

Hydro-Upgrading of Algal Biocrude in Tetralin for the Production of High-Quality Liquid Fuel: Process Intensification

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November 15, 2020

Abstract

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ABSTRACT

Herein, we report a new process for intensified hydro-upgrading of a biocrude produced from the hydrothermal processing of *Auxenochlorella pyrenoidosa* (AuP) in tetralin at a mass ratio of 1:1 with the addition of 10 wt.% Pt/C and 8 MPa H₂ at different temperatures (300-480 °C) and times (1-8 h). Under the selected reaction conditions, the gaseous products were replaced with fresh H₂ at regular time intervals; this process was then continued until the total reaction time was over. Increasing the number of H₂ replacement times decrease the C, N, O, and S contents and increased the H content. The treated bio-oil mainly consisted of aromatic, saturated and unsaturated hydrocarbons. Overall, H₂ replacement removed some of the denitrogenation, desulfurization, and deoxygenation products and avoided secondary reactions of gaseous products with the bio-oil, thus promoting the hydrogenation reaction and N, O, and S removal from the treated bio-oil.

Keywords: *Microalgae; hydrothermal liquefaction; biocrude; hydro-upgrading; H₂ replacement; treated bio-oil*

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Introduction

Microalgae are an alternative and promising way to solve the energy crisis and environmental pollution caused by the extensive utilization of fossil fuels due to their widespread availability, high efficiency of photosynthesis, short growth cycle, easy adaptation to the environment, large biomass production per acre and carbon neutrality^{1,2}. Thermochemical conversion is one of the most promising and efficient ways to realize energy utilization with microalgae^{3,4}, among which hydrothermal processing (e.g., hydrothermal liquefaction (HTL), hydrothermal carbonization, and hydrothermal gasification) is one of the most popularly employed methods because it can directly use high-moisture microalgae as feedstock⁵. During the HTL process, all the biochemical components, such as lipids, proteins and carbohydrates, contained in the microalgae can be simultaneously converted and transferred into an energy-dense material, biocrude⁵, thus using as much of the organic matter in the microalgae as possible.

However, large proportions of nitrogen (N), sulfur (S), and oxygen (O) in the microalgae are converted into the biocrude during the HTL process, resulting in the biocrude having high concentrations of N, O, and S. Therefore, catalysts were directly added during the HTL of microalgae, aiming to reduce the N, O, and S concentrations of the biocrude in situ. Unfortunately, poor catalyst performance regarding the removal of N, O, and S was observed⁶. Biocrude with a high oxygen content will lead to a high total acid number, high viscosity, low calorific value, and poor stability. Furthermore, biocrudes with high N and S contents will lead to significant quantities of nitrogen oxides and sulfur oxides when burned, causing environmental pollution. Therefore, algal biocrude needs to be further treated to address its several disadvantages prior to use.

To date, many techniques have been used to improve the quality of algal biocrudes, among which hydrotreatment is one of the most effective; most of these techniques involve one-pot treatment of the whole biocrude⁷ in the presence of a catalyst, high-pressure hydrogen, and sometimes a reaction medium. Li and Savage⁸ investigated the hydrotreatment of algal biocrude in the absence of a medium. The advantages of this process mainly include no need for additional medium and no hydrogen partial pressure during the reaction, while the disadvantages are also obvious, such as easy coke deposition, fast catalyst deactivation, and difficulty in reducing the N content of the product oil. The N content of the treated bio-oil remained at 1.6 wt.% after optimization of the reaction conditions. Many researchers have carried out hydrotreatment of biocrudes derived from different biomass feedstocks in different organic media⁹⁻¹¹. The reaction medium selected for hydrotreatment of algal biocrude in the early stage was water because water has many advantages, such as cleanliness, good heat and mass transfer properties and being inexpensive and easy to obtain. Duan and Savage¹²⁻¹⁵, Duan et al.¹⁶, Xu et al.¹⁷, and Bai et al.¹⁸ studied the hydrotreatment of algal biocrude in supercritical water. The results indicated that supercritical water could suppress coke formation, and noble metals such as Pt, Pd, Ru, Ir, and Rh showed high performance toward denitrogenation, while molybdenum-based catalysts such as Mo₂C and MoS₂ showed better performance toward deoxygenation and desulfurization. Under optimal conditions, the N content could be reduced from 4.8 wt.% in the biocrude to 1.5 wt.% in the treated bio-oil, and the effective hydrogen value (H/C)_{eff}¹⁹ could be increased from 1.43 in the algal biocrude to 1.71 in the treated bio-oil. However, the disadvantage of using water as the reaction medium is that water can react with the bio-oil and raise the O content of the final treated bio-oil⁹. In contrast, hydrogen-donor solvents show considerable promise for the hydrotreatment of biocrude as they can not only dilute the biocrude and decrease the viscosity of the feedstock but also transform molecular hydrogen into active hydrogen and improve the hydrogenation efficiency of the feedstock¹⁰.

