



Article

Catalytic Hydrodeoxygenation of Fast Pyrolysis Bio-Oil from *Saccharina japonica* Alga for Bio-Oil Upgrading

Hoang Vu Ly ^{1,2}, Jinsoo Kim ^{2,*}, Hyun Tae Hwang ³, Jae Hyung Choi ⁴, Hee Chul Woo ⁴ and Seung-Soo Kim ^{1,*}

- ¹ Department of Chemical Engineering, Kangwon National University, Samcheok, Gangwon-do 25913, Korea; lyhoangvu87@gmail.com
- ² Department of Chemical Engineering, Kyung Hee University, Giheung-gu, Yongin, Gyeonggi-do 17104, Korea
- ³ Department of Chemical and Materials Engineering, University of Kentucky, 4810 Alben Barkley Drive, Paducah, KY 42002, USA; hyun-tae.hwang@uky.edu
- ⁴ Department of Chemical Engineering, Pukyong National University, 365 Sinseon-ro, Nam-gu, Busan 48513, Korea; jhchoe@pknu.ac.kr (J.H.C.); woohc@pknu.ac.kr (H.C.W.)
- * Correspondence: jkim21@khu.ac.kr (J.K.); sskim2008@kangwon.ac.kr (S.-S.K.); Tel.: +82-31-201-2492 (J.K.); +82-33-570-6544 (S.-S.K.)

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Abstract: Biomass conversion via pyrolysis has been regarded as a promising solution for bio-oil production. Compared to fossil fuels, however, the pyrolysis bio-oils from biomass are corrosive and unstable due to relatively high oxygen content. Thus, an upgrading of bio-oil is required to reduce O component while improving stability in order to use it directly as fuel sources or in industrial processes for synthesizing chemicals. The catalytic hydrodeoxygenation (HDO) is considered as one of the promising methods for upgrading pyrolysis bio-oil. In this research, the HDO was studied for various catalysts (HZSM-5, metal, and metal-phosphide catalysts) to improve the quality of bio-oil produced by fast pyrolysis of *Saccharina japonica* (SJ) in a fluidized-bed reactor. The HDO processing was carried out in an autoclave at 350 °C and different initial pressures (3, 6, and 15 bar). During HDO, the oxygen species in the bio-oil was removed primarily via formation of CO₂ and H₂O. Among the gases produced through HDO, CO₂ was observed to be most abundant. The C/O ratio of produced bio-oil increased when CoMoP/ γ -Al₂O₃, Co/ γ -Al₂O₃, Fe/ γ -Al₂O₃, or HZSM-5 was used. The Co/ γ -Al₂O₃ showed high HHV (34.41 MJ/kg). With the use of catalysts, the kerosene-diesel fraction (carbon number C₁₂-C₁₄) was increased from 36.17 to 38.62–48.92 wt.%.

Keywords: S. japonica alga; fast pyrolysis; upgrading bio-oil; catalytic hydrodeoxygenation; autoclave

1. Introduction

Biomass has attracted considerable attention as an alternative energy resource to replace nonrenewable fossil fuels. Biomass feedstocks including agricultural residues [1], forestry waste [2,3], plastic [4], aquatic plant [5,6], and sewage sludge [7], are inexpensive and can be further utilized to produce a variety of valuable chemicals and biomaterials as well as energy [5,8]. Among the various resources for renewable energy, macroalgae offers great promise as feedstock for biofuel production due to its higher growth rate even in wastewater and seawater, higher yield, and shorter harvesting cycle, compared to terrestrial biomass. Thermal conversion via pyrolysis has received a lot of attention as a promising technique to produce biofuel from macroalgae. Kim et al. [9,10] investigated the pyrolysis

characteristics and kinetics of *Saccharina japonica* (SJ) alga and *Sargassum* sp. and found that the bio-oil produced at optimum conditions showed a higher heating value (HHV) of 31.9 MJ/kg and an O/C molar ratio of 0.16. Ly et al. [5] produced bio-oils with HHVs in the range of 24.75–28.72 MJ/kg by fast pyrolysis of SJ. By pretreating *Enteromorpha clathrata* alga with diluted HCl, Cao et al. [11] enhanced the yield of the bio-oil by 9.6%.

