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Catalytic Hydrothermal Liquefaction of a Microalga in a Two-Chamber Reactor

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ABSTRACT: We carried out catalytic hydrothermal liquefaction of *Nannochloropsis* sp. at 350 °C in a two-chamber batch reactor that physically separated the 5% Pt/C catalyst from the algae and any solid material by a porous metal frit. This two-chamber arrangement provided a higher biocrude yield, a gaseous product richer in hydrocarbons, a biocrude with a larger "light" (hexane-soluble) portion, and a larger portion of biocrude consisting of small molecules than did an equivalent system where algae and catalyst were in physical contact. At the temperature investigated, a longer reaction time reduced the nitrogen and oxygen content in the biocrude, as has been observed in previous studies. Taken collectively, these results demonstrate that physically separating the heterogeneous catalyst and the biomass improves the catalytic hydrothermal liquefaction of microalgae, likely by more effectively doing the separate tasks of biomass liquefaction and biocrude upgrading in a single vessel.

1. INTRODUCTION

Plant biomass is an abundant, renewable material that could be a more carbon-neutral alternative to petroleum as a feedstock for liquid fuels. The first generation of these liquid biofuels derives from edible biomass (e.g., sugar, starch, vegetable oil), whereas the second generation derives from nonedible feedstocks (e.g., lignocellulosic biomass, agricultural residues). Much research is now focused on third-generation biofuels, which are derived from algal biomass. In addition to being a feedstock for biofuels, algae can provide environmental services such as CO_2 removal,[1,2] phytoremediation,[3] and wastewater treatment[4] during their growth. Moreover, algae grow more quickly than terrestrial biomass and can be cultivated on nonarable land and with brackish or salt water.[5]

Algae contain proteins, polysaccharides, and lipids. In some instances, exclusively the lipid fraction is targeted for liquid fuels (e.g., to make biodiesel), as algae can provide a higher oil yield than terrestrial oilseeds commonly used as biodiesel feedstock.[6] Processing the entire algae cell, however, allows the protein and polysaccharide fractions to contribute to biofuel formation, resulting in biocrude yields that exceed the lipid content of the algae.[5] Hydrothermal liquefaction (HTL) is one such process that converts portions of all of the cellular components into biocrude.[7−9] This process accepts a wet algae paste (about 10−20 wt % solids) as a feedstock, and it produces an energy-dense biocrude along with an aqueous-phase coproduct. This aqueous phase contains nutrients (N, P) and can be recycled to the algae growth facility to produce more biomass.[10] The biocrude typically has a higher heating value of ∼35−40 MJ/kg and a carbon content of ∼75 wt %.

HTL operates in hot compressed liquid water at temperatures of ∼300−350 °C. The hot, compressed water can play the roles of catalyst precursor (dissociating to form H^+ for acid-catalyzed reactions), H-donor, and solvent.[11] Additionally, performing the biomass conversion reactions in water eliminates the need to dry the biomass, which would otherwise make a net-energy-positive algal biorefinery unlikely. The literature on HTL ofa microalgae has been expanding rapidly in recent years, and some attempts have been made to use heterogeneous metal catalysts to increase biocrude yields. Different heterogeneous catalysts (Pd/C, Pt/C, Ru/C, Ni/SiO_2−Al_2O_3, CoMo/Al_2O_3, and zeolite)[12] have been applied in the HTL of *Nannochloropsis* sp., and the addition of catalysts promoted higher yields. The elemental compositions and heating values of the crude bio-oil, however, were largely insensitive to the catalyst used. HZSM-5, Fe/ZSM-5, and Ni/ZSM-5 have also been tested in the liquefaction of the macroalga *Laminaria japonica*,[13] and the presence of catalyst promoted the biocrude yield and prevented char formation. Jena et al.[14] tested Na_2CO_3, $Ca_3(PO_4)_2$, and NiO as potential catalysts for the HTL of *Spirulina platensis* and found that Na_2CO_3 increased the biocrude yield compared to noncatalytic HTL.