Recently, a two-stage process was adopted by Yang et al²⁰ to enhance N and O removal from algal biocrude via hydrotreatment in the absence of a medium. That is, biocrude generated from the HTL of microalgae was first processed at 360 °C with added Ni/Mo/γ-Al₂O₃ and 4 MPa H₂. The treated bio-oil collected during the first round of the upgrading process was used as the feedstock for the second round of upgrading under the same reaction conditions as the first run. This approach of two consecutive hydrotreatments of the algal biocrude effectively reduced the N, S, and O contents of the final treated bio-oil and increased the (H/C)_{eff} value from 1.47 in the biocrude to 1.62 in the treated bio-oil separated from the first-round upgrading process and 1.85 in the treated bio-oil separated from the second-round upgrading process. These interesting results provided

inspiration: the equilibrium of denitrogenation, deoxygenation, and desulfurization reactions was broken in this two-stage batch hydrotreatment process of algal biocrude as the denitrogenation, deoxygenation, and desulfurization products were removed when the reactor was opened after the first round of treatment, avoiding the occurrence of secondary reactions of these products with the bio-oil.

Therefore, in the present study, we designed a new process to break the equilibrium of denitrogenation, deoxygenation, and desulfurization in algal biocrude upgrading to substantially decrease the N, O, and S concentrations of the final treated bio-oil. At a given temperature, the algal biocrude was dissolved in tetralin and hydrotreated with added catalyst and pressurized H₂ for a period of time. Then, the reactor was cooled to room temperature, the gaseous products in the reactor were vented, and the reactor was charged with high-pressure fresh H₂. The reactor loaded with fresh H₂ was operated for another period of time and then cycled down when needed. After several rounds of runs, the N, O, and S contents in the treated bio-oil could be significantly reduced. Pt/C (Pt, 10 wt.%) was used as the upgrading catalyst as it showed high performance toward the N, O, and S removal from the algal biocrude^{13,14}. Tetralin was used as the reaction medium to enhance the hydrogenation reaction and made the separation of treated bio-oil easier by enabling the use of centrifugal separation instead of solvent extraction, whose superiorities had been evidenced when used as a reaction medium for hydrotreatment of straw bio-oil fraction. The influence of temperature (300-480 °C), reaction time (1-8 h), and frequency of H₂ replacement (for a given reaction time) on the product distribution and characteristics of the treated bio-oil were examined. Finally, the chemical compositions of treated bio-oil were characterized by elemental analysis and comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry (GC×GC-TOF-MS). Physical properties such as density, viscosity, moisture, total acid number, and freezing point of the treated oil were also tested.

Experimental

Materials

The microalga *Auxenochlorella pyrenoidosa* (AuP) was used as feedstock for the production of biocrude and was purchased from Tianjian Biotechnology Co., Ltd. (Binzhou, Shandong, North China). The received AuP was heated in an oven at 110 °C for 12 h to remove moisture, pulverized to a particle size of 100 mesh and stored in a vacuum desiccator. Table 1 provides the proximate and ultimate analysis of AuP. Pt/C was purchased from Zhengzhou Alfachem Co., Ltd. (Zhengzhou, Henan, China) and received at a moisture content of ~65 wt.% to avoid spontaneous combustion. This high-moisture Pt/C catalyst was processed at 80 °C for 12 h in a vacuum drying oven prior to analysis and use. The Pt/C had 10 wt.% Pt, a particle size of 200 mesh, and a specific surface area of 1200 m²/g. High-purity tetralin ([?]99.5%) was obtained from Aladdin Co., Ltd. (Shanghai, China) and used as received without any further treatment. Ultrapure water prepared in the lab was used for the HTL of AuP.

A GS1L-type stainless-steel batch reactor with a magnetic mixer was employed to conduct the HTL of microalgae. The total internal volume of this reactor was 1000 mL, with rated temperatures and pressures of 400 degC and 25 MPa, respectively. An electrical heater jacket with a power of 3 kW was used to heat the reactor. A photo of this GS1L reactor is provided in Fig. S1(a).

A 60 mL mini stainless-steel batch reactor with a rated temperature and pressure of 500 degC and 40 MPa was employed to conduct the hydrotreatment experiments, and no mixer was installed due to its limited internal space. This mini reactor was heated with a molten-salt bath consisting of KNO₃ and NaNO₃ at a mass ratio of 5:4. A photo of this mini reactor and the molten-salt bath is provided in Fig. S1(b). The two batch reactors were treated with supercritical water at 400 degC for 4 h before use to ensure that the organic impurities in the reactors were totally removed and reactor wall catalysis was deactivated.

Methods

Hydrothermal liquefaction

A total of 100 g of AuP and 200 g of ultrapure water were added into the 1000 mL reactor and sealed. Nitrogen was used to flush the residual air in the head space of the reactor. The reaction was initiated by

connecting a power source. The mixer speed was set at 600 r/min. Approximately 80 min later, the reactor temperature reached 350 degC, and the time was set to zero at this point. The temperature was controlled at 350+3 degC by an Omega temperature controller using a thermocouple inserted into a thermal well on the top cover of the reactor. The reaction time was 60 min. The reaction pressure changed between 19 and 20 MPa during the whole HTL process. After the reaction was completed, the reactor was removed from the electrical heater jacket and placed into an ice water bath to cool to room temperature. The gaseous products in the reactor were vented prior to opening. The oil phase, water phase, and solid residue could be easily separated due to their different densities. The separated biocrude was subjected to centrifugal separation at a speed of 12000 r/min to isolate the residual water and scum. This algal biocrude was stored in a refrigerator for subsequent use.

