

Research Article

Ni-Ru/CeO₂ Catalytic Hydrothermal Upgrading of Water-Insoluble Biocrude from Algae Hydrothermal Liquefaction

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Received 22 November 2017; Accepted 28 March 2018; Published 8 May 2018

Academic Editor: Chun-Fei Wu

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Hydrothermal liquefaction (HTL) of algae is a promising crude bio-oil (biocrude) production technology, which can convert wet algae into water-insoluble biocrude and other coproducts. In this work, algae HTL at 350°C and 20 min was conducted to obtain water-insoluble biocrude (B₁), which was then hydrothermally upgraded at 450°C, 60 min, or with added H₂ and/or homemade catalyst (i.e., Ni-Ru/CeO₂ or Ni/CeO₂) for the first time. The characteristics (e.g., yield, elemental component, energy recovery, and molecular and functional group compositions) of upgraded water-insoluble biocrude (B₂) as well as light biocrude thereof were analyzed comprehensively. The results show that Ni-Ru/CeO₂+H₂ led to the highest yield and HHV (higher heating value), the best elemental compositions quality of B₂, and the largest fraction and the best light of light biocrude in B₂. Ni-Ru/CeO₂+H₂ had good catalytic desulfurization effect and could transform high-molecular-weight compounds into low-molecular-weight compounds in B₁ upgrading. At the condition above, 46.2% of chemical energy in the initial algae could be recovered by B₂, while average 54.9% of chemical energy in B₂ was distributed in its light biocrude (hexane-soluble) portion. On the whole, Ni-Ru/CeO₂+H₂ can be considered as the optimal additive in all tested cases.

1. Introduction

Hydrothermal liquefaction (HTL) of algae for crude bio-oil (biocrude) production has increasingly drawn much attention due to its benign raw material properties, high bio-oil yield, avoidance of drying step, and so on. It can chemically convert high moisture algae into water-insoluble biocrude and coproducts (i.e., gases, aqueous phase, and solids) in hot compressed water. However, the obtained biocrude does not meet biodiesel standards in some aspects such as heteroatoms content and heating value, so it requires further biorefinery via proper approaches. An effective method is hydrothermal upgrading, in which biocrude reacts in water, either thermally or with added H₂ and/or catalyst to remove heteroatoms and improve heating value, and so on [1].

Typically, after algae HTL of 1–4 h at around 350°C, total biocrude (both water-insoluble and water-soluble biocrudes)

is collected by organic solvent (e.g., dichloromethane) extraction from all postreaction products and followed hydrothermal upgrading with 2–6 h at a supercritical temperature [2–7]. Notably, the water-insoluble biocrude can spontaneously separate from aqueous phase by gravity upon cooling after algae HTL and commonly accounts for more than 85 wt% of the total biocrude and has remarkably distinct characteristics in comparison to the water-soluble biocrude extracted from the aqueous phase by organic solvent [8, 9]. Due to pollution and cost restrictions of extraction solvent, it is more feasible to adopt solvent-free method to collect and upgrade the water-insoluble biocrude (as the majority of the total biocrude) in actual industrial production. On the other hand, it is convenient and economic to directly use the aqueous phase instead of water in hydrothermal upgrading, because it is easy to separate part of the aqueous phase after algae HTL and to use the rest for following

hydrothermal upgrading. However, relevant investigation about water-insoluble biocrude upgrading with the aqueous phase and catalyst is very scarce now, except for our latest research about catalytic hydrothermal upgrading of water-insoluble biocrude in supercritical water at 400°C, 60 min with commercial catalysts (i.e., Mo₂C, Ru/C, and Pt/C) [1].

As an extension, this work conducted 20 min of algae HTL at 350°C to obtain water-insoluble biocrude and then upgraded it at the higher temperature of 450°C, 60 min with added H₂ and/or Ni-Ru bimetallic catalyst homemade for the first time. The yields, elemental components, energy recoveries, and molecular and functional group compositions of the upgraded water-insoluble biocrudes at various conditions were analyzed systematically. The characteristics concerning the light biocrude in the upgraded biocrude and gaseous products were examined as well. This information is valuable for optimizing processes design and operation parameters of the hydrothermal upgrading of the water-insoluble biocrude from algae HTL.

2. Experimental Section

2.1. Experimental Procedures. The adopted algae (*Nannochloropsis* sp.) slurry had 30.5 ± 2.5 wt% of biomass content, which was determined by drying three separate samples at 65°C in an oven for 48 h. The dry basis algae (about 23.30 MJ/kg) contained approximately 52.85, 7.43, 8.78, and 0.62 wt% of C, H, N, and S contents, respectively. High purity solvents (i.e., dichloromethane (DCM), n-hexane, and deuterated chloroform (CDCl₃)) were obtained from commercial sources. High purity (≥99.999%) hydrogen and helium were purchased from Baoguang Gas Co., Ltd. Several 4.1 ml mini-batch reactors were assembled for the HTL experiments by using 1/2-in. 316 stainless steel Swagelok port connectors and caps. Subsequent biocrude upgrading experiments were conducted in the same reactors, but upgrading reactions with added H₂ or with gas analysis were implemented by additionally equipping each reactor with a length of stainless steel tubing and a high-pressure gas valve.