In addition to this prior work on catalytic HTL, there are reports of catalytic hydrothermal upgrading of biocrude following its formation by HTL.[15] This approach involves a two-step process wherein the biomass is first liquefied to make crude bio-oil and then this crude bio-oil is catalytically upgraded. These studies have shown that the heating value and hydrocarbon content of the upgraded biocrude are generally superior to those of biocrude produced directly by catalytic HTL. It seems that having catalyst present in the reactor with the original biomass feedstock is less effective than using a two-step approach and using catalyst exclusively with the biocrude.

In this work, we use a novel two-chamber reactor in an attempt to combine HTL and catalytic upgrading together in a

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single reactor. Algal biomass is loaded into one chamber, and catalyst is loaded into the other. We selected Pt/C as the catalyst for this study because it is active for hydrogenation and deoxygenation under hydrothermal conditions.[12,16] The two reactor chambers are separated by a porous metal frit, which allows the biocrude components to experience both chambers in the reactor, but confines the biomass and catalyst to their respective chambers. This process intensification idea was inspired by Sawai et al.,[17] who proposed a batch reactor with two compartments for gasification of sewage sludge. We report herein on results obtained with this two-chamber reactor and compare them with the results obtained in a conventional one-chamber catalytic HTL experiment.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials. Algae (*Nannochloropsis* sp.) was purchased from Reed Mariculture, Inc., as a preservative-free slurry with roughly 32.5 wt % solids content and used as received. The ash content was 2.15 wt %. Freshly deionized water, prepared in house, was used throughout the experiments. Dichloromethane and hexane were obtained commercially and used as received. The Pt/C (5 wt %) catalyst was obtained from Sigma-Aldrich and used as received. Previous work[18] indicated that the as-received Pt/C catalyst was just as active as the prereduced catalyst for the hydrothermal deoxygenation of fatty acids.

2.2. Reactors. We fashioned the two-chamber reactor in Figure 1 from stainless steel Swagelok components. The reactor

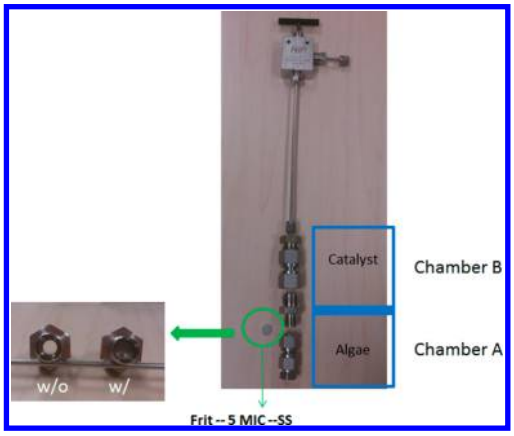

Figure 1. Two-chamber batch reactor.

body consisted of a $^3/_8$-in. port connector (chamber A) connected to a $^1/_2$-in. port connector (chamber B) through a reducing union fitted with a stainless steel frit ($^3/_8$ in., 5-μm pores, from Dale Foster Sales). Individual microalgae cells are about 1 μm in size, but when heated in a hydrothermal environment, they very quickly agglomerate into larger multicellular particles that are unable to pass through the frit.[19,20] The reactor body was attached to a high-pressure valve by a length of stainless steel tubing.

2.3. Procedure. Algae paste (0.6 g) was loaded in chamber A, and the catalyst (15 mg) was loaded in chamber B. Water was loaded in both chamber A (400 μL) and chamber B (1600 μL). Enough water was loaded so that its expansion at the reaction temperature of 350 °C rendered the reactor 87.5% full of the liquid. After the reactors had been loaded and sealed, the residual room air was replaced with He by three repeated cycles of evacuation and pressurization using the high-pressure gas valve. This treatment was then followed by H_2 pressurization and evacuation three times if H_2 was desired in the headspace during the HTL reaction. The reaction mixture was then immersed in a 350 °C preheated isothermal fluidized sandbath, and after the desired reaction time, the reactors were removed from the sandbath and quenched in cold water.

