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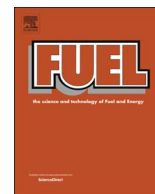
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Full length article

Nanoparticles of Pd supported on bacterial biomass for hydroprocessing crude bio-oil



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ABSTRACT

A process of much future-potential for upgrading of biofuels derived from hydrothermal liquefaction (HTL) is catalytic hydrotreatment. HTL bio-oil, manufactured from *Chlorella* microalgae in a reactor operating in continuous flow mode was processed via hydrotreatment using a bio-Pd/C catalyst. This catalyst comprises a bacterial biomass support decorated with Pd(0) nanoparticles. The hydrotreatment performance of commercial Pd/C catalyst and bio-Pd/C was compared in order to benchmark the latter catalyst preparation. Oil:catalyst ratio, time and temperature were investigated as three variables for optimization. Similar conversion was observed for both Pd/C (76% liquid yield, 4.2% O) and bio-Pd/C (77% liquid yield, 3.9% O) catalysts under equivalent conditions (4 h reaction time, 5 wt% Pd loading, 325 °C). The oxygen content was reduced by 65%, whilst the nitrogen content decreased by 35%, with a bio-oil:catalyst ratio of 20, at a temperature of 325 °C and reaction time of 4 h. The upgraded oil was further studied by elemental analysis, Simulated Distillation and GC–MS, in order to quantify the improvement in fuel properties. The fresh and spent catalysts were analyzed using elemental analysis, TGA and ICP–MS, showing that the bio-oil yield was augmented by conversion of the biomass component from bio-Pd/C.

1. Introduction

In order to meet the demands of future fuel requirements, the large requirement for fossil fuels [1–4] could be progressively replaced by biofuels with reduced carbon footprint [5,6]. Biomass can be provided via agri-food wastes, forestry residues or by using purpose-grown bioenergy crops, or microalgae growing rapidly in bioreactors, or potentially farmed as seaweed in the oceans [7]. Hydrothermal liquefaction (HTL) and fast pyrolysis are two promising techniques that are extensively used for biofuel production. Microalgae have been identified as a particularly suitable feedstock for HTL [8–11]. However, the quality of bio-oil is an issue even though the energy recovery is high from this material. It contains around 5 wt% nitrogen, 10 wt% oxygen and presents a high viscosity at ambient temperature. Use of heterogeneous and homogeneous catalysts in-situ to achieve improved bio-oil quality is one of the most commonly reported research approach in this field [12,13]. Due to the high cost associated with catalytic in-situ techniques, attention has shifted towards catalytic upgrading of

biocrude oils [14–18], utilizing catalysts such as CoMo, NiMo Pd/C [11,19,20].

The high cost of refinery catalysts and higher coke formation during catalytic upgrading reactions prompts investigation into alternative low cost catalyst [21–23]. As a potential alternative to traditional homogeneous catalysts, the immobilization of metallic nanoparticles upon micron-sized bacterial cells leads to a nanoparticle array that has been shown to be active as a catalyst [24]. Ortiz-Moreno et al. [21] investigated the use of Mo precursors at 400 °C which increased gasoline production but did not improve the liquid yield in comparison to similar thermal hydrotreatment without catalyst. Palladium based catalysts are extensively used for bio-oil upgrading processes. The use of nanoparticles of palladium in catalysis has been of great interest, due to the very low loadings of 0.001–0.1 mol% requirements for catalytic activity and improved activity over the bulk metal [25,26]. A bio-scaffolded catalyst is considered to be intermediate between homogeneous and heterogeneous catalysts. Bennett et al. [24] and Deplanche et al. [27] investigated the catalytic properties of biogenic

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nanoparticles of palladium supported upon the surface of bacterial biomass (bio-Pd), for organic synthesis, while Hart et al. [28] and Omajali et al. [29] reported activity in catalytic upgrading of heavy oil. In each case the activity of the bio-catalyst was comparable to commercial equivalents. These bio-catalysts use green and economical support material and metals can be recycled and reused from various waste sources [29]. After use, metals for such catalysts can be recovered again by incineration, sonication, or microwaving and reused to make another batch of catalyst. Recovering precious metals from waste sources, such as electronics, catalytic converters, sewage sludge ash, street sweeper dust, waste water, etc. and reusing in such catalysts could prove lucrative, given the fact that global supplies of precious metals are limited.