First of all, one set of experiments were carried out to obtain water-insoluble biocrude from algae HTL at 350°C, 20 min, and 14.1 wt% of algae loading in the reactor (corresponding to 1.2354 g algae slurry and 1.3990 g deionized water). After being sealed, the reactor was placed in a Techno fluidized sand bath (Model SBL-2) preheated up to 350°C for the desired residence time (20 min). Herein, the corresponding reaction pressure was about 16.5 MPa and the reactor heating-up time was 2-3 min. The postreaction reactor was removed from the sand bath and quenched in an ambient-temperature water bath for 15 min and then equilibrated at room temperature for at least 1 h before products collection and analysis. The reactor was kept in a vertical position as it was cooled so that little biocrude would adhere to the inner surface of the reactor top cap. We then opened the reactor and removed 1.875 g aqueous phase via a pipette. The water-insoluble biocrude (about 0.1505 g) from algae HTL (with a little solids residue) and the aqueous phase residue (around 0.3750 g) in the reactor were never in contact with DCM and were used in situ for the following upgrading experiments.

0.0225 g catalyst (if necessary, about 15 wt% of B₁ mass) was loaded into the reactor, and then the reactor was vacuumed and filled either with helium (10 KPa) to eliminate the effect of reactor inside air in the test without H₂ addition or with H₂ to 2.0 MPa to check the effect of H₂ addition. The upgrading experiments were carried out in the sand bath at 450°C, 60 min under different conditions such as catalyst and/or H₂ addition, and the corresponding reaction pressure was approximately 22.5 MPa (based on steam tables). We then removed the reactor from the sand bath and cooled it and followed the previously described method 2 procedure [8] for products collection. In this procedure, the contact between the aqueous phase and DCM is avoided by removing the aqueous product via a pipette, prior to the recovery of the water-insoluble biocrude from the reactor. Eventually, water-insoluble biocrude (B₂) was obtained from B₁ upgrading products, and light biocrude in B₂ (B₂^L) could be further gained by n-hexane extraction.

The mainly used catalysts were 10 wt%Ni0.1Ru/CeO₂ and 10 wt%Ni/CeO₂, which were prepared in house and detailed procedures had been described by our previous report [10]. Herein, 10 wt% represents the mass percentage of active metal (Ni+Ru or Ni) in the catalyst, and 0.1 is the mass ratio of Ru/Ni. For simplification, Ni-Ru/CeO₂, Ni/CeO₂, and “none” were adopted to separately represent 10 wt%Ni0.1Ru/CeO₂, 10 wt%Ni/CeO₂, and the case without catalyst and H₂ in this work. Herein, the cases of Ni/CeO₂ and “none” were tested for comparison with that of Ni-Ru/CeO₂.

2.2. Analysis Methods. Elemental compositions (i.e., C, H, N, and S) of dry basis algae and all biocrude samples were determined by a cube CHNS elemental analyzer (Elementar Vario EL) with uncertainties of <3% of the reported value. Compound components of biocrude were identified via a gas chromatography-mass spectrometer (GC-MS, Agilent Technologies 6890N) equipped with an autosampler, an autoinjector, a mass spectrometric detector, and an Agilent HP-5 capillary column (50 m × 200 μm × 0.33 μm). Nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopic analyses of biocrude were conducted to characterize functional group compositions. Detailed information on these instruments and procedures was introduced in our previous research [8]. Gaseous products were identified and quantified by an Agilent Technologies model 6890N gas chromatograph equipped with a thermal conductivity detector, following the method reported previously [11].

Biocrude yield and energy recovery were defined as follows:

$$\begin{aligned} \text{Biocrude yield} &= \frac{\text{Mass of biocrude}}{\text{Mass of dry basis algae loaded into the reactor}} \\ &\times 100\% \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Energy recovery} &= \frac{\text{HHV of biocrude} \times \text{the biocrude yield}}{\text{HHV of dry basis algae}} \times 100\% \end{aligned}$$

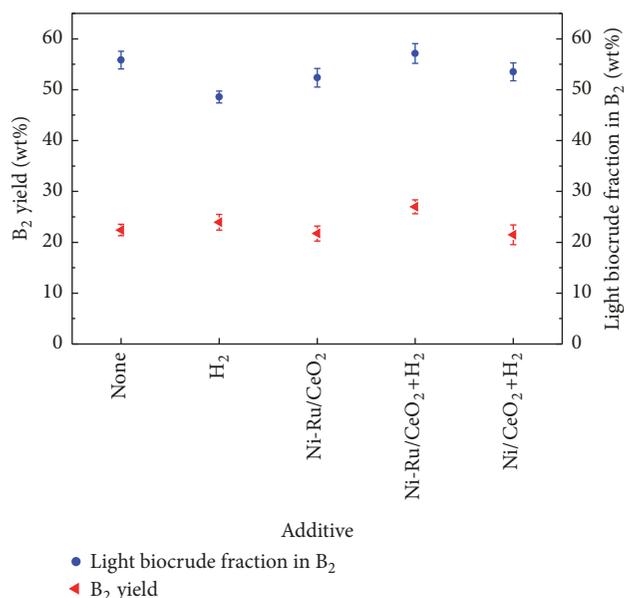


FIGURE 1: B₂ yield and light biocrude fraction in B₂ after B₁ (derived from algae HTL at 350°C, 20 min) upgrading at 450°C, 60 min with or without H₂ and/or catalyst.