Hydrotreatment of algal biocrude

In an example experiment, 5.0 g of algal biocrude, 5.0 g of tetralin, and 0.5 g of Pt/C were fully mixed and charged into the 60 mL mini stainless-steel batch reactor, which was tightly sealed. H₂ was used to flush the reactor head space to eliminate the residual air and then charged to 8 MPa, which was in excess of the amount required for the complete removal of N, O, and S in the biocrude. During the hydrotreatment process, tetralin could also be hydrogenated to naphthane with added Pt/C¹⁰. Therefore, we assumed that all the loaded hydrogen was completely consumed by the algal biocrude and tetralin to calculate the gas yield after the reaction. The loaded reactor was put into the preheated molten-salt bath so as to submerge the reactor body. A thermocouple, which was connected to a temperature controller, was inserted into the thermal well on the top cover of the reactor to control the temperature. The preheating time varied from 5 to 15 min depending on the reaction temperature. After the completion of the reaction time, the reactor was removed from the molten-salt bath and put into an ice water bath to cool to room temperature. The gaseous product weight was quantified from the weight difference before and after gas exhaust. The reaction mixture was subjected to centrifugal filtration at a speed of 12000 rpm. The solid residue and catalyst remained in the filter basket, which was dried at 105 degC for 12 h and weighed. The weight of the solid residue was obtained by subtracting the catalyst's weight. The liquid remaining at the bottom of the centrifuge tube was the treated bio-oil. The collected treated bio-oil was weighed and stored in a refrigerator for further characterization. The yields of treated bio-oil, solid residue, and gas were estimated using their mass divided by the mass of the feedstock (biocrude+tetralin) charged into the reactor.

For the hydrogen replacement experiment, once the selected reaction time was over, the reactor was moved out of the molten-salt bath and put into an ice water bath to cool to room temperature. The gas in the reactor was ventilated and then charged with fresh hydrogen to 8 MPa. The goal of this process was to remove the denitrogenation, deoxygenation, and desulfurization products from the reactor and avoid their secondary reactions with the oil. Since the hydrogen was assumed to be completely consumed in the first round of the hydrotreatment process, the fresh hydrogen loaded into the second-round reaction was assumed to not be consumed. Therefore, the real gas weight produced in the second round was calculated by subtracting the amount of fresh H₂ (~0.258 g) charged into the reactor. This freshly H₂-charged reactor was placed into the molten-salt bath again at the same temperature as that of the first stage for another period of time, and then the H₂ replacement process was repeated. Once the total reaction time was over, the reactor was moved out of the molten-salt bath and placed into the ice water bath to cool to room temperature. The subsequent procedure for product recovery was the same as that described above for the first round.

Catalyst characterization

The morphology images of the as-prepared sample were obtained on a field-emission scanning transmission electron microscope (Zeiss GeminiSEM 500). Transmission electron microscopy (TEM), high-angle annular dark-field scanning TEM (HAADF-STEM) and energy-dispersive X-ray spectrometry (EDS) analysis were taken using a Field Emission Transmission Electron Microscope under 200 kV (ThermoFisher Talos-F200X). The surface compositions of samples were collected by a Kratos spectrometer (AXIS Ultra DLD) photoelectron spectrometer with a monochromatic Al K α (1486.6 eV) X-ray source, and the shift of binding energy was calibrated using the C1s level at 284.6 eV as an internal standard.

Product analysis

A Thermo Fisher Scientific FLASH 2000 organic elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA) was used to quantify the C, H, and O contents in the alga, algal biocrude, and treated bio-oils. A TN-3000 chemiluminescence nitrogen analyzer and TS-3000 fluorescence sulfur analyzer (TNS-3000 N, S autoanalyzer, Jiangsu Guochuang Analytical Instrument Co., Ltd., China) were employed to confirm the N and S contents in the treated bio-oil as their concentrations were beyond the detection limit of the organic elemental analyzer. The higher heating value (HHV) was calculated by using the Dulong formula:

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

where C, H, O, and S represent the weight contents of the corresponding elements in the sample.

GC×GC-TOF-MS (LECO Pegasus-IV, LECO, USA) was used to analyze the molecular composition of the algal biocrude and treated bio-oils. Two columns were installed in this GC×GC-TOF-MS system. The first column was a middle-polar VF-17 MS column (30 m × 0.25 mm ID × 0.25 μm film thickness) that separates compounds based on their boiling points. The second column was a nonpolar Rxi-1 MS column (1.79 m × 0.15 mm ID × 0.15 μm film thickness) that separates compounds based on their polarity. Dichloromethane was used to dilute the oil samples at a concentration of 20 wt.%. One microliter of sample was injected each time. The inlet temperature was 300 °C, and the inlet was operated in spitless mode. A 240 s solvent delay was used to protect the filament. He at a flow rate of 1 mL/min served as the carrier gas. The ion source and transmission wire temperatures were 250 °C and 280 °C, respectively. For the one-dimensional oven temperature program, the temperature was held at 40 °C for 3 min, then raised to 280 °C at 4 °C/min and held for 3 min. The mass spectrometry acquisition rate was 100 spectra per second. Each compound was selected from the 10 most similar substances from mainlib and replib for identification. Substances were positively identified with a similarity of 700 or more.

