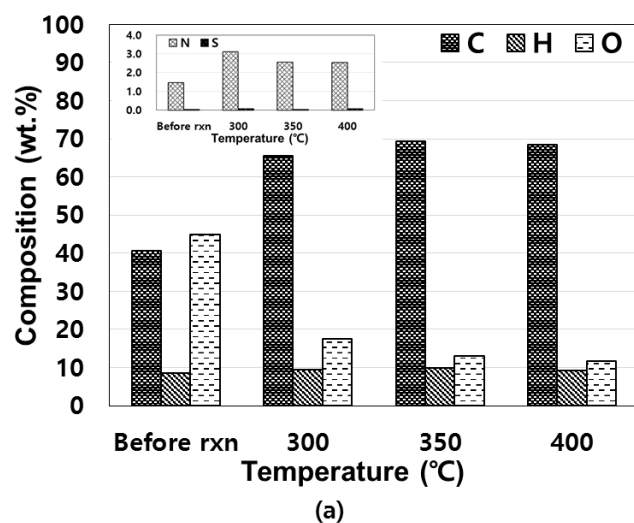


Fig. 2. Effect of reaction temperature on elemental percentages of (a) oil and (b) aqueous phase over 5 wt% $\text{Pd/Al}_2\text{O}_3$ and CuCr_2O_4 catalysts.

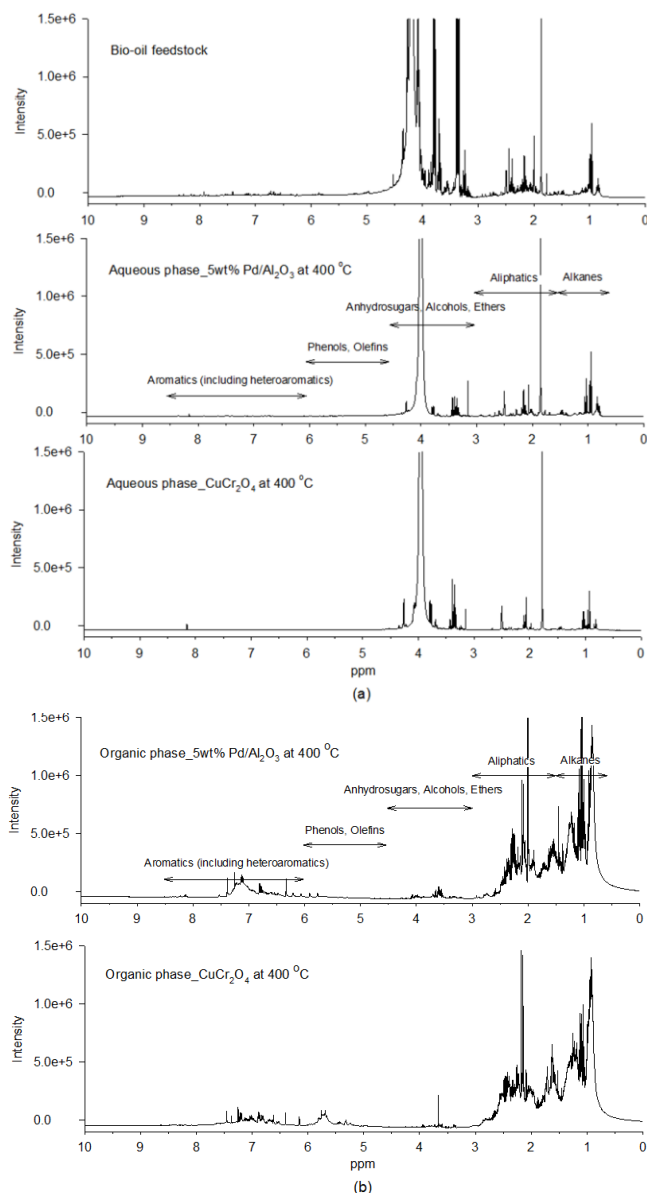


Fig. 3. $^1\text{H-NMR}$ spectra of (a) bio-oil feedstock and aqueous phases, (b) organic phases of catalytic hydrotreatment over 5 wt% $\text{Pd/Al}_2\text{O}_3$ and CuCr_2O_4 at 400 °C and 10 MPa H_2 .

δ 4.2-3.0 ppm range decreased with increasing hydrotreating temperature, and represents the methoxy and/or hydroxyl groups related to carbohydrate derivatives. In addition, the intensity of δ 6.0-8.0 ppm has increased relatively, in line with hydrogenation of carbon-carbon double bonds to hetero-aromatics.

4. CONCLUSIONS

The supported palladium and copper chromite catalysts applied for the improvement of bio-oil properties such as high oxygen and sulfur content, higher heating value (HHV), viscosity and density. The two different metal catalysts based on Pd and CuCr have a

strong activity for HDO and hydrogenation, and show the different selectivity of C=C and C=O hydrogenation, respectively. The pyrolysis and catalytic upgrading as a part of processes for production of liquid biofuel from biomass feedstock can produce the alternative biofuel for both fuel blend stocks and refinery intermediates.

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REFERENCE

- [1] Wei N, Quarterman J, Jin Y-S. Trends Biotechnol 2013;31:70-77.
- [2] Gao K, McKinley KR. J Appl Phycol 1994;6:45-60.
- [3] Huber GW, Iborra S, Corma A. Chem Rev 2006;106:4044-98.
- [4] Canabarro N, Soares JF, Anchieta CG, Kelling CS, Mazutti MA. Sustain Chem Process 2013;1:22.
- [5] Choi JH, Kim S-S, Woo HC. J Ind Eng Chem 2017;51:206-215.
- [6] Zhang Q, Chang J, Wang T, Xu Y. Energy Convers Manag 2007;48:87-92.
- [7] Wildschut J, Mahfud FH, Venderbosch RH, Heeres HJ. Ind Eng Chem Res 2009;48:10324-10334.
- [8] Elliott DC. Energy Fuels 2007;21:1792-1815.
- [9] Choi JH, Kim S-S, Suh DJ, Jang E-J, Min K-I, Woo HC. Korean J Chem Eng 2016;33:2691-8.
- [10] Channiwala SA, Parikh PP. Fuel 2002;81:1051-1063.
- [11] Venderbosch RH, Ardiyanti AR, Wildschut J, Oasmaa A, Heeres HJ. J Chem Technol Biotechnol 2010;85:674-686.
- [12] Pstrowska K, Walendziewski J, Łuzny R, Stolarski M. Catal Today 2014;223:54-65.
- [13] Furimsky E. Appl Catal A Gen 2000;199:147-190.