



Catalytic upgrading of fractionated microalgae bio-oil (*Nannochloropsis oculata*) using a noble metal (Pd/C) catalyst



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ABSTRACT

Pyrolytic bio-oil was chemically upgraded after physically distilled upgrades to meet the petroleum transportation fuel substitute. A Pd/C catalyst was used to upgrade the microalgae pyrolytic bio-oil to determine the effect of different distillation fractions and catalytic upgrading conditions on the yields and properties. The middle distillation fraction (F2) was upgraded under various temperature (130 to 250 °C) and pressure (4.1 to 8.3 MPa) conditions based on response surface methodology (RSM). The light distillation fraction (F1) and raw bio-oil were also catalytically upgraded for the comparison. The distillation step prior to catalytic upgrading led to a better quality of upgraded bio-oil compared to the direct bio-oil upgrades. Both the oxygen and hydrogen contents of light and middle fraction upgrades were improved, while the upgraded raw bio-oil showed limited improvement. The other properties of HHV and TAN with the middle fraction upgrades were improved to 42.9 MJ/kg and 1.09 mg KOH/g, respectively, at the severe condition as most of the ketones in upgrades were removed. Also, paraffin and aromatic chemical groups were significantly produced at the expense of the olefin groups through hydrogenation and hydrodeoxygenation. Thus, the catalytic upgrading after a distillation stage enhanced the quality of biofuel that can be a petroleum fuels substitute or additives.

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1. Introduction

Microalgae, as a source of third generation biofuels, have obtained much attention as an alternative energy source because they overcome the drawbacks of first and second generation biofuels. With simple conditions required for growth, light, sugar, CO₂, N, P, and K, photosynthetic microalgae microorganisms grow rapidly even on non-arable land. The large amounts of lipids, proteins and carbohydrates in microalgae can be processed into biofuel, medicine, and food [1]. Many microalgae biofuels were studied in the form of biodiesel from lipid transesterification [2], bio-oil from the thermal conversion process of pyrolysis [3–5] and hydrothermal liquefaction (HTL) [6]. The transesterification process for biodiesel produced a large amount of residue, while the bio-oils showed high viscosity, high acidity, and high nitrogen and sulfur contents [7,8].

An upgrading of thermally converted bio-oils is required for them to be used as potential fuel substitutes or additives. A physical method of distillation and a chemical method of catalytic upgrading were used to upgrade pyrolytic bio-oil by reducing the O/C ratio and increasing the H/C ratio, which also enhances the other fuel properties of viscosity, acid number, heating value, and water content. Distillation as a physical separation process upgrades bio-oils based on the relative volatility of chemicals at various temperatures. Several techniques were used to upgrade the microalgae bio-oil with direct, fractional, steam, vacuum, and molecular distillations. Bio-oil (*Spirulina* sp. and *Tetraselmis* sp.) from hydrothermal liquefaction (HTL) was fractionated using a vacuum distillation at temperature conditions of 300 °C and 350 °C [9]. The maximum yields of an HTL bio-oil and its distillates were 58% and 73%, respectively, whereas each HHV (higher heating value) were 32 MJ/kg and 40 MJ/kg with a 97% deoxygenation of bio-oil. In our previous study [8], the bio-oil of *Nannochloropsis oculata* microalgae was physically upgraded using fractional and vacuum distillation setups. Both the techniques showed similar distillate properties, while a higher product yield was obtained from fractional distillation when better separation was made with vacuum distillation. The lower operating temperature of vacuum distillation prevented polymerization in the heavy fraction. The HHV and the lowest total acid number (TAN) were

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41.2 MJ/kg and 0.1 mg KOH/g obtained through deoxygenation and de-hydration. Still, the fuel needed a further bio-oil upgrading step to be used as a petroleum fuel substitute due to the existence of oxygen and nitrogen contents, and high acidity in a certain bio-oil fraction.