The gas composition after the hydrotreatment reaction was also qualified by the GC×GC-TOF-MS system as mentioned above. The gas sample was injected using a microsyringe injector. For the one-dimensional oven temperature program, the temperature was held at 40 °C for 2 min, raised to 280 °C at 16 °C/min and held for 1 min. The other parameters were the same as in the oil analysis.

A GC-7900 gas chromatograph (Shanghai Techcomp Scientific Instrument Co., Ltd.) was used to quantify the ammonia in the gaseous products. A stainless-steel packed ammonia analysis column was used to separate the gas components. A constant inlet temperature of 120 °C and oven temperature of 60 °C were used. Argon served as the carrier gas at a flow rate of 15 mL/min. The filament current of the thermal conductivity detector (TCD) was set at 50 mA, and the inlet pressure was 0.20 MPa.

The density of the algal biocrude and treated bio-oil was tested by evaluating the weight of one milliliter of sample at 25 °C. The total acid number (TAN) and moisture contents were determined according to Ref.²¹ The viscosity of the algal biocrude and treated bio-oil was determined using NDJ-8S rotary viscometer (Shanghai Changji Geological Instrument Co. LTD, Shanghai, China) at 25 °C according to ASTM D7042-20.²² The freezing point of the algal biocrude and treated bio-oil was estimated using BCQ-600B tester (Shandong Benchuan Instrument Co., LTD, Zibo, Shandong province, China) according to ASTM D2386-19.²³

Results and discussion

Characterization of the Pt/C

The micromorphology of the prepared Pt/C nanomaterial was further characterized by the FE-SEM and TEM measurements. As showed in Fig 1 (a, b), the as-obtained Pt/C sample presented the morphology of nanoparticles with the size of 50-100 nm. TEM image confirms the particle-like structure of the as-prepared sample (Fig. 1c). The bright spots in the STEM images (Fig. 1d) demonstrated that the platinum particles of ultrafine size were tightly anchored on the AC support. Moreover, the EDS elemental mapping analysis (Fig. 1e and f) evidenced that the Pt and C elements were homogeneously dispersed throughout the present catalyst material, which agreed well with the results of STEM.

In order to elucidate the surface electronic state of Pt species on the as-obtained sample, the XPS experiments were performed and the results were shown in Fig. 2. From the core-level spectrum of Pt 4f, the Pt element exists in two types of chemical environments after reduction treatment. A couple of peaks located at binding energies of 74.5 and 71.2 eV were observed, which were ascribed to the Pt⁰ reported on the C²⁴. Furthermore, the other pair of Pt 4f_{5/2} and Pt 4f_{7/2} located at higher binding energies of 75.9 and 72.7 eV was the signal of PtO or Pt(OH)₂. The Pt⁰ / (Pt⁰+Pt²⁺) area for the Pt/C catalyst was 68.8%, verifying that most of the Pt precursor were transformed into Pt⁰ after reduction treatment.

Effect of temperature on product distribution

The influence of reaction temperature on product distribution was first examined by varying the temperature from 300 to 480 °C for 4 h with the addition of 10 wt.% catalyst (Pt/C/biocrude) and 8 MPa H₂ based on the optimization of parameters for the hydrotreatment of algal biocrude¹³. For the hydrogen replacement experiments, at each reaction temperature, after 2 h of reaction, the gas products in the reactor were vented, and the reactor was charged with 8 MPa fresh H₂; the other parameters were kept the same as in the non-H₂ replacement experiments. As expected, three products, oil, solid residue, and gas, were produced during this hydrotreatment process. Fig. 3 provides all the results.

For the non-H₂ replacement experiments, the treated bio-oil yield increased from 93.4 to 67.6 wt.% as the temperature increased from 300 to 480 °C, as macromolecules were easily cracked into smaller macromolecules and finally gases at high temperatures. The same result was also observed for the hydrotreatment of the biocrude fraction of crop straw in tetralin¹⁰, and the yield from the hydrotreatment of pure biocrude also varied as a function of temperature⁸. A higher treated bio-oil yield was always achieved when the algal biocrude was hydrotreated in tetralin¹⁰ than when treated in supercritical water or with pure biocrude alone¹⁴, indicating that tetralin was beneficial for liquid product production as it suppressed coke and gas formation, as proved by a previous study that processed the biocrude fraction of crop straw in tetralin¹⁰. As expected, the gas yield increased from 3.5 wt.% at 300 °C to 27.7 wt.% at 480 °C. A rapid increase in gas yield was found upon increasing the temperature from 400 to 450 °C as gasification was significantly accelerated in this temperature range, which was consistent with the significant reduction in the treated bio-oil yield. The gas yield produced at 400 °C when the biocrude was processed in tetralin was lower than those obtained when biocrude was produced in supercritical water or with pure biocrude alone¹⁸, indicating that tetralin suppressed the gasification reaction by stabilizing the oil intermediates. The gas products primarily comprised unreacted H₂ and CH₄, CO, CO₂, and C₂₋₅hydrocarbons¹²⁻¹⁸, together with denitrogenation, desulfurization, and deoxygenation products. The solid residue yield initially decreased from 3.7 wt.% at 300 °C to 1.9 wt.% at 400 °C and increased again with further increasing temperature. At 300 °C, some of the high-molecular-weight compounds could not be totally cracked into smaller compounds, and thus, a large amount solid residue was produced. Increasing the temperature between 300 and 400 °C promoted the cracking reaction of high-molecular-weight compounds. At temperatures >400 °C, polymerization prevailed, and a higher solid residue yield was again observed. Higher solid residue production was undesirable as it would cover the catalyst and thus could inactivate the catalyst.