After analyzing the gas phase by opening the valve and admitting a gas-phase sample into the gas chromatograph, we opened the reactor and used 15 mL of dichloromethane to recover the biocrude in both chambers. This mixture was then centrifuged, and the organic phase was withdrawn and filtered through a Buchner funnel. A 1 mL aliquot of the biocrude solution was collected in a gas chromatography (GC) vial for later analysis. The remaining material was subjected to vacuum vaporization to remove the solvent. The material that did not evaporate was the biocrude, and its mass was determined gravimetrically. The biocrude yield was calculated as its mass divided by the mass of algae loaded into the reactor, on a dry, ash-free basis. Next, hexane was added to the solvent-free biocrude to dissolve the "light" fraction. The insoluble portion that remained after removal of the hexane solution was the "heavy" biocrude. The light and heavy biocrude yields were determined gravimetrically. Some HTL experiments were performed in the same reactor but in a single-chamber mode. In these instances, both algae and catalyst were loaded into chamber A. All other conditions and procedures were the same as outlined above.

Control experiments were conducted to make sure that the molecules can go through the frit as expected. Palmitic acid (0.1 g) was loaded in chamber A, and catalyst (0.015 g) was loaded in chamber B. The other conditions and procedures were identical to those used with algae, except that we collected the products from the two chambers separately.

All experiments were repeated at least twice. We report the mean values, and the uncertainties displayed represent standard deviations.

2.4. Analytical Chemistry. The gas-phase products were analyzed with an Agilent 6890N gas chromatograph equipped with a thermal conductivity detector (TCD). A 15-ft × $^1/_8$-in.-i.d. stainless steel column, packed with 60 × 80 mesh Carboxen 1000 adsorbent (Supelco), separated the components in the mixture. Argon served as the carrier gas for the analysis. Mole fractions of the gaseous products were determined from calibration curves obtained by analysis of gas standards with known compositions.

An Agilent 6890N gas chromatograph with a 5973 mass spectrometry (MS) detector and an Agilent HP-5 MS (50 m × 0.2 mm × 0.33 μm) capillary column were used to identify products. The injection port temperature was 310 °C, and the temperature program consisted of a 4 min soak at 40 °C followed by a 4 °C min^{-1} ramp to 300 °C, which was held for 3 min.

An Agilent 7890 gas chromatograph, equipped with a HP-5 capillary column (50 m × 0.2 mm × 0.33 μm), a flame ionization detector (FID), and an autoinjector, served to quantify the mass of light compounds (i.e., palmitic acid and compounds eluting before it). We used pentadecane as a calibration standard and assumed that the FID response was proportional to the mass of carbon in each molecule.

^{13}C nuclear magnetic resonance (NMR) spectra of biocrude were recorded at 110.6 MHz on a 400-MHz NMR spectrometer (Inova 400, Varian) at 25 °C. The sample was dissolved in deuterochloroform ($CDCl_3$). About 10^5 scans were

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accumulated for the spectrum using a 45° pulse width together with broadband proton decoupling. Tubes of 5-mm diameter were used. Atlantic Microlab, Inc., performed elemental analyses of solvent-free biocrude samples.

3. RESULTS AND DISCUSSION

This section first provides results from a control experiment and then compares results from HTL using the two-chamber reactor with those obtained from operation in one-chamber mode and from HTL in the absence of added catalyst.

3.1. Control Experiment. Chamber A was loaded with palmitic acid and no catalyst, and chamber B initially contained catalyst but no palmitic acid. Pt/C is an active catalyst for the hydrothermal decarboxylation of fatty acids,[16,18] so if palmitic acid traveled across the frit, one would expect pentadecane to be formed. After reaction at 350 °C for 1 h, the products were collected from both chambers. Chamber A contained both palmitic acid and pentadecane, as did chamber B. This outcome shows that palmitic acid passed through the frit and reacted with catalyst in chamber B to produce pentadecane. Some of the pentadecane then passed through the frit into chamber A. It is clear that molecules can freely pass through the frit.