The current investigation presents results for upgrading the low lipid microalga *Chlorella* bio-oil (produced from a continuous reactor) with nanosized bio-Pd/C catalyst. The bio-oil is upgraded via hydro-treatment using commercial and bio catalysts at various reaction times and temperatures. A comprehensive analysis is carried out on the bio-oil and upgraded fuel to investigate its fuel properties, nitrogen and oxygen concentration and carbon species present following hydro-treatment. The objective is to study the effectiveness of bio-catalyst towards upgrading of algal bio-oil and report changes in the catalyst recovered post-reaction. The results are discussed in context of potential replacement of commercial catalysts with alternative biobased Pd/C catalyst.

2. Materials and methods

HTL bio-oil produced from *Chlorella* microalga was obtained from the University of Leeds, UK. The custom built continuous reactor used for the biocrude oil production was described previously [11]. Bio-supported nanoparticles of palladium on bacterial biomass were prepared in University of Birmingham, UK [24,27]. A 5 wt% bio-Pd/C (Pd/biomass) with an average metal particle size of 3.34 ± 0.09 nm and a mean size Pd/biomass (i.e., bacterial cells decorated with Pd nanoparticles) of $2.8 \mu\text{m}$ was prepared by reducing a solution of sodium tetrachloropalladate (II) (Na_2PdCl_4) on cells of an anaerobic bacterium (*Desulfovibrio desulfuricans* NCIMB 8307). The produced Pd/biomass was air-dried and ground into powder for use. Details of the production procedures of the nano sized Pd(0) supported on bacterial biomass are reported elsewhere [24,27].

2.1. Hydroprocessing

For each batch experiment, approximately 15 g of bio-oil and 5 wt% (0.75 g) or 10 wt% (1.5 g) catalyst were placed in a 300 mL Parr high-pressure reactor (Moline, IL). The reactor was purged with N_2 twice and with H_2 three times. The initial H_2 pressure was adjusted to approximately 1069 Psi. The reactor was stirred continuously, heated to two different temperatures (300 and 325 °C) and maintained for either 2, 4, or 16 h. The ideal gas law was used to calculate a final operating pressure of 2000 Psi at operating temperature. The heating rate of the reactor was approximately 5–7 °C/min. Upon completion of the reaction, the reactor was cooled using internal cooling coils; the cooling rate was approximately 15 °C/min. The final gas pressure and temperature were recorded, and the reactor was vented. The reactor contents were recovered, separated from the catalyst by decanting and analyzed. Dichloromethane (DCM) was used to recover the remaining oil on the reactor walls, catalysts, and stirrer, after which the DCM was evaporated. Both parts were combined to determine the yield

2.2. Bio-oil characterization

The bio-oil from HTL and upgraded bio-oil from the hydroprocessing were analyzed by elemental analyzer, GC–MS, GC-FID (simulated distillation), FT-IR and ^1H NMR. Samples were processed for total CHN

(carbon/hydrogen/nitrogen) using an Exeter Analytical (Chelmsford, MA) CE-440 Elemental Analyzer. Sulfur analysis was carried out using PerkinElmer (SCIEX ELAN DRcE ICP-MS). Oxygen was calculated by mass balance closure. The calorific value or high heating value (HHV) was determined using the DuLong formula based on the CHNSO analysis [30].

The boiling point distribution of crude and upgraded samples was obtained by performing simulated distillations according to ASTM 7169. The analysis was performed on 1% (w/w) sample solutions in carbon disulfide (CS_2) using an HP 5890 Series II FID gas chromatograph equipped with a temperature programmed vaporizer injector, HP 7673 autosampler, and a Durabond DB-HT-SimDist column by Agilent J & W Scientific (5 m \times 0.53 mm id, 0.15 μm film) as described by Vardon et al. [31,32].