For the H₂replacement experiments, raising the temperature from 300 to 480 °C reduced the treated bio-oil yield from 96.8 to 73.9 wt.%, which is consistent with the trend obtained without H₂replacement. Interestingly, however, the treated bio-oil yield generated with H₂ replacement was always higher than that generated without H₂ replacement at the same reaction temperature due to reduced gas and solid residue yields. The gas product yield during the first 2 h was always lower than that at a total reaction time of 4 h. This is reasonable, as a longer reaction time would favor gas production at a given temperature. The gas product yield was significantly lower in the second 2-h stage than in the first 2-h stage, as almost no hydrogen was consumed in the second 2-h stage. The same solid yield variation trend was observed as that obtained without H₂ replacement, but the solid residue yield was always lower than that obtained without H₂ replacement. With H₂ replacement, the denitrogenation (HCN, NH₃) and desulfurization (SO₂) products would be removed from the reactor, which would decrease the possibility of catalyst poisoning and thus retard the polymerization reaction of the coke precursor. Therefore, a lower solid residue yield was always

observed for the H₂ replacement experiments than the non-H₂ replacement experiments at the same reaction temperature.

Comprehensively considering the yield and quality of the treated bio-oil (see Table 2), 400 °C was chosen as the temperature for subsequent optimization of the hydrotreatment parameters.

Effect of time on the product distribution

The influence of reaction time on product distribution was examined at 400 °C with the addition of 10 wt.% catalyst (Pt/C/biocrude) and 8 MPa H₂ for 1, 2, 4, 6, and 8 h. For the H₂replacement experiments, the gas products in the reactor were vented, and the reactor was subsequently charged with fresh H₂; this process was performed every 2 h for total reaction times of 4, 6, and 8 h and every 0.5 and 1 h for total reaction times of 1 and 2 h, and the other parameters were kept the same as in the non-H₂replacement experiments. Fig. 4 provides all the results.

For the non-H₂replacement experiments, time had less of an effect on product distribution than did temperature. Extending the time from 1 to 4 h gradually reduced the treated bio-oil yield from 92.6 to 86.2 wt.% as a longer reaction time favored the cracking of macromolecules to smaller ones. Further extending the time had almost no effect on the product distribution, as the reaction was thermodynamically controlled at a reaction time of [?]4 h. A treated bio-oil yield of 83.7 wt.% was observed when the same algal biocrude was treated at 400 degC for 2 h in tetralin with 10 wt.% added Ru/C, indicating that external hydrogen was necessary to obtain a higher treated bio-oil yield²¹. The gas product yield increased from 6.8 to 10.9 wt.% as the reaction time increased from 1 to 4 h and exhibited almost no variation with further extension of the reaction time. The solid residue yield consistently increased from 0.6 to 4.5 wt.% as the reaction time increased from 1 to 8 h, indicating that the polymerization reaction always existed during the reaction. The solid residue yield produced at 2 h (1.1 wt.%) was markedly lower than that generated under the same reaction conditions without the addition of external hydrogen²⁵, indicating that the hydrogen source played a very important role in the suppression of solid residue formation during the hydrotreatment process.

For the H₂ replacement experiments, extending the time from 1 to 8 h reduced the treated bio-oil yield from 94.4 to 87.6 wt.%, which is consistent with that trend produced without H₂replacement. Interestingly, however, the treated bio-oil yield produced with H₂ replacement was always higher than that without H₂ replacement at the same reaction time due to reduced gas and solid residue production. The total gas yield increased from 5.1 to 9.5 wt.% with increasing time from 1 to 4 h. Further extending the time had almost no effect on the gas yield. The total gas yield was never higher than that produced without H₂ replacement at the same total reaction time, as only a small amount of hydrogen was consumed after the first round of H₂ replacement. The solid residue yield presented the same trend as in the non-H₂ replacement experiments, increasing from 0.1 to 2.3 wt.% as the reaction time increased from 1 to 8 h. A lower solid residue yield was also achieved relative to that produced without H₂ replacement at the same reaction time due to removal of denitrogenation, deoxygenation, and desulfurization products.

Effect of H₂ replacement frequency on the product distribution

The influence of H₂ replacement frequency on the product distribution was examined at 400 degC for a total reaction time of 6 h with 10 wt.% added catalyst (Pt/C/biocrude) and 8 MPa H₂. Every 3, 2, 1.5, 1.2, and 1 h, the gas products in the reactor were vented, and the reactor was charged with fresh H₂. Fig. 5 presents all the results.