The higher heating value (HHV) of dry basis algae or biocrude was estimated by the following Dulong formula:

$$\text{HHV (MJ/kg)} = 0.338C + 1.428 \left(H - \frac{O}{8} \right) + 0.095S, \quad (2)$$

where C, H, O, and S are the wt% composition of each element in the material. The O content was calculated by the differences from the C, H, N, and S values and reserving 1 wt% for other elements not assessed.

Three independent experiments were carried out at the same conditions to determine the uncertainties of experimental data. The results reported herein are mean values and their uncertainties are the sample standard deviations.

3. Results and Discussion

All experiments about algae HTL and biocrude upgrading produced water-insoluble biocrude, gases, aqueous phase, and solids, and total mass balance exceeded 91.0 wt% in products collection.

3.1. Biocrude Yield. Algae HTL at 350°C, 20 min, and 14.1 wt% of algae loading led to 37.5 ± 0.21 wt% of B₁ yield. Figure 1 shows B₂ properties after B₁ upgrading at 450°C, 60 min, with or without H₂ and/or catalyst. It can be found that Ni-Ru/CeO₂+H₂ led to the highest B₂ yield (27.0 wt%, corresponding to about 72.0 wt% of B₁ yield), likely due to catalytic hydrogenation effect during B₁ upgrading. The much lower B₂ yield (21.72 wt%) appeared at the Ni-Ru/CeO₂ condition, and this might be attributed to a large amount of gases formation promoted by the catalyst in supercritical water [10]. Based on the B₂ yield (23.94 wt%) in the case of H₂ addition, there seemingly was synergetic effect between H₂ and Ni-Ru/CeO₂ on B₂ yield improvement because their coexistence

probably inhibits gases formations. Light biocrude fraction in biocrude, which was defined as the measured mass of light biocrude (hexane-soluble) divided by the biocrude mass, is a proxy for biocrude quality because these hexane-soluble compounds are less polar and of moderate boiling point and thus more desirable for fuel use, compared with heavy biocrude (hexane-insoluble) compounds [9]. As indicated in Figure 1, Ni-Ru/CeO₂+H₂ could obviously increase the light biocrude fraction in B₂ and led to the highest value (57.14 wt%), meaning the remarkable improvement of B₂ quality. Herein, similar synergetic effect between H₂ and Ni-Ru/CeO₂ on the promotion of the light biocrude fraction in B₂ was found as well, probably due to the conversion of hexane-insoluble biocrude to hexane-soluble biocrude in hydrothermal upgrading at the Ni-Ru/CeO₂+H₂ condition. Thereby, we could adopt the Ni-Ru/CeO₂ catalyst together with H₂ to regulate the properties of the upgraded water-insoluble biocrude. It is worthy noticing that the upgrading without H₂ and catalyst (i.e., none) rendered considerably high B₂ yield and light biocrude fraction in B₂, so it may be considered as a pre-upgrading process of B₁ in actual large scale production.

3.2. Elemental Composition and HHV. Table 1 indicates elemental compositions and HHVs of B₂ and B₂^L after B₁ upgrading under different conditions. It can be observed that hydrothermal upgrading could increase the C content and simultaneously reduce S and O contents. Deoxygenation can be realized by forming CO₂, H₂O, and CO through complex reactions such as decarboxylation and dehydration [12, 13]. Note that the Ni-Ru/CeO₂ catalyst had the best catalytic desulfurization effect and Ni-Ru/CeO₂+H₂ was also much better for sulfur removal. This has good agreement with the findings that the S content in bio-oil by Ni/SiO₂-Al₂O₃ catalytic upgrading is below detection limit [14] and Ru/C has good desulfurization performance [15]. Ni-Ru/CeO₂+H₂ rendered the highest C content, the largest HHV, the lowest O content, and the second lowest N+S content, so totally exhibiting the best catalytic upgrading effect in all tested cases. Consistently, H₂ addition together with catalyst is desirable for hydrogenation and hydrodeoxygenation behaviors in biocrude upgrading [3, 4, 6]. Apparently, based on the higher C, H contents and HHV but lower heteroatoms (i.e., N, O, and S) contents, each B₂^L had better quality than its corresponding B₂. Thus, the tested catalysts (i.e., Ni-Ru/CeO₂ and Ni/CeO₂) had substantially positive effect on the improvement of B₂^L quality in B₁ upgrading in the presence of H₂, due to the increase of C, H contents, and HHVs and the decrease of N, S, and O contents. The combined Ni-Ru/CeO₂+H₂ led to the best B₂^L quality with the highest C+H content, the largest HHV, and the lowest N+S+O content. Overall, the best catalytic effect of Ni-Ru/CeO₂+H₂ is likely attributed to positive reactions such as hydrogenation, deoxygenation, denitrogenation, and desulfurization in B₁ upgrading.

Energy recovery is a key indicator of the effectiveness of a hydrothermal process in capturing the chemical energy of initial algae in the produced biocrude [16]. Due to little

TABLE 1: Elemental compositions, HHVs, and energy recoveries of B₁ (derived from algae HTL at 350°C, 20 min) and B₂ and B₂^L (obtained from B₁ upgrading at 450°C, 60 min with different additives).