3.2. Comparison between One- and Two-Chamber Reactors. This section provides results on the yields and compositions of biocrude produced from HTL in single- and two-chamber catalytic batch reactors and in conventional uncatalyzed HTL.

3.2.1. Oil Yield. Figure 2 compares the biocrude yields obtained in different atmospheres and at different initial loading

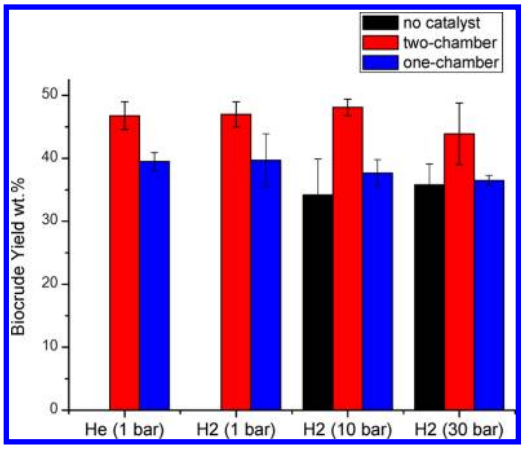

Figure 2. Biocrude yields from HTL at 350 °C for 1 h in one- and two-chamber reactors under different atmospheres.

pressures in a one-chamber reactor and in the two-chamber reactor. For a given reactor, catalytic HTL in either He or H_2 gave biocrude yields nearly equal to those obtained from catalytic HTL with 1, 10, and 30 bar of added H_2. The differences in yields for the different conditions were smaller than the uncertainties in the measured yields. For example, the biocrude yield varied only from 48% to 44% in the two-chamber reactor, indicating that it was largely insensitive to the amount and identity (He or H_2) of gas added to the reactor. It is clear, however, that the biocrude yields in the two-chamber reactor always exceeded those in the one-chamber reactor under the same conditions.

HTL experiments with no added catalyst produced biocrude yields of 34.2% and 35.8% with H_2 loadings of 10 and 30 bar, respectively. The biocrude yields in Figure 2 from the one-chamber catalyzed HTL experiments were 37.7% and 36.5%, whereas those from the two-chamber catalyzed HTL experiments were 48.1% and 43.9%, respectively. Thus, addition of catalyst, even in a one-chamber reactor, can enhance biocrude yields modestly, but the two-chamber arrangement performed much better.

Physical segregation of the catalyst from the biomass seems to enhance the biocrude yield. We speculate that this outcome occurs because the segregation makes it impossible for the biomass itself to deactivate the catalyst by plugging pores or coking the surface. Rather, only biomolecules and their decomposition products are able to diffuse across the porous frit and come into contact with the catalyst. Regrettably, postreaction analysis of the catalyst, which might provide important clues regarding any deactivation, was not possible for the one-chamber reactor because the catalyst was mixed with the solid byproducts from algae at the end of the experiment. It was not possible to isolate just the catalyst alone for postreaction characterization.

3.2.2. Heavy versus Light Biocrude. Figure 3 shows the fraction of biocrude containing light (hexane-soluble) compo-

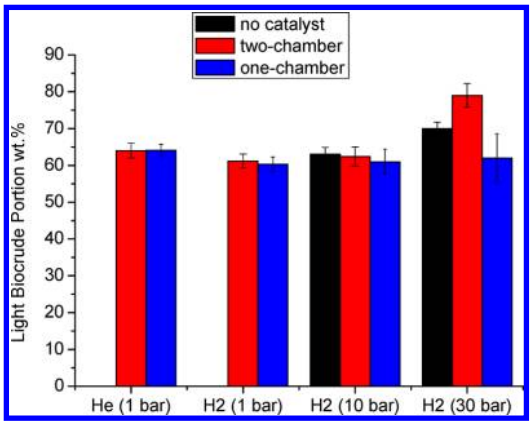

Figure 3. Light biocrude fractions from HTL at 350 °C for 1 h in one- and two-chamber reactors under different atmospheres.

nents. In all but one case, the light fraction constituted about 60−65% of the biocrude. The one exception, catalytic HTL in the two-chamber reactor with the highest H_2 loading, produced a biocrude for which the light fraction accounted for 80% of the material. Evidently, the combined effects of more H_2 and better accessibility to the catalyst promoted reactions (e.g., hydrogenation, hydrodeoxygenation) that produced more of the light biocrude. This result demonstrates another advantage of the two-chamber catalytic reactor. In addition to giving higher biocrude yields, it also can produce a higher-quality biocrude.