However, pyrolytic bio-oils contain a lot of oxygen-containing compounds, leading to a decrease in the bio-oil quality [3,12]. For this reason, in order for bio-oil to be directly used as transportation or boiler fuel, an upgrading process to lower the oxygen content in bio-oil is required. Catalytic pyrolysis is known as one of the most promising methods for upgrading bio-oil. In the presence of catalyst, the O-species in the bio-oils are released as forms of CO₂, CO, and/or H₂O, or converted directly to hydrocarbons at atmospheric pressure, resulting in improvement of bio-oil quality [12]. Ly et al. [3] also studied the catalytic pyrolysis of tulip tree (*Liriodendron*) in a fluidized-bed reactor with dolomite catalyst. They reported that oxygen content in the bio-oil was mostly removed as water via dehydration. In addition, gaseous products released together were found to have a high H_2/CO ratio. The effect of HZSM-5 as a catalyst on the composition of pyrolyzed bio-oil from microalgae with high contents of nitrogen and oxygen was investigated by Lorenzetti et al. [13]. They found that the upgraded bio-oil contained high amounts of aromatic hydrocarbon, while contents of oxygen and nitrogen were relatively small. The catalytic deoxygenation over hydrotreating, known as catalytic hydrodeoxygenation (HDO), has been accepted as a potential method for efficient removal of oxygen in bio-oil. Due to high catalytic activity along with inexpensive material cost, alumina, zeolites, silica, and activated carbon have been commonly employed as supports for various HDO catalysts. Selecting 2-furyl methyl ketone (FMK) as a model compound, Ly et al. [14] obtained relatively high conversion (>83%) of FMK with Ni-based catalysts (Ni/ γ -Al₂O₃). They also found that HDO was enhanced by addition of phosphorous, which influences the structural properties of active phase [14]. In particular, transition metal phosphide catalysts have been reported to show excellent activities on HDO [14–16]. The HDO processes with supported-metallic catalysts were investigated to upgrade pyrolytic bio-oils [17,18]. Cheng et al. [18] studied the HDO of bio-oil from pine sawdust with Fe-Co/SiO₂ catalysts and found that the bimetallic Fe-Co/SiO₂ catalysts (Fe/Co ratio of 1:1) showed better performance, as compared to monometallic catalysts (e.g., Fe/SiO₂ and Co/SiO₂).

In the present study, different catalysts including HZSM-5, metal (Fe and Co), and metal phosphide (Fe₂P, CoP, and CoMoP) supported on γ -Al₂O₃ were examined for upgrading bio-oil obtained by pyrolysis of SJ. In addition, the feasibility of applying inexpensive catalysts to HDO processes was investigated, by testing in an autoclave at 350 °C and pressure varying from 3 to 15 bar. Finally, the compositions of the products and the catalysts were systematically analyzed using various techniques.

2. Results and Discussion

2.1. Catalysts and Sample Characterization

The X-ray diffractogram of catalysts was reported in Figure 1. The peaks at $2\theta = 31.93^{\circ}$, 37.67° , 45.78° , and 66.35° were associated with γ -Al₂O₃ support. Two main peaks for HZSM-5 were displayed at 22.86° and 23.89° [19]. The peaks related to Fe phase in 10 wt.% Fe/ γ -Al₂O₃ catalyst were observed at $2\theta = 44.64^{\circ}$ and 65.05° . The peaks of Fe₃O₄ appeared at 2θ values of 18.77° , 35.87° , 57.64° , and 62.91° . This result indicates that the Fe₂O₃ phase was transformed into Fe₃O₄ phase and further to Fe metallic phase. The peak corresponding to Fe₂P could be observed at 38.4° . In the XRD patterns for Co-containing catalysts, the peaks of CoP phase appeared at $2\theta = 31,62^{\circ}$, 35.23° , 40.12° , 48.19° , and 56.69° , Co at 42.39° , 51.24° , 54.01° , and 75.45° , and the peaks of spinel Co₃O₄ at 31.89° , 37.02° , 59.64° , and 65.86° . The peaks 25.94° , 36.98° , and 69.88° were attributed to MoO₂, while the signals at 28.03° , 32.28° , and 43.20° for the spinel MoP. These XRD results were consistent with those reported in previous studies [14–16].



Figure 1. XRD patterns of (**a**) HZSM-5 and γ -Al₂O₃-supported catalyst with (**b**) 10 wt.% Co, (**c**) 10 wt.% CoP, (**d**) 10 wt.% CoMoP, (**e**) 10 wt.% Fe, and (**f**) 10 wt.% Fe₂P.