Additive	Biocrude	Element (wt%)					N/C	O/C	HHV (MJ/kg)	Energy recovery (%)
		C	H	N	S	O				
–	B ₁	77.05	9.76	4.82	0.53	6.84	0.063	0.089	38.81	62.46
None	B ₂	79.74	9.44	4.24	0.37	5.21	0.053	0.065	39.54	38.03
H ₂	B ₂	79.19	9.59	4.37	0.41	5.44	0.055	0.069	39.53	40.61
Ni-Ru/CeO ₂	B ₂	79.63	9.55	4.03	0.19	5.6	0.051	0.070	39.57	36.89
Ni-Ru/CeO ₂ +H ₂	B ₂	80.23	9.57	4.12	0.22	4.86	0.051	0.061	39.94	46.24
Ni/CeO ₂ +H ₂	B ₂	79.27	8.87	4.55	0.45	5.86	0.057	0.074	38.46	37.80
None	B ₂ ^L	80.26	9.49	4.04	0.25	4.96	0.050	0.062	39.82	32.11
H ₂	B ₂ ^L	80.63	9.77	3.59	0.35	4.66	0.045	0.058	40.41	30.10
Ni-Ru/CeO ₂	B ₂ ^L	81.26	9.57	3.54	0.18	4.45	0.044	0.055	40.35	23.24
Ni-Ru/CeO ₂ +H ₂	B ₂ ^L	81.9	9.73	3.62	0.19	3.56	0.044	0.043	40.96	29.25
Ni/CeO ₂ +H ₂	B ₂ ^L	81.4	9.6	3.89	0.16	3.95	0.048	0.049	40.53	24.75

variation of biocrude HHVs under different conditions, the energy recovery is largely tracked with the biocrude yield, as displayed in Table 1. It can be noticed that the energy recovery of B₁ was 62.5% after algae HTL, but after B₁ upgrading at various conditions, the energy recoveries of B₂ ranged from 36.9 to 46.2% (average 39.9%) of the heating value of the algae initially loaded into the reactor. Ni-Ru/CeO₂+H₂ addition led to the high energy recovery of 46.2% owing to the largest B₂ yield in this case (see Figure 1). Moreover, the energy recoveries of B₂^L ranged from 23.2 to 32.1% (average 27.9%) of the heating value of the algae loaded initially. Notably, it can be calculated that 49.7–58.6% (average 54.9%) of chemical energy in B₂ was distributed to B₂^L (i.e., its light biocrude portion). Hence, taking into account the yields, elemental compositions, HHVs, and energy recoveries of both B₂ and B₂^L, Ni-Ru/CeO₂+H₂ can be regarded as the optimal additive in all tested cases.

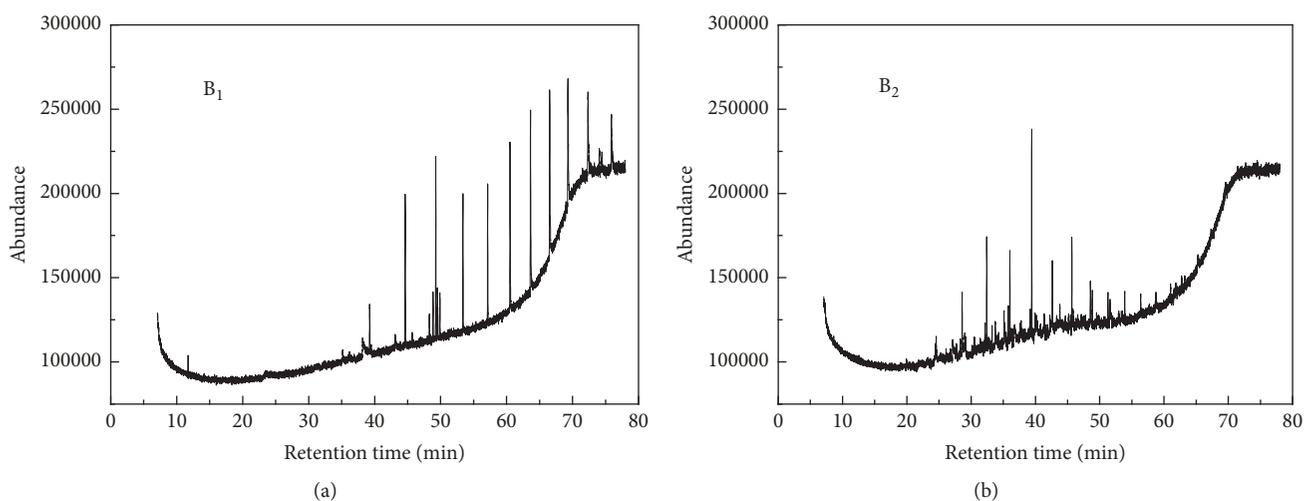
3.3. Gas Analysis. Note that Ni-Ru/CeO₂ is favorable for organic matters gasification to produce a flammable gas mixture in supercritical water [10], so gaseous products are also concerned in this research. Table 2 provides gaseous products after hydrothermal upgrading of B₁ at different conditions, so major gases compositions included H₂, CH₄, CO₂, C₂H₂, C₂H₆, CO, and C₂H₄ at the condition in absence of H₂. Compared with the case without catalyst and H₂ (i.e., none), the Ni-Ru/CeO₂ catalyst could significantly improve H₂ mole fraction (from 29.6% to 41.1%), and meanwhile the postreaction pressure increased from about 2.2 to 3.5 bar. This suggests that Ni-Ru/CeO₂ led to much more H₂ and C-containing gases formation during B₁ upgrading probably mainly via promoting water-gas shift and decarbonation reactions. This outcome is in good accord with the findings that Ru/C [17] and Ni-Ru/CeO₂ [10] are effective for hydrothermal gasification and the relatively low B₂ yield in Figure 1 as well. Notably, it reminds us that these flammable gases formed in the water-insoluble biocrude upgrading should be disposed properly in large scale production processes. In the case of H₂ addition, major identified gaseous products were CH₄, CO₂,