A chemical upgrading of catalytic hydrotreatment is performed by removing the oxygen, nitrogen, and sulfur contents from bio-oil, which is also used in the conventional petroleum refining process. Catalytic upgrading generally requires the reactions between hydrogen gas and bio-oil at high pressure and temperature with enough reaction time. Various alumina, silicate, and carbon based catalysts for bio-oil upgrading were evaluated from many studies. A catalyst screen study by Bai et al. [7] used 12 different catalysts for HTL bio-oil (*Chlorella pyrenoidosa*) upgrading. The highest product yield (77%) and a HHV of 45.3 MJ/kg for upgraded bio-oil were obtained with a mixed catalyst of Ru/C and Raney-Ni, and the lowest O/C (0.01) and N/C (0.017) were achieved with Ru/C and Raney-Ni, respectively. An HTL bio-oil (*Nannochloropsis* sp.) upgrading in supercritical water also conducted by Duan and Savage [10] to determine the effect of Pt/C, H₂ pressure (3.5 MPa), and the pH of bio-oil on the bio-oil upgrades at 400 °C. The upgraded bio-oil showed a substantially decreased acid number, 25 mg KOH/g, with a decrease in O/C (0.041) and H/C (1.64) contents, which led to an increase the HHV (43 MJ/kg). They also conducted a similar study using Pd/C at the same temperature and pressure conditions to find the effect of reaction time (1–8 h) and catalyst loading (5–80%) on the hydrotreatment products [11]. The upgraded bio-oil properties with Pd/C upgrading showed 43.5 MJ/kg for HHV, 0.028 for O/C, and 1.79 H/C, which had a somewhat better result compared to the Pt/C upgrading. Barreir et al. [12] conducted HTL bio-oil upgrading (*Scenedesmus Almeriensis* and *Nannochloropsis Gaditana*) using Pt/Al₂O₃ and HZSM-5 at 400–450 °C with 4–8 MPa. The addition of water for the catalytic upgrading at a lower H₂ pressure produced more oxygen chemicals compared to the upgrading under only H₂ pressure. Also, Lin et al. [13,14] produced green diesel from hydrodeoxygenation of extracted microalgae oil using various catalysts (NiMo, Pt and Rh) in a continuous flow microreactor. The optimum yield of hydrocarbon ranging from C₁₃ to C₂₀ was 56% at operating conditions of 500 psi, 360 °C, and 1 s contact time. Maguyon [15] studied the pyrolysis bio-oil upgrading (*Nannochloropsis oculata*) with an HZSM-5 catalyst at a constant pressure (4.1 MPa) to determine the effect of temperature (200–300 °C) and reaction time (1–4 h). Mass balance was achieved based on the amount of upgraded bio-oil, coke, tar, and gas. The upgraded bio-oil showed a basic pH level (7.7–8.9) and the HHV ranged from 37.5–40 MJ/kg with a 1.46 H/C and 0.032 O/C.

Even though many upgrading methods with various catalysts were studied based on the various operating conditions, few catalytic upgrading studies of distilled bio-oil have been reported. As a continuing distillation study of Nam et al. [8], the distilled bio-oil of light and middle fractions were used for chemical catalytic upgrading. The current study can expand the understanding of the effectiveness of the catalytically upgraded bio-oil from distilled bio-oil. The objectives of the study were to,

- 1) assess the effects of distilled bio-oils through Pd/C catalytic upgrading on the properties of bio-oil,
- 2) evaluate the performance of the catalyst at various conditions of temperature and pressure on the deoxygenation, hydrogen consumption, and turnover frequency, and,
- 3) to investigate the catalyst deactivation after catalytic upgrading.