Fourier-Transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy were used to get information on the chemical functionality. ^1H NMR data were collected using a Varian Unity Inova Advance-400 spectrometer running Topspin 1.4 pl8 software operating at 400 MHz using a 5-mm BBO probe. Samples were dissolved in deuterated chloroform (CDCl_3) and all spectra were acquired at ambient temperature. Chemical shifts (δ) are reported as parts per million (ppm) from tetramethylsilane based on the lock solvent. FT-IR spectra were obtained on a Thermo-Nicolet Nexus 670 FT-IR spectrometer (Madison, WI) with a Smart ARK accessory containing a 45 ZeSe trough in a scanning range of 650–4000 cm^{-1} for 64 scans at a spectral resolution of 4 cm^{-1} as described earlier [33].

GC–MS analysis was carried out using an Agilent (6890N GC/5973 MS) GC–MS instrument. 2 wt% solutions of bio-oil in DCM were prepared and 2 μl injected. The split/splitless injector was set to 280 °C and a split ratio of 20:1 was used. The products were separated on a Zebron ZB-5 ms column (60 m \times 0.32 mm i.d., 0.25 μm film thickness) using a temperature program of 50 °C (2 min) to 320 °C (held 5 min) at 10 °C/min and a constant column head pressure of 17.49 psi. The ion source was at 230 °C and the interface 250 °C, with a scan rate of 1 s over m/z 50–550. Peaks were assigned using the NIST mass spectral database.

2.3. Catalyst characterization

Recovered catalysts were dried and examined along with fresh catalysts by scanning electron microscopy in a Hitachi S-4700 High Resolution Scanning Electron Microscopy (SEM) at 10 kV. The amount of coke produced from the upgrading reaction of HTL bio-oil was determined using thermogravimetric analysis (TGA) of fresh and reclaimed catalyst using a Q50 TGA instrument. The analysis was carried out with air flow rate of 50 mL/min and a linear increase in temperature from 25 °C to 900 °C at a rate of 25 °C/min. At 900 °C, an isothermal condition was maintained for 20 min to enable total burn off of the materials deposited on the reclaimed catalysts. Thermo Elemental PQ ExCell ICPMS was used to determine the metal percent in fresh and reclaimed catalysts. An Exeter Analytical (Chelmsford, MA) CE-440 Elemental Analyzer was used to determine the carbon percent in the catalysts before and after the reactions.

3. Results and discussion

Degree of upgradation is visible from color and viscosity of upgraded bio-oil. Good conversion is reflected by lower viscosity and light color. Also the odor approaches the smell of petroleum crude oil. Degree of upgradation has been studied through chemical characterization of upgraded bio-oil and compared with neat bio-oil.

3.1. Bio-oil characterization.

Hydroprocessing parameters of the bio-oil and the yields of hydro-processed bio-oil are listed in Table 1. At the lower temperature of 300 °C, higher yields (87%) of refined bio-oil were obtained for Pd/C

Table 1
Bio-oil and upgraded sample: ultimate and proximate analysis.

Catalyst	Temp (°C)	Time (h)	Catalyst wt%	Yield wt%	%C	%H	%N	%O [*]	%S	HHV ^{**} (MJ/kg)
Bio-oil					73.5	8.9	6.6	10.8	0.72	35.7
Pd/C	300	2	5	87	74.6	10.2	4.6	10.4	0.11	38.0
	325	2	10	82	79.3	10.8	5.1	4.7	0.11	41.3
	325	4	10	78	79.2	10.1	4.2	6.2	0.29	40.0
	325	16	10	74	82.6	10.7	3.2	3.5	0.07	42.5
	325	2	5	81	80.6	10.0	5.2	3.9	0.05	41.2
	325	4	5	76	80.9	10.5	4.3	4.2	0.2	41.5
	325	16	5	72	82.0	11.2	3.9	2.3	0.05	43.1
Bio-Pd/C	325	4	5	77	80.7	10.1	4.9	3.9	0.3	41.0

* %O: Determined by difference.