C₂H₆, C₂H₄, CO, and unreacted H₂, but there was no C₂H₂ due to hydrogenation effect. Similar gases compositions are also found in catalytic upgrading of duckweed biocrude in subcritical water [18]. The far high H₂ mole fraction (about 70%) is mainly attributed to initial H₂ addition (2.0 MPa). Nonetheless, the remarkable reduction of the postreaction pressure in contrast to that before reaction suggests a large amount of H₂ consumption for heteroatoms removal (likely in the forms of H₂O, NH₃, and H₂S) and hydrogenation in B₁ upgrading. Certainly, at the same time, there is also H₂ formation due to biocrude gasification in supercritical water (see the “none” group).

3.4. GC-MS Analysis. Biocrude is produced by complex reactions such as oligomerization, depolymerization, decomposition, and reformation reactions [19–21]. Its compounds compositions are mainly dependent on feedstock feature, since not only lipids but also proteins and carbohydrates are converted into biocrude in algae HTL [22]. Figure 2 exhibits total ion chromatograms of B₁ and B₂ derived from B₁ upgrading at the Ni-Ru/CeO₂+H₂ condition. The characteristics of the upgraded water-insoluble biocrude are explored here for the first time. In combination with Table 3 (tentative GC-MS analysis results), it can be confirmed that B₁ consisted of large amounts of complex compounds such as propanal, 2,2-dimethyl-, oxime; cycloheptasiloxane, tetradecamethyl-, cyclooctasiloxane, hexadecamethyl-, heptadecane; 2-hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-, 7,8-didehydro-4,5-epoxy-17-methyl-3,6-bis[(trimethylsilyloxy)-, (5.alpha.,6.alpha.)-; cycloheptasiloxane, tetradecamethyl-, cyclodecasiloxane, eicosamethyl-, and cyclotrisiloxane, hexamethyl-, 2-methyl-6-(5-methyl-2-thiazolin-2-ylamino)pyridine. Some of them contained N, O, and both them, which is consistent with high N and O contents in this material (see Table 1). Some existing cyclic nitrogenous compounds (e.g., 7,8-didehydro-4,5-epoxy-17-methyl-3,6-bis[(trimethylsilyloxy)-, (5.alpha.,6.alpha.)-; 2-methyl-6-(5-methyl-2-thiazolin-2-ylamino)pyridine) are likely produced

TABLE 2: Gaseous products compositions after B₁ upgrading at 450°C, 60 min with different additives.

Additive	H ₂ (%)	CO (%)	CH ₄ (%)	CO ₂ (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	Pressure after reaction (bar)
None	29.6 ± 1.2	5.0 ± 0.8	18.7 ± 2.2	16.1 ± 1.1	12.2 ± 1.8	4.3 ± 0.4	12.5 ± 1.1	2.2 ± 0.2
H ₂	70.7 ± 6.9	2.8 ± 0.4	9.2 ± 2.4	6.6 ± 1.2	–	2.91 ± 0.3	6.5 ± 1.0	9.7 ± 0.4
Ni-Ru/CeO ₂	41.1 ± 2.7	3.2 ± 0.5	16.6 ± 1.9	21.8 ± 1.4	5.7 ± 1.0	2.7 ± 0.2	8.4 ± 1.5	3.5 ± 0.3
Ni-Ru/CeO ₂ +H ₂	70.4 ± 7.7	1.1 ± 0.6	9.0 ± 1.7	9.7 ± 1.3	–	1.8 ± 0.3	6.5 ± 0.9	8.8 ± 0.3
Ni/CeO ₂ +H ₂	69.8 ± 7.2	2.1 ± 0.4	8.75 ± 1.2	8.9 ± 1.1	–	1.9 ± 0.3	6.2 ± 0.8	8.2 ± 0.4

FIGURE 2: Total ion chromatograms of (a) B₁ derived from algae HTL at 350°C, 20 min, and (b) B₂ obtained from B₁ upgrading at 450°C, 60 min, Ni-Ru/CeO₂+H₂ conditions.

by Maillard reactions between amino acids and reducing sugars, which are separately formed by the hydrolysis of proteins and carbohydrates [20].

Apparently, the total ion chromatogram of B₂ looks completely different from that of B₁, because most compounds appearing in the range of 45–75 min in B₁ disappeared or reduced. Major compounds in B₂ appeared in the range of 28–55 min, where the peaks areas sum of all identified compounds took up 95.7% of the total peak area. Main compounds involved pentadecane, tridecane, tetradecane, heptadecane, and dodecane, in which pentadecane and tridecane seem to be the most abundant two species. Thus, hydrothermal upgrading of B₁ with Ni-Ru/CeO₂+H₂ is able to transform high-molecular-weight compounds into low-molecular-weight (i.e., low-boiling-point) compounds, meaning the quality improvement of the upgraded biocrude. More importantly, this catalytic upgrading helps to remove heteroatoms (e.g., O and N) in B₁ to form the upgraded biocrude with abundant presence of a series of aliphatic saturated hydrocarbons. Reactions such as decarboxylation, dehydroxylation, and deamination contribute to the heteroatoms removal, hydrocarbons formation, and so corresponding increase in carbon content and HHV after hydrothermal upgrading.