The BET surface area (S_{BET}), the pore volume, and the average pore size of HZSM-5 were determined to be 132.49 m²/g, 0.14 cm³/g, and 6.70 nm, respectively. As presented in Table 1, the prepared catalysts (Co, CoP, Fe, Fe₂P, and CoMoP on γ -Al₂O₃) showed the textual properties with specific surface area ranging from 184.82 to 211.08 m²/g, the pore volume 0.40–0.43 cm³/g, and the average pore size 7.05–8.09 nm. As reported in our prior study [9], the moisture and ash contents of SJ sample were 6.90 wt.% and 20.21 wt.%, respectively. Table 2 shows the characteristics of SJ and SJO. As shown in Table 2, the HHV of SJO was determined to be 26.10 MJ/kg, which was higher than that of woody biomass such as tulip tree (18.87 MJ/kg) [3] and *Pinyon pine* (18.94 MJ/kg) [2].

Table 1. Pore structure data of different catalyst
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Catalyst	Calcination Temperature (°C)	Surface Area (m²/g)	Pore Volume (cm ³ /g)	Average Pore Size (nm)
HZSM-5	550	132.49	0.04	6.7
10 wt.% Co/γ-Al ₂ O ₃	600	184.82	0.40	7.79
10 wt.% Fe/γ-Al ₂ O ₃	600	203.71	0.43	8.09
10 wt.% CoP/γ-Al ₂ O ₃	600	209.87	0.43	7.05
10 wt.% Fe ₂ P/ γ -Al ₂ O ₃	600	204.72	0.41	7.67
$10 \text{ wt.}\% \text{ CoMoP/}\gamma\text{-Al}_2\text{O}_3$	600	211.08	0.42	7.56

Proximate Analysis (wt.%)	Moisture ^a	4 -1 b	Volatile	Fixed	Elem	HHV			
		Ash ^v	Matter ^c	Carbon ^c	С	Н	Ν	O ^e	(MJ/kg)
S.J [9]	6.90	20.21	68.79	4.10	32.89	6.17	0.93	60.01	12.11
Raw SJO	2.14	-	-	-	61.96	8.02	2.21	27.81	27.45

Table 2. Characteristics of Saccharina japonica (SJ) and raw Saccharina japonica bio-oil (SJO).

^a ASTM E1756, Standard test method for the determination of the total solids of biomass. ^b ASTM E1755, Standard test method for determination of ash content of biomass. ^c Calculating based on sample after drying. ^d On dry, ash free basis (for biomass material). ^e By difference.

2.2. Thermogravimetric Analysis of Biomass Samples

The thermogravimetric analysis (TGA) combined with differential thermogravimetric analysis (DTG) is a high-precision technique to understand the characteristic of thermal decomposition of solid materials. The TGA enables to monitor the degree of conversion with temperature, while the differential rate of conversion (dX/dt) vs. temperature is expressed by DTG. Both TGA and DTG curves for original SJ and SJO at a heating rate of 20 °C/min are illustrated in Figure 2. Starting at -40 °C, most of SJO conversion was obtained below 500 °C, which is ascribed to the decomposition of organic components in the SJO. According to the simulated distillation by TGA [3,12,20], this decomposition temperature range (40–500 °C) corresponded to the boiling point of the organic products with carbon numbers from C₅ to C₃₈. It is also noteworthy that 80% of SJO was recovered within 350 °C, and the maximum differential rate of conversion was observed at 200.43 °C in the DTG curve (b).



Figure 2. TGA and differential thermogravimetric analysis (DTG) of weight loss curves at a heating rate of 20 °C/min: (**a**) *Saccharina japonica* (SJ) macroalgae and (**b**) *Saccharina japonica* bio-oil (SJO).

2.3. Effect of Reaction Conditions on Product Distribution

The effect of initial pressure on the HDO of SJO was investigated. With increasing reactor pressure, the gas yield decreased, while the liquid yield increased. It is likely because increased pressure results in the suppression of volatiles. The moisture content in the oil decreased with increasing reaction pressure, whereas the content of organic matter increased. The HHV of the bio-oil was in the range of 33.09–33.99 MJ/kg, which was little influenced by the pressure. As compared to raw bio-oil, however, the HHV of the bio-oil upgraded by HDO increased because oxygen species are reduced via dehydration, decarboxylation, and decarbonylation. The HHV of the upgraded bio-oils was higher than that of pyrolysis bio-oils from biomass such as tulip tree (24.37 MJ/kg) [3] and *S. japonica* (26.1–28.27 MJ/kg) [9].