For the given time of 6 h, increasing the H₂ replacement frequency from 1 to 5 times gradually increased the treated bio-oil yield from 86.1 to 91.0 wt.%, although this yield increase was small, because the gas and solid residue production was reduced. The more frequent replacement was, the shorter the gas products stayed in the reactor, and the lower the possibility of catalyst poisoning. As expected, the yields of gas and solid residue products consistently decreased with increasing H₂ replacement frequency. The gas products were mainly produced before the first round of H₂ replacement due to prevailing denitrogenation, deoxygenation, and desulfurization reactions at this stage. The solid residue yield was reduced from 2.4 to 1.6 wt.% as the

H₂ replacement frequency increased from 1 to 5 times at a given total reaction time of 6 h. That is, if the gas products were removed from the reaction system as soon as possible, they would not poison the catalyst, and secondary reactions with the oil would be avoided, thus prolonging the activity of the catalyst for the hydrogenation reaction. Correspondingly, a lower gas and solid yield and higher treated bio-oil yield would be achieved.

Characterization of the algal biocrude and treated bio-oils

Physical properties

The algal biocrude had a density of 1.05 g/cm³, viscosity of 21.80 mpa.s, moisture of 2.13 wt.%, total acid number (TAN) of 47.10 mgKOH/g, and freezing point of -8.4 degC, which agreed with a previous study²¹. In contrast, the treated bio-oil was found to have approximately 1.32-2.34 wt.% moisture depending on the hydrotreatment conditions. The density of the treated bio-oil varied between 0.88 and 0.95 g/cm³, smaller than that of the blended biocrude and tetralin feedstock (~1.02 g/cm³). The viscosity of the treated bio-oil varied from 8-18 mpa.s, and raising the temperature and extending the time reduced the viscosity of the treated bio-oil. A much lower TAN of the treated bio-oil was also found, which varied between 4 and 13 mgKOH/g due to the removal of acidic compounds. The freezing point of the treated bio-oil was reduced to -14-22 degC which is similar with -20 # diesel.

Elemental analysis

Table 2 provides the elemental composition, H/C molar ratio, and HHV of the alga, biocrude, and treated bio-oils generated under different reaction conditions. Approximately 60% of the N, 77% of the S, and 40% of the O that were originally contained in the alga were converted into the biocrude during the HTL process at 350 degC. Thus, the biocrude had a certain amount of N (52541 ppm), O (9.04 wt.%), and S (5180 ppm). The addition of tetralin to the biocrude at a mass ratio of 50% halved the N, S, and O contents of the biocrude. Under all experimental conditions examined, the treated bio-oil always had a higher C content and lower H, N, O, and S contents than did the algal biocrude and tetralin blend, implying that deoxygenation, denitrogenation, and desulfurization took place during the hydrotreatment process.

For the non-H₂replacement experiments, the C content consistently increased from 84.99 wt.% at 300 degC to 89.75 wt.% at 480 degC. A slight increase in H content was found as the temperature increased from 300 to 350 degC. However, a further elevation in temperature gradually reduced the H content of the treated bio-oil. Hydrogenation and dehydrogenation reactions took place simultaneously during the hydrotreatment process. Heat is released in the hydrogenation reaction; thus, a lower temperature is favorable for the occurrence of this reaction. At temperatures >350 degC, dehydrogenation reactions prevailed, and more aromatics (see Table 3) were formed²⁵, thus decreasing the H content of the treated bio-oil. The reduced H/C molar ratio of the treated bio-oil with increasing temperature again proved the increasing aromaticity of the treated bio-oil. The HHV of the treated bio-oil was accordingly reduced from 44.55 MJ/kg at 350 degC to 41.60 MJ/kg at 480 degC. The S content of the treated bio-oil consistently decreased from 477 ppm at 300 degC to 2 ppm at 480 degC, indicating that a higher temperature was favorable for the desulfurization reaction. The N and O contents also decreased from 2.19 wt.% and 22448 ppm at 300 degC to 0.70 wt.% and 6778 ppm at 480 degC. However, a further increase in temperature increased the O and N contents of the treated bio-oil, possibly due to the secondary reaction of deoxygenation and denitrogenation products with the bio-oil at the severe temperature of 480 degC, indicating that severe temperatures would not guarantee obtaining treated bio-oil with lower concentrations of N and O. The same variation trend as a function of temperature was observed for the elemental composition of the biocrude fraction of crop straw treated in tetralin with added Pt/C and high-pressure H₂²⁶.

For the H₂ replacement experiments, the C, H, N, O, and S contents presented the same variation trend as in the non-hydrogen replacement experiments. Generally, the treated bio-oil had higher concentrations of C and H and lower concentrations of N, O, and S than did treated bio-oils produced without hydrogen replacement, indicating that the removal of denitrogenation, deoxygenation, and desulfurization products avoided their secondary reactions with the bio-oil. The S content of the treated bio-oil generated at 480

degC was 0 ppm. However, the N content of the treated bio-oil generated at 450 degC was 3122 ppm, indicating that N was more difficult to remove than S. Sharp reductions in N, O, and S concentrations were found as the temperature increased from 300 to 400 degC regardless of H₂ replacement, indicating that denitrogenation, deoxygenation, and desulfurization reactions mainly happened in this temperature range. The treated bio-oil generated at 350-480 degC with H₂ replacement always possessed a higher H/C molar ratio than did that generated without hydrogen replacement, indicating that the hydrogenation reaction was promoted with hydrogen replacement. The HHV of the treated bio-oil produced with hydrogen replacement was always higher than that produced without hydrogen replacement.