3.2.3. Gas Distribution. Gas yields from algae HTL are generally low. In the case of HTL in a He atmosphere, the most abundant gaseous product was CO_2 (82.2 mol %), which is commonly formed from the hydrothermal processing of biomass.[12] The second most abundant gaseous product was H_2 (15.2 mol %), followed by CH_4 (2.1%) and C_2H_6 (0.5%). Figure 4 shows the mole percentages of CH_4 and C_2H_6 in the gas phase from each experiment. The balance of the gaseous product was largely CO_2. The Pt/C catalyst clearly promoted cracking reactions to form methane and ethane, as the gas phase from catalytic HTL was richer in these components than were the gaseous products formed in the absence of added

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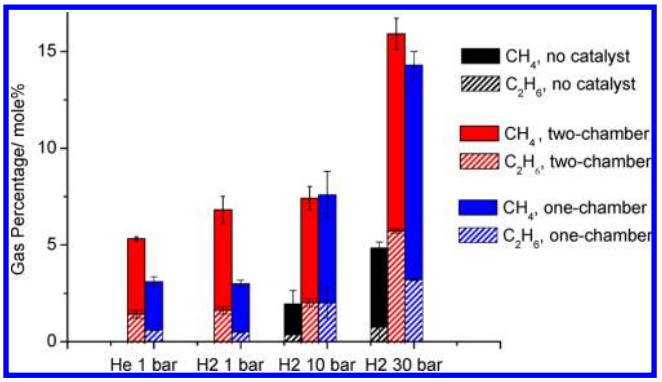

Figure 4. Methane and ethane compositions from HTL at 350 °C for 1 h in one- and two-chamber reactors under different atmospheres.

catalyst (at 10 and 30 bar H_2) . The percentages of CH_4 and C_2H_6 in the gas phase from catalytic HTL were typically larger in the two-chamber than the one-chamber reactor. This result is consistent with the suggestion that the catalyst in direct contact with the biomass in the one-chamber reactor experienced more deactivation than did the catalyst in the separate chamber of the two-chamber reactor. Figure 4 also shows that increasing the pressure of H_2 increased the proportion of alkanes in the gas phase, which is consistent with the catalyst remaining more active for hydrocracking reactions in the two-chamber reactor

3.2.4. Yield of Light Compounds. Previous work on the HTL of this species of algae showed that only about 35% of the mass of the biocrude elutes from the capillary GC column used in our analyses.[21] The balance of the biocrude consists of heavier compounds that are not sufficiently volatile to be amenable to analysis by GC. Accordingly, GC analysis provides a means of comparing the effectiveness of HTL in producing lighter molecules that would be in the range desired for liquid transportation fuels. We used GC analysis to estimate the total yield of compounds in the biocrudes produced in the present work that eluted with or before palmitic acid. We take increases in this total yield as a rough measure of the extent of cracking that occurred during the HTL process. Figure 5 shows that higher loadings of H_2 produced higher yields of light compounds, which is consistent with H_2 playing a role in their formation, perhaps through hydrogenation or cracking. Figure 5 also shows that the two-chamber reactor always produced yields of light compounds that exceeded those from the one-chamber reactor by about 1−2 wt %. This result demonstrates that higher yields of lighter compounds in the biocrude are yet another advantage of using the two-chamber reactor. Indeed, the yields of light compounds from catalytic HTL in the one-chamber reactor were not appreciably different from those obtained in the absence of catalyst.