The effect of catalysts on the HDO of SJO was also investigated for HZSM-5 and various catalysts with 10 wt.% metal loading at 350 °C and the initial pressure of 15 bar. As shown in Table 3, the product distributions were different for the catalysts tested, which were likely due to different reaction pathways. When HDO of SJO was conducted without catalyst, the liquid yield decreased, whereas the gas yield increased, compared to catalytic HDO. The maximum liquid yield was 78.60 wt.%, observed for HZSM-5. The highest value of gas yield was 15.21 wt.%, achieved by HDO using Co/Al₂O₃. As a result, the addition of metal on γ -Al₂O₃ support (Co/ γ -Al₂O₃ and Fe/ γ -Al₂O₃) decreased the liquid and char yields, while the gas yield was increased. This might be due to the catalytic cracking reaction, which produced lower molecular weight compounds and non-condensable gas, followed by a series of deoxygenation reactions [12]. When HZSM-5 was applied, the liquid yield was decreased, but the char yield was increased, compared to HDO in the absence of the catalyst. An increase in the char yield might be due to the formation of coke on the surface of HZSM-5 by repolymerization and aromatization of aromatic compounds in liquid products [12].

When phosphorus was added into the metal catalysts, however, significant changes in the solid yield were observed. The solid yield of P-containing catalysts was higher than those of the P-free counterpart. The solid yields for Co/γ -Al₂O₃ and Fe/ γ -Al₂O₃ were determined to be 15.21% and 14.39%, respectively. On the other hand, they were decreased to 8.8% and 7.92% with an addition of phosphorus (CoP/ γ -Al₂O₃ and Fe₂P/ γ -Al₂O₃). This might be because the addition of phosphorus enhanced the acidity of catalyst, leading to the decrease of solid yield on active sites of catalysts. The HHVs of bio-oils through HDO were determined to be 34.41 MJ/kg (Co/ γ -Al₂O₃) and 34.28 MJ/kg (Fe/ γ -Al₂O₃), while for phosphide catalysts in the range of 28.87–33.94 MJ/kg.

Reaction Conditions		350 °C, 3 Bar	350 °C, 6 Bar	350 °C, 15 Bar	350 °C, 15 Bar, HZSM-5	350 °C, 15 Bar, Co/γ-Al ₂ O ₃	350 °C, 15 Bar, Fe/γ-Al ₂ O ₃	350 °C, 15 Bar, CoP/γ-Al ₂ O ₃	350 °C, 15 Bar, Fe ₂ P/γ-Al ₂ O ₃	350 °C, 15 Bar, CoMoP/γ-Al ₂ O ₃
	Liquid	77.24 ± 0.21	78.09 ± 0.18	80.17 ± 0.08	78.60 ± 0.11	74.28 ± 0.20	73.63 ± 0.16	75.14 ± 0.11	72.76 ± 0.07	68.58 ± 0.16
Product Vield	Moisture	19.87 ± 0.08	17.61 ± 0.10	11.52 ± 0.05	19.57 ± 0.19	22.39 ± 0.22	17.89 ± 0.13	17.33 ± 0.09	21.22 ± 0.10	31.97 ± 0.25
(w/t %)	Organic	80.13 ± 0.08	82.39 ± 0.10	88.48 ± 0.05	80.43 ± 0.19	77.61 ± 0.22	82.11 ± 0.13	82.67 ± 0.09	78.78 ± 0.10	68.03 ± 0.25
(Wt.70)	Solid	13.93 ± 0.28	13.87 ± 0.14	13.29 ± 0.15	14.97 ± 0.28	10.51 ± 0.37	11.98 ± 0.27	16.06 ± 0.18	19.42 ± 0.26	25.23 ± 0.40
	Gas	8.83 ± 0.07	8.04 ± 0.31	6.54 ± 0.22	6.43 ± 0.17	15.21 ± 0.18	14.39 ± 0.42	8.8 ± 0.30	7.82 ± 0.20	6.19 ± 0.23
	С	72.44	71.46	72.60	73.16	73.39	73.42	70.16	63.83	72.48
Elemental	Η	8.46	8.39	8.59	8.38	8.54	8.42	8.43	8.22	8.58
Analysis (wt.%)	Ν	3.21	3.27	3.37	3.19	3.44	3.62	3.07	2.97	3.03
	О	15.89	16.88	15.44	15.26	14.63	14.54	18.34	24.98	15.91
HHV (MJ/kg)		33.74	33.09	33.99	33.99	34.41	34.28	32.51	28.87	33.94
	CH ₄	7.61	8.25	10.32	9.05	10.24	12.05	9.27	5.22	5.17
	C_2H_4	0.76	0.82	1.05	1.02	0.62	0.64	0.82	0.77	0.97
Cas Soloctivity	C_2H_6	1.69	1.75	2.10	2.08	1.79	1.77	1.43	1.35	1.10
(mol ⁹)	C_3H_6	1.46	1.54	1.92	1.95	2.05	1.85	1.02	1.38	0.97
(1110176)	C_3H_8	0.54	0.56	0.62	0.83	0.87	0.60	0.37	0.47	0.29
	CO	0.18	0.49	1.67	0.83	0.72	0.90	1.36	0.17	1.83
	CO ₂	87.76	86.59	82.32	84.24	83.71	82.19	85.73	90.64	89.67