Increasing the reaction time increased the C concentration and decrease the H, O, N, and S concentrations of the treated bio-oil under H₂ replacement or non-H₂ replacement conditions. Higher H concentrations and lower C, O, N, and S concentrations in the treated bio-oil were observed with hydrogen replacement than under non-hydrogen replacement conditions, again indicating that H₂ replacement was helpful for hydrogenation reactions and the removal of N, O, and S in the bio-oil. A sharp reduction in S concentration was observed as the time was extended from 1 to 4 h for both H₂ replacement and non-hydrogen replacement reactions. Further extension of the reaction time only slightly reduced the S concentration. The S concentrations of the treated bio-oil generated at reaction times of 6 and 8 h were almost the same regardless of H₂ replacement, indicating that desulfurization reached equilibrium at 400 degC. A slight reduction in N concentration was found as the reaction time was extended from 1 to 2 h for both non-hydrogen replacement and hydrogen replacement reactions. A sharp reduction in N concentration was found as the reaction time increased from 2 to 4 h for both non-H₂ replacement and H₂ replacement reactions. Small variations in the O concentration of treated bio-oil were observed as the reaction time was extended from 1 to 8 h for both non-H₂ replacement and H₂ replacement reactions as the deoxygenation product H₂O was difficult to remove from the reactor because most of the H₂O existed in the liquid state. The H/C molar ratio and HHV of the treated bio-oil also decreased with increasing reaction time regardless of H₂ replacement.

Increasing the number of H₂ replacement times decreased the C, N, O, and S concentrations and increased the H concentration of the treated bio-oil. The greater the number of H₂ replacement times was, the lower the N, O, and S contents of the treated bio-oil. That is, the denitrogenation, desulfurization, and deoxygenation products would be removed as rapidly as possible by increasing the number of H₂ replacement times, avoiding secondary reactions with the bio-oil and decreasing the possibility of poisoning the catalyst. The N, S, and O concentrations were reduced by 68%, 49%, and 24% as the number of H₂ replacement times increased from 1 to 5 times, indicating that the number of H₂ replacement times had a greater influence on the N concentration of the treated bio-oil than on the concentrations of S and O. The H/C molar ratio and HHV of the treated bio-oil also increased with increasing number of H₂ replacement times due to the acceleration of hydrogenation reactions.

GC-MS analysis

Comprehensive GCxGC-TOF-MS analysis was employed to analyze the molecular composition of the biocrude and treated bio-oils produced under different reaction conditions. Fig. S2-6 show the results. The dense dots on the two-dimensional chromatogram represent different compounds with different boiling points and polarities. The advantage of using GCxGC-TOF-MS is that compounds with similar properties typically stay together in a specific area and avoids co-eluting peaks. It should be noted that compounds with a boiling point >300 degC might not have been detected as the inlet temperature was set at 300 degC. Furthermore, compounds with a retention time <240 s could also not be detected due to the 240 s solvent delay. To more intuitively explain the relative proportion of substances in treated bio-oil, one-dimensional total ion chromatograms are also presented in Fig. S2-6.

To clearly demonstrate the influence of reaction conditions on the molecular composition of the treated bio-oil, Table 3 lists the relative content of each compound class in the biocrude and treated bio-oils. Clearly, the biocrude contained a significant quantity of amide (e.g., N-methyldodecanamide, octadecanamide, and hexadecanamide)¹⁸ (26.28%) and O-containing compounds (11.44%), and approximately 0.23% S-containing (e.g., allylphenyl sulfide) compounds were also observed, which was consistent with a previous study^{17,18}.

These compounds are mainly generated from the direct decomposition of proteins, lipids, and carbohydrates in algae or secondary reactions between these decomposition products. Only 6.98% aromatic hydrocarbons and 23.46% saturated hydrocarbons were observed in the biocrude. In contrast, after the biocrude was hydrotreated in tetralin, the contents of amides, unsaturated hydrocarbons, and O-containing compounds were reduced, and the contents of aromatic and saturated hydrocarbons increased in the treated bio-oil. The increase in aromatic hydrocarbons is mainly due to the presence of tetralin and its hydrogenation products. The saturated hydrocarbons in the treated bio-oil were mainly composed of n-alkanes starting from C7, which correspond to many regularly spaced peaks in the one-dimensional total ion chromatograms.

Increasing the temperature increased the aromatic hydrocarbon content and reduced the unsaturated hydrocarbon content in the treated bio-oil, which agreed with the reduced H/C molar ratio of the treated bio-oil regardless of H₂ replacement. The saturated hydrocarbon content in the treated bio-oil increased as the temperature increased from 300 to 400 degC due to the dominant hydrogenation reactions. A further increase in temperature gradually decreased the saturated hydrocarbon abundance in the treated bio-oil due to the acceleration of aromatization at severe temperatures. A sharp reduction in N-containing compounds was also found as the temperature increased from 300 to 400 degC regardless of H₂ replacement, which was consistent with the N content observed by the elemental analysis. Zhao et al. showed that amides could be converted to nitrile compounds at approximately 300 degC and that the nitrile compounds at 350 degC almost completely disappeared and were converted into hydrocarbons, which is consistent with the results of the present study²⁷. The N-containing compounds in the treated bio-oil produced at 480 degC mainly consisted of hydrazine, carbazole, pyrazole, and naphthylamine; these kinds of compounds were extremely difficult to remove. Almost no S-containing compounds were detected in the treated bio-oil at temperatures above 400 degC, which agreed with the elemental analysis.