3.5. NMR Analysis. ¹H-NMR and ¹³C-NMR analysis of biocrude was conducted to identify the types of functional groups. Chemical shift provides information concerning functional group identification, and corresponding peak area can roughly reflect its relative abundance.

3.5.1. ¹H NMR Analysis. Figure 3 illustrates ¹H NMR spectra of B₁ and B₂ derived from B₁ upgrading at the Ni-Ru/CeO₂+H₂ condition. The resonances at 0.8 and 1.2 ppm are characteristics of protons in terminal methyl groups and methylene groups in alkyl chains, respectively [23]. The peak at around 2.1 ppm is consistent with resonance expected from protons on carbon atoms α to an acyl group [15]. There was a peak near 7.2 ppm in B₁ and B₂, which arises from aromatic protons or conjugated dienes [15, 24], and herein the much smaller peak area in the B₂ spectrum suggests that the catalytic hydrothermal upgrading by Ni-Ru/CeO₂+H₂ can effectively reduce the compounds containing the functional groups above. This is consistent with the findings in the GC-MS analysis. Differently, in the B₂ spectrum, a clear peak emerged at around 5.2 ppm representing phenolic -OH [24], possibly due to the existence of hydroxyketone in the upgraded biocrude. The appearance of these peaks above reveals the

TABLE 3: Tentative products identifications by GC-MS analysis of B₁ and B₂ in Figure 2.

Retention time (min)	Compound	Relative peak area (%)
11.7223 ^a	Propanal, 2,2-dimethyl-, oxime	0.3283
38.1796 ^a	Benzoic acid, 4-methyl-2-trimethylsilyloxy-, trimethylsilyl ester	1.337
39.2486 ^a	Cycloheptasiloxane, tetradecamethyl-	3.2133
43.1274 ^a	Diethyl phthalate	0.0338
44.6316 ^a	Cyclooctasiloxane, hexadecamethyl-	7.5681
45.6930 ^a	Heptadecane	0.6365
48.2967 ^a	1-Dodecanol, 3,7,11-trimethyl-	1.3641
48.8617 ^a	Hexadecane, 2,6,10,14-tetramethyl-	1.862
49.2741 ^a	Cyclononasiloxane, octadecamethyl-	7.8494
49.5718 ^a	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	5.1915
57.1387 ^a	Cyclodecasiloxane, eicosamethyl-	5.7078
60.5213 ^a	Morphinan, 7,8-didehydro-4,5-epoxy-17-methyl-3,6-bis[(trimethylsilyl)oxy]-, (5.alpha.,6.alpha.)-	8.6591
63.6290 ^a	Cycloheptasiloxane, tetradecamethyl-	10.5962
66.5381 ^a	Cyclodecasiloxane, eicosamethyl-	10.0725
69.3022 ^a	Cyclotrisiloxane, hexamethyl-	12.5258
69.7069 ^a	Tetrasiloxane, decamethyl-	0.5209
71.5088 ^a	Arsenous acid, tris(trimethylsilyl) ester	0.3042
72.3411 ^a	(p-Methoxyphenyl)-acetyl-dimethylsilane	6.9254
72.5015 ^a	2-Methyl-6-(5-methyl-2-thiazolin-2-ylamino)pyridine	1.0923
75.8993 ^a	2,4,6-Cycloheptatrien-1-one, 3,5-bis-trimethylsilyl-	5.2647
24.5728	Undecane	2.7899
28.6044	Dodecane	6.3133
32.1702	Benzene, 1-(2-butenyl)-2,3-dimethyl-	4.0373
32.4222	Tridecane	10.9529
33.2621	2,4,6(1H,3H,5H)-Pyrimidinetrione, 5-butyl-5-ethyl-1,3-bis(trimethylsilyl)-	3.2033
33.7432	Spiro(9-methylenetricyclo[6.2.1.0(2,7)]undeca-2,4,6-triene)-11,1'-cyclopropane	2.7049
35.1252	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	3.9456
35.7742	2-Tetradecene, (E)-	3.7452
36.0338	Tetradecane	7.816
39.1873	Cyclododecane	3.3313
39.4240	Pentadecane	17.3115
39.9509	2H-1,2,5-Oxasilaborole, 5-tert-butyl-4-ethyl-2,2,3-trimethyl-	3.3719
42.6309	Hexadecane	4.6292
45.6699	Heptadecane	7.1577
48.5485	Octadecane	5.014
48.8539	Hexadecane, 2,6,10,14-tetramethyl-	4.3843
51.2897	Nonadecane	3.2509
51.5951	3-Butyn-1-ol	2.025
53.8934	Eicosane	2.5267
56.3826	Heptadecane, 2,6,10,15-tetramethyl-	1.4892

^aThe peaks are for Figure 2(a) and other peaks are for Figure 2(b).

existence of alkyl moieties, carbonyl functionalities, and aromatic or unsaturated molecules in the biocrudes, though in different amounts [9]. Overall, in B₁ and B₂ obtained from B₁ upgrading with Ni-Ru/CeO₂+H₂, alkane functionality (0.5–1.5 ppm) and aliphatic α -to-heteroatom/unsaturated functionality (1.5–3.0 ppm) [25] were very abundant, due to

the presence of alkanes and other compounds with aliphatic methylene and methyl groups.