Table 3. Product distribution of *Saccharina japonica* bio-oil for different conditions in an autoclave reactor at reaction time of 60 min.

2.4. Compositions of Gas Product

Table 3 also shows gaseous product distributions by non-catalytic and catalytic HDO of SJO. The gas compositions mostly consisted of CO, CO₂, CH₄, and other hydrocarbon gases and varied depending on the reaction conditions. The CH₄ was formed by cracking and hydrocracking of alkyl groups during the upgrading process. Without a catalyst, CH₄ content in gas products increased from 7.61 to 10.32 mol% with increasing pressure from 3 to 15 bar. This was probably due to the increase in the demethylation reaction rate. The demethylation was favored in HDO with Co/ γ -Al₂O₃ (10.24 mol%) and Fe/ γ -Al₂O₃ (12.05 mol%) catalysts. In this study, CO₂ was identified as a major component among produced gases (82.19–90.64 mol%), indicating that the organic compounds in raw SJO underwent decarboxylation [12]. For the HDO with catalysts, on the other hand, the decarboxylation reaction was more predominant than decarbonylation. Particularly for Fe₂P/ γ -Al₂O₃ and CoMoP/ γ -Al₂O₃ catalysts, high selectivity to carbon dioxide was observed, which is likely to be attributed to promoted dehydration and decarboxylation by addition of phosphorus [21,22].

2.5. Bio-Oil Analysis

The atomic C/O ratio of bio-oils obtained by HDO was calculated based on the result of the elemental analysis of the bio-oil. By performing catalytic HDO, the C/O ratio of bio-oil increased from 4.12 (without catalyst) to 4.75 (HZSM-5), 6.34 (Co/ γ -Al₂O₃), 5.67 (Fe/ γ -Al₂O₃), and 6.75 (CoMoP/ γ -Al₂O₃), while decreasing to 3.77 and 3.71 for CoP/Al₂O₃ and Fe₂P/ γ -Al₂O₃, respectively. The decrease in O content after HDO reaction was due to the removal of oxygenates from the gas (CO, CO₂) or H₂O via deoxygenation and dehydration reactions. The carbon and oxygen balances of the reactant and products were shown in Table 4.

Reaction Condition	s	350 °C, 3 Bar	350 °C, 6 Bar	350 °C, 15 Bar	350 °C, 15 Bar, HZSM-5	350 °C, 15 Bar, Co/γ-Al ₂ O ₃	350 °C, 15 Bar, Fe/γ-Al ₂ O ₃	350 °C, 15 Bar, CoP/γ-Al ₂ O ₃	350 °C, 15 Bar, Fe ₂ P/γ-Al ₂ O ₃	350 °C, 15 Bar, CoMoP/γ-Al ₂ O ₃
Gas	С	0.31	0.27	0.23	0.22	0.64	0.88	0.3	0.4	0.21
Product (g)	0	0.54	0.51	0.45	0.41	0.63	0.91	0.51	0.43	0.33
Char	С	1.344	1.261	1.115	1.261	1.053	1.011	1.471	1.86	2.013
Product (g)	0	0.06	0.09	0.49	0.16	0.11	0.09	0.1	0.08	0.06
Moisture	С	0.05	0.05	0.05	0.04	0.06	0.09	0.05	0.04	0.03
Phase (g)	0	1.36	1.22	0.82	1.37	1.48	1.17	1.16	1.37	1.95
Organic	С	4.43	4.55	4.74	4.60	4.39	4.19	4.31	3.82	3.86
Phase (g)	0	0.95	1.09	1.15	0.97	0.69	0.74	1.14	1.03	0.57
C/O Ratio		4.68	4.18	4.12	4.75	6.34	5.67	3.77	3.71	6.75

Table 4. Carbon and oxygen balance of the reactant and product during HDO reaction.