Extending the reaction time increased the aromatic hydrocarbon content and decreased the saturated hydrocarbon and unsaturated hydrocarbon contents, implying that a longer reaction time was also beneficial to aromatization reactions. A higher aromatic hydrocarbon content was always observed for the treated bio-oil produced without H₂ replacement. Increasing the number of H₂ replacement times could also decrease the aromatic hydrocarbon and unsaturated hydrocarbon contents and increase the saturated hydrocarbon content of the treated bio-oil. The saturated hydrocarbon content in the treated bio-oil produced with 5 rounds of H₂ replacement reached as high as 71.62%.

Overall, the GC-MS analysis agreed with the results of the elemental analysis. H₂ replacement was beneficial for reductions in the aromatic and unsaturated hydrocarbon contents and an increase in the saturated hydrocarbon content.

Evidence of the reaction of gaseous products with the bio-oil

The gaseous products produced from hydrotreatment of biocrude and tetralin blended at a mass ratio of 1:1 at 400 °C for 6 h with 10 wt.% added Pt/C and 8 MPa H₂ were analyzed by GCxGC-TOF-MS and GC-TCD at the same time. The relative quantity of each component in the gas products detected by GC-MS is listed in Table S1. GC-TCD analysis indicated that the gaseous products were largely composed of unreacted H₂, CH₄, and CO₂ together with trace amounts of CO and C2-C5 hydrocarbons, which was consistent with the results produced from hydrotreatment of the biocrude fraction of crop straw in tetralin²⁵. A certain amount of NH₃ was also detected in the gaseous products by GC-TCD, which was derived from the denitrogenation of N-containing compounds in the biocrude. GC-MS analysis of the gaseous products indicated that a certain amount of N-containing compounds, such as C₂H₄N, C₃H₇N, and C₆H₇N rather than NH₃, also existed. S-containing compounds such as thiocyanic acid and sulfur dioxide were also observed in the gaseous products. If these N- and S-containing gases were removed during the reaction, the possibility of reaction between these gases and bio-oil would be avoided.

To verify the reaction between the hydrotreatment gaseous products and bio-oil, the gaseous products produced from hydrotreatment of biocrude and tetralin blended at a mass ratio of 1:1 at 400 °C for 6 h with 10 wt.% added Pt/C and 8 MPa H₂ were used as the gas environment for the treatment of a model oil at 400

for 4 h with 10 wt.% added Pt/C and 8 MPa H₂. The model was a mixture consisting of 3 g of n-C₁₂, n-C₁₄, and n-C₁₆ (mass ratio of 1:1:1) and 3 g of tetralin. After the reaction, the oil products were combined and analyzed by GCxGC-TOF-MS. Fig. 6 presents the total ion chromatograph of this treated model oil. As expected, N- and S-containing compounds were found in the treated model oil products, indicating that reactions between the model oil and the gaseous products occurred. Therefore, H₂ replacement could remove some of the N- and S-containing compounds from the reaction system, avoiding secondary reactions of the gaseous products, and thus favored N and S removal from the bio-oil.

These above results suggest that a new reactor configuration is needed to realize the in situ removal of gaseous products during the hydrotreatment of biocrude and avoid the loss of oil products at the same time. Fig. S7 shows a schematic diagram of this new reactor configuration suitable for the in situ removal of gaseous products. High-pressure H₂ is continuously charged into the reactor during the hydrotreatment of the biocrude, and the gaseous products are carried out of the reactor by H₂ together with part of the oil fraction. The flowed out oil fraction is condensed to liquid and flowed back to the reactor. After a certain amount of time, most of the N- and S-containing compounds are removed from the reaction system, and deep removal of N, S, and O would be expected.

Conclusion

Tetralin is a promising medium for the upgrading of biocrude derived from HTL of microalgae by diluting the biocrude, transforming H₂ into active hydrogen, controlling coke formation, and favoring denitrogenation, desulfurization, and deoxygenation. Increasing temperature and time decreased the yield but improved the properties of the treated bio-oil, such as by decreasing the N, O, and S contents, regardless of H₂ replacement. Raising the temperature and time could also increase the aromaticity of the treated bio-oil by decreasing its H/C molar ratio, but a lower aromaticity and higher H/C molar ratio of the treated bio-oil were observed for H₂replacement experiments. H₂ replacement removed the hydrodenitrogenation, hydrodesulfurization, and hydrodeoxygenation products from the reaction system, avoided their secondary reactions with the oil products and decreased the possibility catalyst poisoning and would thus be favorable for hydrogenation reactions, an increased treated bio-oil yield, and N, O, and S removal from treated bio-oil. With H₂ replacement, 88% of the O, 92% of the N, and 100% of the S originally contained in the algal biocrude were removed under optimal reaction conditions. The treated bio-oil mainly consisted of aromatic and saturated hydrocarbons, making up more than 80% of the treated bio-oil. However, the N content of the treated bio-oil was still higher than that of commercially available fossil diesel. Thus, future work should concentrate on the in situ removal of hydrodenitrogenation, hydrodesulfurization, and hydrodeoxygenation products from the reaction system.

Acknowledgments

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (21776063; 22078082; U1704127), the Scientific and Technological Innovation Team of the University of Henan Province (18IRTSTHN010).

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