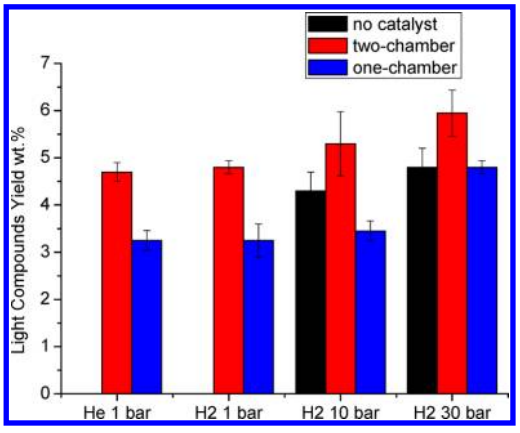

Figure 5. Light compound yields from HTL at 350 °C for 1 h in one- and two-chamber reactors under different atmospheres.

3.2.5. Distribution of Molecular Products. Analysis of the bio-oil by GC-MS permitted identification of many of the individual molecular products, which included alkanes, alcohols, aromatics, phenols, and indoles. The alkanes detected were pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, eicosane, heneicosane, and cholestane. The alcohols detected were mainly benzyl alcohol and phenylethyl alcohol. The aromatics detected were mainly naphthalene, anthracene, ethylbenzene, and styrene. The types of products formed from HTL in the one- and two-chamber reactors exhibited some similarities and some differences. Regardless of which reactor type was used, the biocrude always contained products with carbon chains containing 4−5, 12−17, and 20 backbone carbon atoms; sulfur-containing compounds; and naphthalene and anthracene. Note that the number given for the carbon chain length is a descriptor solely for that part of the molecule. For example, we would classify both pentane and 2-methylpentane as C_5 products. We use this classification system as a rough way to assess the distribution of hydrocarbon chain lengths present in the biocrude and, hence, the extent of cracking.

Hexadecanoic acid (palmitic acid) and C_{27} compounds appeared in the biocrude from HTL in the one-chamber reactor, but not in the biocrude from the two-chamber reactor. The absence of palmitic acid would be consistent with the Pt/C catalyst being better able to decarboxylate fatty acids in the two-chamber reactor. Likewise, the absence of C_{27} compounds suggests that these were readily cracked to smaller molecules in the two-chamber reactor. Interestingly, C_{7-11} and C_{18-19} compounds always appeared in the biocrude produced in the two-chamber reactor but rarely appeared in the biocrude from the one-chamber reactor. The sole exception is for C_{7-11} compounds, which were evident in the one-chamber reactor at the highest H_2 pressure of 30 bar.

3.2.6. ^{13}C NMR Analysis of Biocrude. Figure 6 displays the ^{13}C NMR spectra for the light and heavy biocrude produced in the two-chamber reactor from catalytic HTL at 350 °C and 30

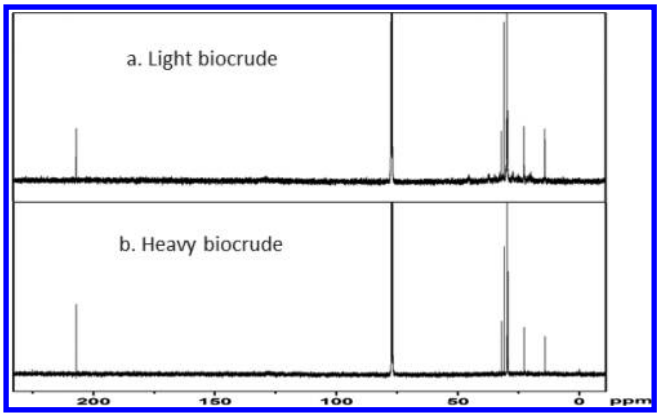

Figure 6. ^{13}C NMR spectra of biocrude (1 h, 30 bar H_2, two-chamber reactor) in $CDCl_3$: (a) light biocrude fraction, (b) heavy biocrude fraction.