The pyrolysis bio-oil is known as a complex mixture consisting of hundreds of components with a wide range of molecular weight. Table 5 shows the GC–MS analysis data of the bio-oils produced by HDO reaction at 15 bar and 350 °C with/without catalysts (based on peak area %). The bio-oil mainly contained components such as fatty acids, dianhydromannitol, isosorbide, 2-furyl methyl ketone (2-FMK), and derivatives of ketones. It can be observed that HZSM-5 was effective in the conversion of dianhydromannitol and isosorbide and the production of aromatic compounds such as derivatives of pyrazine, pyridinamine, and indole. This result was in good agreement with other literature [12]. An increase in the alkane selectivity, resulting in a decrease in the selectivity to fatty acids, might be explained by decarboxylation of fatty acids by catalytic activity of metal catalysts (Fe/Al₂O₃ and Fe₂P/Al₂O₃) [23]. As shown in Table 4, the selectivity of ketone derivatives in the produced bio-oils after HDO, especially 2-FMK, was found to be lower than that of raw SJO. This result was also in good agreement with our previous study on HDO of bio-oil model compounds [14–16].

Composition of Bio Oil	Bio-Oil at 450 °C	w/o	Catalysts						
	$4.0 imes U_{mf}$	Catalyst	HZSM-5	Co/γ - Al_2O_3	CoP/y-Al ₂ O ₃	$CoMoP/\gamma-Al_2O_3$	Fe/γ - Al_2O_3	Fe ₂ P/γ-Al ₂ O ₃	Structure
2-methyl-2-cyclopenten-1-one	1.84	0.41	0.49	0.61		2.14	2.41	2.44	
3-methyl-Butanal					3.53		3.66		<i>}_</i> ≡0
2-Furyl methyl ketone	12.7	6.53	5.62	2.45	5.22	7.7	4.36	6.11	\rightarrow
3,4-dimethyl-2-cyclopentenone			1.64					1.32	0=
2-hydroxy-3,4-dimethyl-2-Cyclopenten-1-one	2.33	2.75							но
2-Hydroxy-3-ethyl-2-Cyclopenten-1-one	1.25	1.82							0= HO
2,3,6-Trimethylpyrazine			3.47						N N N N N N N N N N N N N N N N N N N
2,3-dimethyl-2-cyclopenten-1-one	3.29	1.93	2.93	1.05	2.04	1.59	2.18	2.02	Ţ.
2,3,4-trimethyl-2-cyclopenten-1-one	2.29	2.05	1.21	0.9	2.71		2.26	2.15	\rightarrow
3-ethyl-2,5-dimethyl-Pyrazine	4.23	1.76	0.67						
2-methoxy-Phenol				0.26		3.14	0.77		HO O
2,4-Dimethyl phenol	1.01	0.98					1.09	1.23	HO

Table 5. Compounds identified by gas chromatograph/mass spectrometry (GC–MS) of bio-oil produced from HDO of *Saccharina japonica* bio-oil in an autoclave at 350 °C under pressure of 15 bar using various catalysts (results are based on peak area %).

Composition of Bio-Oil	Bio-Oil at 450 °C	w/o	Catalysts						
	$4.0 imes U_{mf}$	Catalyst	HZSM-5	Co/y-Al ₂ O ₃	CoP/y-Al ₂ O ₃	CoMoP/y-Al ₂ O ₃	Fe/y-Al ₂ O ₃	Fe ₂ P/γ-Al ₂ O ₃	Structure
2,3-Dimethyl-5-ethyl-Pyrazine	1.95	1.89	1.76						N
1-Acetyl-1-cyclohexene			2.61						\sim
4-Ethyl-2,5,6-Trimethylpyrimidine			2.42						$\rightarrow N \rightarrow N$
Isosorbide	3.48	2.66		4.03	11.91	6.96	6.12	18.52	HO H OH
Dianhydromannitol	22.26	20.73	3.35	17.33	19.67	23.82	20.68	20.64	HO OH
3-ethoxy-2-Pyridinamine			2.57						HIN
1,2-dimethoxy-Benzene			1.23						
6,7-dihydro-2,5-dimethyl-5H-cyclopentapyrazine			2.63						<i>™™</i>
Tetradecane n-Pentadecane n-Hexadecane			1.87 1.42	1.97 0.7		1.18 1.04 2.61	2.5 0.71		C ₁₄ H ₃₀ C ₁₅ H ₃₂ C ₁₆ H ₃₄
2-Ethylhexyl 2-ethylhexanoate						2.83			mary
Methyl n-tetradecanoate			1.09	1.78	2.49	1.78	1.97	1.02	Å
Tetradecanoic acid			1.29		2.04				HO
4-Benzylaniline						6.35			H ₂ N_
1,1-Diphenylhydrazine						2.65			N NH2

Table 5. Cont.