3.5.2. ¹³C NMR Analysis. Figure 4 displays ¹³C-NMR spectra of B₁ and B₂ (at the Ni-Ru/CeO₂+H₂ condition). They have larger chemical shift regions and thus provide more details

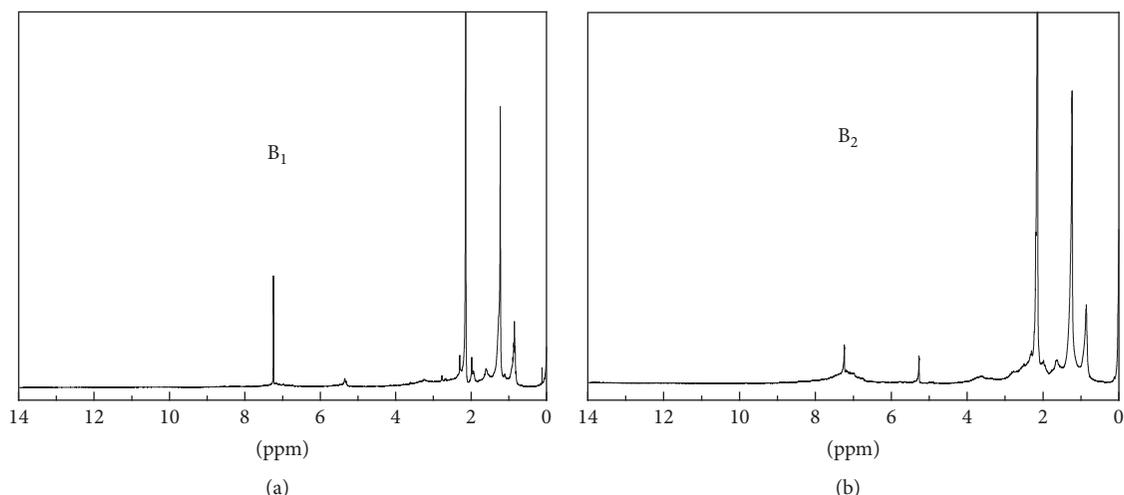


FIGURE 3: ^1H -NMR spectra of (a) B_1 obtained from algae HTL at 350°C , 20 min, and (b) B_2 derived from B_1 upgrading at 450°C , 60 min, and Ni-Ru/ CeO_2+H_2 conditions.

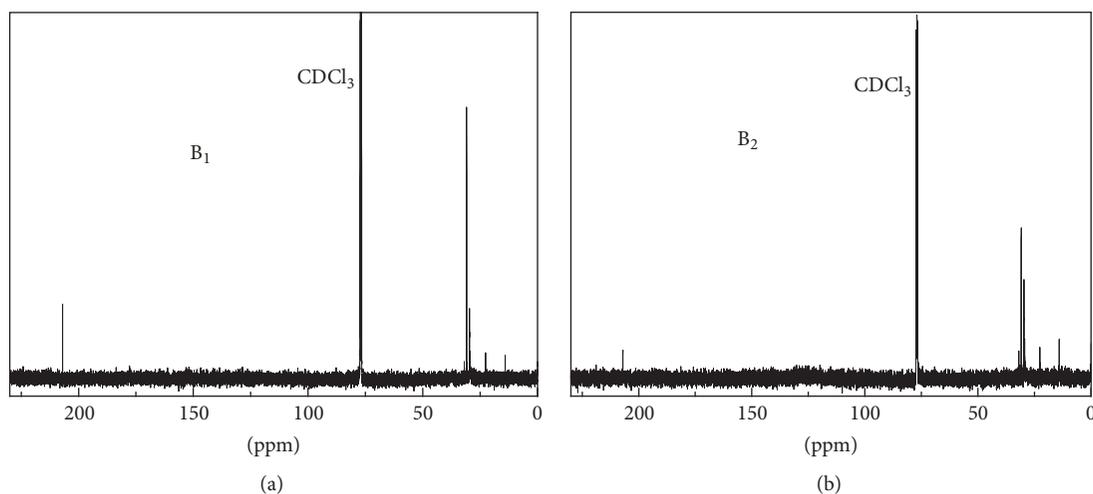


FIGURE 4: ^{13}C -NMR spectra of (a) B_1 derived from algae HTL at 350°C , 20 min, and (b) B_2 obtained from B_1 upgrading at 450°C , 60 min, and Ni-Ru/ CeO_2+H_2 conditions.

about C-related functional groups. The two spectra possessed some peaks in the 0–55 ppm region, where aliphatic methyl and methylene carbon (such as alkane carbons) atoms appear [4]. This suggests that aliphatic linkage variability lies with chain length or degree of branching within the linkers [24]. In detail, the region above can be divided into 0–28 ppm (short aliphatics) and 28–55 (long and branched aliphatics), and these aliphatic carbon atoms contribute significantly to energy content [25]. Except for the solvent peak at around 77 ppm, there was no signal in the 55–95 ppm region, where carbohydrate carbons appear [25]. Moreover, each biocrude also indicated a peak at about 207 ppm, where carbonyl carbons in ketones and aldehydes appear [8]. The drop of the peak area implies the content reduction of the O-containing compounds above after B_1 upgrading with Ni-Ru/ CeO_2+H_2 .