2. Experimental

2.1. Sample preparation

An algae species, *Nannochloropsis oculata*, from the Texas A&M Agrilife pond in Pecos, Texas, was obtained for pyrolysis and bio-oil distillation. The wet algae sample was first dried and processed through a batch type pyrolysis reactor, which was also used in other studies

[3,16]. The mass recovery and HHV (higher heating value) of bio-oil from pyrolysis was 20% and 38.6 MJ/kg. The bio-oil was then fractionated using a fractional distillation setup as shown in Fig. 1(b). The light ($T < 120$ °C) and middle (120 °C $< T < 200$ °C) fractions after fractional distillation were used in this study. The distillation mass recovery was 23% for the light fraction (fraction 1 or F1), 52% for the middle fraction (fraction 2 or F2) and 19% for the heavy fraction (fraction 3 or Fe), while the HHVs were 40.0 and 41.2 MJ/kg, respectively. A study by Nam et al. [8] showed a detailed fractional and vacuum distillation study for the fractionated microalgae bio-oils.

2.2. Experimental setup and procedure

A batch type reactor (Micro Robinson-Mahoney, Autoclave Engineers) was used for the current catalytic upgrading study. The volume of the batch was 50 mL, which can handle a maximum pressure to 5000 psi at 343 °C or a maximum temperature to 538 °C as shown in Fig. 1(c). The temperature of the reactor was controlled by an electric heating band with a PID temperature controller. Two K type thermocouples were used; one for the temperature inside the reactor, and the other for the temperature of the electric heater. An internal stirrer was placed inside the batch to help in uniform reactions, and was set at around 300 rpm during the experiment.

Each pressurized catalytic experiment was conducted with 7 g of bio-oil with 5% of 5%Pd/C catalyst (Sigma Aldrich, USA). Before the start of the experiment, hydrogen gas was used to flush as much air as possible from inside the reactor. Then the reactor was pressurized with 4.1, 6.2, or 8.3 MPa of hydrogen gas at room temperature. Once the experiment was ready to run, the heater jacket heated the inside reactor to 130, 190, or 250 °C with a stirring of 400 rpm. A constant reaction time was set at 4 h based on Duan and Savage [11], who state that the properties of upgraded bio-oil were not improved much after 4 hour reaction time. At the end of the 4 hour reaction time, the system was shut down and the temperature reduced to room temperature with the help of a water jacket. First, the pressure at room temperature after each experiment was noted to compute the amount of hydrogen gas used. The gas samples were then collected for analysis. Last, the upgraded bio-oil was collected after filtering out the catalyst using a pre-weighted Buchner glass filter. Then the remaining catalyst and bio-oil in the reactor were washed out thoroughly using acetone as solvent. Both the Buchner glass filter and washed bio-oil were then dried in a 60 °C oven to completely remove the acetone solvent. The weight of the dried catalyst in the glass filter after solvent wash was considered as coke. The solvent washed bio-oil was indicated as tar. The complete mass balance was made with upgraded bio-oil, coke, tar, and produced gas + loss.

2.3. Analytical methods

The pyrolytic bio-oil and upgraded fractions were analyzed using the following analytical methods. A higher heating value (HHV) was obtained using a PARR bomb calorimeter 6200 in accordance with ASTM D 711. The ultimate analysis (for C, H, N and S) was obtained from a Vario MICRO Elemental analyzer based on the standards of ASTM D5373. The liquid products after upgrading were analyzed according to ASTM E203 for water content and ASTM D974 for total acid number (TAN). The pH of the bio-oil was measured using a digital pH meter. A Shimadzu IRAffinity-1 FTIR spectrophotometer was used to understand the changes of functional groups of the liquid products. The chemical compositions were analyzed using a GC-MS (Shimadzu QP2010Plus, ZB5MS 30 m × 0.25 mm diameter × 0.25 μm thick). The same temperature program of a previous distillation study was used [8]. The gas composition was analyzed using an SRI multiple gas chromatograph (GC) equipped with a TCD and a GC column containing a 6' molecular sieve and a 6' silica gel column. The size characterization of raw and used Pd/C catalyst was analyzed using a Quantachrome Instrument

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