Composition of Pio Oil	Bio-Oil at 450 °C	w/o	Catalysts						
	$4.0 imes U_{mf}$	Catalyst	HZSM-5	Co/y-Al ₂ O ₃	CoP/y-Al ₂ O ₃	CoMoP/y-Al ₂ O ₃	Fe/γ-Al ₂ O ₃	Fe ₂ P/γ-Al ₂ O ₃	Structure
3,7,11,15-tetramethyl-2-Hexadecene	1.2	2.49	4.99	1.65			2.72		ю{
Methyl hexadecanoate	0.46	0.87	1.28	1.44	3.42	2.3	2.64	1.21	Å
Hexadecanoic acid	5.16	3.44	1.47	1.91	2.23	1.09			l.
9-Octadecenoic acid	4.65	3.41							HOLINA
Methyl-9-octadecenoate		1.67	0.67	2.19	3.35	1.09	2.96		۰ ۱
1-Methyl-2-phenyl-1H-indole			6.55						
3-Nitrophthalic acid				37.4					O _{≤N⁴} HO [−] OOH

Table 5. Cont.

The simulated distillation using TGA, which is based on the boiling point of a carbonaceous liquid, has been conducted for the SJ bio-oil [3,12]. As shown in Figure 3, the carbon number distribution of bio-oil could be classified into three groups such as C_5-C_{11} , $C_{12}-C_{18}$, and $C_{20}-C_{38}$, corresponding to gasoline, kerosene-diesel, and heavy oil fractions, respectively. The distribution of these fractions in the SJO (without catalyst) was 36.24 (C_5-C_{11}), 36.17 ($C_{12}-C_{18}$), and 27.38 wt.% ($C_{20}-C_{38}$), respectively. However, there were significant changes in the carbon number distribution for the bio-oils by catalytic HDO. The fractions of C_5-C_{11} , $C_{12}-C_{18}$, and $C_{20}-C_{38}$ for bio-oil (organic phase) upgraded by HDO were in the range of 30.7–44.81, 38.62–48.92, and 14.16–28.64 wt.%, respectively.



Figure 3. Carbon number distribution of bio-oil produced from HDO of *Saccharina japonica* bio-oil in an autoclave at 350 °C under pressure of 15 bar using different catalysts.

3. Material and Methods

3.1. Sample and Catalysts Preparation

The SJ biomass used in this study was provided by the Cleaner Production Institute of Pukyong National University. The samples were subjected to drying at 105 °C overnight to achieve equilibrium moisture before the experiments. The bio-oils (organic phase) were obtained by fast pyrolysis at 450 °C and the HDO was proceeded at the fluidization velocity of $4.0 \times U_{mf}$.

Following the ASTM standard method (ASTM E 1756-1 and ASTM E 1755-01), the ultimate and proximate analyses of biomass samples and bio-oil were conducted. The thermal decomposition of the bio-oil was analyzed using thermogravimetric analyzer (TGA N-1000, SINCO) under a nitrogen flow rate of 20 mL/min, from room temperature up to 700 °C at a heating rate 10 °C/min.

All catalysts tested in this study were ground and sieved to 80–100 mesh (150–180 μ m). The commercial HZSM-5 catalyst was provided by Hyundai Petroleum Chem. Co. (South Korea) and was calcined at 550 °C for 5 h before use [24–28]. Alumina-supported monometallic (Co/ γ -Al₂O₃ and Fe/ γ -Al₂O₃) and metal phosphorus (Co/ γ -Al₂O₃ and Fe/ γ -Al₂O₃) catalysts were synthesized by impregnation method with 10 wt.% metal loading and a molar ratio of phosphorus (P) to metal (M) 1:1. Before the catalysts were used in the HDO process, they were calcined at 600 °C for 3 h and were further treated in the H₂ environment at atmospheric pressure to reduce metal oxides or metal/metal-oxide phosphate to metal or metal phosphide, respectively. More details on catalysts preparation procedure and characterization methods are described in our prior work [15,16]. The specific surface area of the catalyst was determined using the multipoint Brunauer–Emmett–Teller (BET). Powder X-ray diffraction (XRD, MAC-18XHF, Rigaku, Japan) was also employed to understand the crystallographic structure of the catalysts.