3.6. FT-IR Analysis. Figure 5 elucidates FT-IR spectra of B_1 from algae HTL and B_2 obtained from hydrothermal upgrading of B_1 with Ni-Ru/ CeO_2+H_2 . GC-MS and NMR analysis results show that the two biocrudes contained methylene groups in alkanes, which is proved by further FT-IR analysis herein. Asymmetrical and symmetrical C–H stretching vibrations in aliphatic methylene groups appear in the range of $2800\text{--}3000\text{ cm}^{-1}$ [15]. The existence of carbonyl carbon (such as carboxylic acids and esters) is characterized by the bands at $1650\text{--}1760\text{ cm}^{-1}$ [8]. The high intensity in these two regions is in accord with a significant amount of hydrogen in the biocrudes being aliphatic [15]. The spectrum of B_2 also exhibited strong absorbance at approximately 1450 cm^{-1} , where the scissoring band in methylene groups emerges [23]. This is probably attributed to some mononuclear

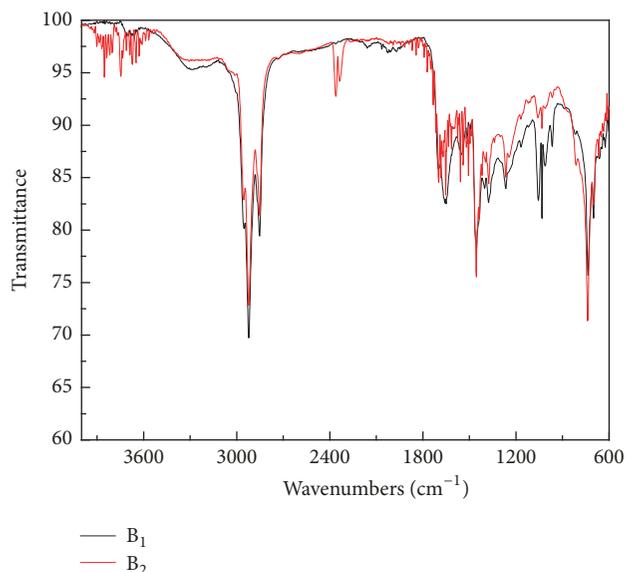


FIGURE 5: FT-IR spectra of B_1 derived from algae HTL at 350°C , 20 min, and B_2 obtained from B_1 upgrading at 450°C , 60 min, and Ni-Ru/ CeO_2+H_2 conditions.

aromatic compounds (e.g., naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl- in Table 3) present in the biocrude. In addition, the two biocrudes also had other different functional groups such as methyl, methylene, aromatic, and alkyne groups appearing at ~ 1378 , ~ 1271 , ~ 1036 , and $\sim 735\text{ cm}^{-1}$, respectively, and their different absorbance intensities imply content variations. Different from B_1 , B_2 presented certain intensity of bands within $2000\text{--}2500\text{ cm}^{-1}$ representing triple bonds or cumulative double bonds and large amounts of absorption peaks within $3600\text{--}3900\text{ cm}^{-1}$ (e.g., O-H stretching vibrations in hydroxyketone [26]). Hence, hydrothermal upgrading of B_1 with Ni-Ru/ CeO_2+H_2 led to obvious variations of functional groups compositions and contents in B_2 .

4. Conclusions

In all tested hydrothermal upgrading (at 450°C , 60 min and with added H_2 and/or catalyst) of B_1 from algae HTL at 350°C , 20 min, Ni-Ru/ CeO_2 had the best catalytic desulfurization effect and could significantly improve H_2 mole fraction and rendered much more H_2 and C-containing gases formation after B_1 upgrading. Ni-Ru/ CeO_2+H_2 led to the highest B_2 yield (27.0 wt%), the best elemental compositions, and the largest HHV (39.94 MJ/kg), as well as the highest B_2^L fraction in B_2 (57.1 wt%) and the best B_2^L quality. At the Ni-Ru/ CeO_2+H_2 condition, 46.2% of chemical energy in initial algae could be recovered in B_2 , and average 54.9% of chemical energy in B_2 was in its light biocrude portion. Ni-Ru/ CeO_2+H_2 was able to transform high-molecular-weight compounds into low-molecular-weight compounds and led B_2 to containing a series of abundant aliphatic saturated hydrocarbons such as pentadecane, tridecane, tetradecane, heptadecane, and dodecane. Overall, Ni-Ru/ CeO_2+H_2 can be regarded as the optimal additive in all tested cases, and there

seemingly was synergetic effect between Ni-Ru/ CeO_2 and H_2 on B_2 yield and quality improvement after B_1 upgrading.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work is supported by the Projects from the National Natural Science Foundation of China (21576219 and 21206132), the Fundamental Research Funds for the Central Universities (no. xjj2016116), the National Key Research and Development Program of China (nos. 2016YFC0801904 and 2017YFB0603604), the Special Financial Grant from the Shaanxi Province Postdoctoral Science Foundation, and the Special Financial Grant from the China Postdoctoral Science Foundation (2014T70922).

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