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Table 1. Elemental Compositions (wt %) of Light and Heavy Biocrude

	light biocrude					heavy biocrude				
	C	H	N	O[a]	H/C	C	H	N	O[a]	H/C
no catalyst,[23] 1 h, He (0.69 bar)	75.7	10.0	4.5	9.8	1.59	73.2	9.0	6.5	11.3	1.48
1 h, H_2 (10 bar)	75.8	9.9	4.5	9.8	1.57	74.6	8.7	6.4	10.3	1.40
4 h, H_2 (10 bar)	77.7	10.6	4.4	7.3	1.63	75.5	8.3	6.5	9.7	1.32
4 h, H_2 (30 bar)	78.0	10.7	4.1	7.2	1.64	76.7	9.3	5.2	8.8	1.45

[a]By difference.

bar H_2 for 1 h. To the best of our knowledge, this is the first report of NMR characterization of the separate light and heavy fractions of biocrude. The two spectra are about the same. Peaks in the 10−35 ppm region show that aliphatic methyl and methylene carbon atoms are present in the biocrude. The peak at ∼75 ppm shows the solvent $CDCl_3$ used to dissolve the biocrude. The peak at about 220 ppm shows that carbonyl groups are present in both fractions of the biocrude. This result is consistent with the literature,[22] in which catalytically treated biocrude showed a ^{13}C NMR peak at ∼220 ppm. Although the algal biomass feedstock was about 12 wt % carbohydrate, there are no peaks in the 70−100 ppm region where carbohydrate carbons appear. The carbohydrate fraction most likely hydrolyzed to form water-soluble compounds that would not appear in the biocrude. We also note that there is no peak at ∼180 ppm where carboxylic acid carbons would be expected to appear. The absence of a peak here indicates that the fatty acids initially produced by HTL from the hydrolysis of lipids went through decarbonylation or decarboxylation paths. Pt/C is known to be an efficient catalyst for the hydrothermal decarboxylation of fatty acids. This explanation is consistent with the GC results in the previous section, which showed that palmitic acid was present in the one-chamber reactor but absent in the two-chamber reactor, which afforded higher catalyst activity.

Table 1 compares the elemental compositions of the light and heavy biocrudes obtained from catalytic HTL in the two-chamber reactor at different batch holding times and hydrogen loadings. The algae had an elemental composition (on a dry basis) of 52.6% C, 7.4% H, and 8.4% N. After the catalytic hydrothermal liquefaction for 1 h with 10 bar H_2, the carbon and hydrogen contents in the light biocrude increased to 75.8% and 9.9%, respectively. When the reaction time increased to 4 h or the H_2 loading increased, there was a further increase in the carbon and hydrogen contents, along with a decrease in nitrogen and oxygen contents. Consistent with previous work, the heavy biocrude was richer in nitrogen and poorer in C and H than the light biocrude.[23]

Table 1 also permits comparison of the results of catalytic and noncatalytic HTL. Valdez et al.[23] analyzed light and heavy biocrudes from the HTL of the same *Nannochloropsis* sp. with 0.69 bar He at 350 °C for 1 h without a catalyst. The compositions of the biocrude fractions are about the same for the catalytic and noncatalytic HTL experiments. The largest difference is in the O/C ratio for the heavy biocrude. This ratio was 0.104 for the catalytic experiment and 0.116 for the noncatalytic experiment. The presence of the Pt/C catalyst leading to additional biocrude deoxygenation is consistent with earlier work on catalytic HTL.[12]

4. CONCLUSIONS

Loading catalyst and biomass into separate reactor compartments for hydrothermal liquefaction provided a higher biocrude yield, a larger amount of lighter compounds, and a biocrude with a larger light oil component than did HTL in the same reactor with catalyst and biocrude in the same compartment. Indeed, in many instances, the results of one-chamber catalytic HTL were not appreciably different from those of noncatalytic HTL. We suspect that physically isolating the catalyst from the biomass allows the catalyst to retain its activity for a longer time. This two-chamber approach appears to be a more effective way to perform catalytic HTL of microalgae and biocrude catalytic upgrading in a single reactor vessel.

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Notes

The authors declare no competing financial interest.

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