3.2. Experimental Setup and Analytical Method

Upgrading of *Saccharina japonica* bio-oil (SJO) was carried out in an autoclave reactor. As shown in Figure 4, the system consists of a salt bath, a temperature controller, a mechanical stirrer, and a reactor with an inner volume of 100 mL. A molten salt mixture as heat transfer fluid was prepared from a eutectic salt of KNO₃ (59 wt.%) and Ca(NO₃)₂ (41 wt.%) [6,10]. The experiments were conducted at a fixed temperature of 350 °C under different initial pressures from 3 to 15 bar using hydrogen. With the autoclave submerged in the molten salt bath, a ratio of catalyst to bio-oil of 1:10 (i.e., 1 g of catalyst with 10 g bio-oil sample) was used in the catalytic experiments. The residence time of the reactant in the salt bath was 60 min for each condition. After each run, the reactor was removed from the bath and cooled to room temperature.

The samples after HDO were collected to calculate product yields by determining the ratio of mass of the product to that of the biomass fed to the system. The gas yield was determined by measuring the difference in the weight of the reactor before and after the reaction. To calculate the solid and liquid yields, liquid and solid products were first separated by solvent extraction with acetone using a micro filter paper (pore size: 0.45μ m). Then, the solid yield was calculated by weighing the solid and filter after drying, while the liquid yield was given by difference. For all the calculations presented, each data point was an average of more than two experiments.

The elemental compositions of the upgraded bio-oils were characterized by Flash EA1112, CE Instrument [3,9,10]. The moisture content was measured by a Karl-Fischer (CA-200, Mitsubishi, Seoul, South Korea). The gas compositions were identified by the gas chromatography (YL 6500GC) equipped with dual detectors, a flame ionization detector (FID) using Porapak N column to identify hydrocarbon gases (C_1 – C_4) and a thermal conductivity detector (TCD) using a Molecular sieve 13X column for H₂, CO, CO₂, and CH₄. The FID was operated at 250 °C, using high-purity nitrogen (99.999%) as a carrier gas with flow rate 20 mL/min, while the TCD detector was held constant at 150 °C with a constant flow rate (20 mL/min) of argon (99.999% purity) as a carrier gas. Using helium carrier gas with a constant flow rate of 1.0 mL/min, a gas chromatograph/mass spectrometry (GC/MS, 7890A/5975C,

Agilent, Seoul, South Korea) with a capillary column of HP-5MS ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was applied to identify the compositions of bio-oils [3,5]. Starting at 40 °C, with a heating rate of 10 °C /min, the oven temperature increased to 280 °C and was maintained for 10 min. The temperature of injector was set constant at 280 °C and injection volume was 1 μ L.



Figure 4. Schematic diagram of experimental apparatus for hydrodeoxygenation (HDO) of *Saccharina japonica* bio-oil.

4. Conclusions

The HDO process of *Saccharina japonica* bio-oil was systematically investigated in an autoclave reactor. The HHVs of bio-oils upgraded by HDO were in the range of 33.74–33.99 MJ/kg in the absence of a catalyst. Although the liquid yield decreased, however, the quality of bio-oil increased by using metal catalysts in HDO of *Saccharina japonica* bio-oil. The HHVs of HDO bio-oils were increased to 34.41 MJ/kg by using Co/ γ -Al₂O₃ catalyst but decreased with metal phosphide catalysts. The C/O ratio of HDO bio-oil with CoMoP/ γ -Al₂O₃, Co/ γ -Al₂O₃, Fe/ γ -Al₂O₃ and HZSM-5 were higher than that of raw *Saccharina japonica* bio-oil and HDO bio-oil with CoP/ γ -Al₂O₃ or Fe₂P/ γ -Al₂O₃ catalyst. Metal phosphide catalysts were likely to promote the decarboxylation, while metal catalyst elevating the demethylation reactions. The carbon number distribution of bio-oil was mainly distributed in the range C₅–C₁₁ and C₁₂–C₁₈ fractions. Our results revealed the feasibility of upgrading SJO to high-quality bio-oil using catalysts, and this upgraded bio-oil could be further used as a great source for manufacturing alternative bio-fuels and/or valuable chemicals.

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