** HHV: Calculated using DuLong formula.

catalyzed reaction, compared to higher temperature (325 °C) at all reaction times. The yields are higher (81–82%) at the shorter reaction time (2 h) compared to yields of only 72–74% at 325 °C for 16 h. The variation in percent catalyst does not have an effect on the refined bio-oil yield, elemental composition and calorific value, therefore lower catalyst loading (5%) was used for remaining experiments. Higher yields at low temperatures and short reaction times could be due to lesser cracking at these conditions compared to high temperatures and long reaction times. In our earlier study [11] also, we obtained higher yields at low temperature (350 °C) compared to higher temperature (405 °C). Refined bio-oil yield with bio-Pd/C catalyst was similar to commercial Pd/C catalyst at 325 °C for 4 h. Yields obtained in this study were similar to what has been reported in earlier studies. Elliott et al. [19] reported 80–85% for microalgae biocrude oil processed using a sulfide alumina catalyst at 405 °C, while Li and Savage [34] reported 75% yield of upgraded oil at 400 °C with HZSM-5 catalyst for algal biocrude oil.

Table 1 also presents the elemental analysis of the refined bio-oil along with algal bio-oil. Carbon content in the refined bio-oils ranges from 75 to 81 wt%, increased from 73 wt% in the bio-oil; small increases in H were also observed from 8.9% to 10%. Our results show that up to 41% of N, 79% of O and 93% of S is removed using 5% Pd/C catalyst at 325 °C for 16 h. Reductions in O and S were more pronounced at the higher operating temperature of 325 °C and longer reaction time of 16 h. Denitrogenation did increase at longer processing times with maximum decrease to 3.2% at 300 °C for 16 h from 6.6% in bio-oil. This value was slightly higher than earlier reported by Biller et al. [11], Bai et al. [20], and Li and Savage [34]. To achieve higher degree of hydro-denitrogenation, a higher temperature of 405 °C and higher catalyst loading (20%) may be helpful as used in our earlier study, [11,35] where catalytic and non-catalytic processes at 350 °C decreased nitrogen to same level (4.7%), but on increasing temperature to 405 °C, a clear cut distinction between non-catalytic process (3.6%) and NiMo catalyst (2.4%) was observed. Increased deoxygenation of the bio-oil was observed at the higher processing temperature. This effect has been shown previously on the same bio-oil subjected to non-catalytic hydrotreating temperatures of 350 and 405 °C, which resulted in oxygen contents of 5.0 and 1.5% respectively [11]. These previous results demonstrate that both commercial and bio-Pd catalysts promote catalytic deoxygenation compared to non-catalytic hydrotreatment as the oxygen contents is 3.9% at the same residence time and 25 °C lower processing temperature (compared to 5.0% at 350 °C). Similar or slightly lower oxygen contents (3.9%) was observed in this study (325 °C for 2 h) with both commercial and bio-Pd/C compared to our earlier study [11], where 4.2% oxygen was obtained with NiMo catalyst at 350 °C for 2 h. With trend showing increased deoxygenation at higher temperatures, it is assumed that oxygen content will be even lower at 350 °C than 3.9% obtained at 325 °C, however on increasing temperature to 405 °C thermal hydrodeoxygenation becomes prominent than catalytic hydrodeoxygenation as shown in earlier study [11].

Jensen et al. [35] also reported that incomplete deoxygenation was observed at temperatures lower than 350 °C. Higher desulfurization effect was observed at higher reaction temperature. On comparison with our earlier study [11], it was observed that Pd/C (0.05% at 325 °C) and bio-Pd/C (0.3% at 325 °C) are more efficient hydrodesulfurization catalysts compared to NiMo (0.21% at 350 °C) and CoMo (0.42% at 350 °C) catalysts. Higher temperatures (405 °C) as used in earlier study have potential to further lower the sulfur content to negligible amount. No pronounced difference was observed in the elemental composition and calorific value obtained from catalytic reactions under similar conditions using commercial Pd/C and bio-Pd/C. The HHV was calculated using the measured CHNSO values for bio-oil and refined oils. The HHV increased from the 35.7 MJ/kg of the original bio-oil to 38 MJ/kg (300 °C for 2 h at 5% catalyst) and further to 41.2 (325 °C for 2 h at 5% catalyst) and 41.3 MJ/kg (325 °C for 2 h at 10% catalyst), almost similar to what was obtained by Biller et al. [11] on non-catalytic and catalytic process (41.5 MJ/kg) at 350 °C for 2 h at 20% catalyst, and Jensen et al. [35] in their hydrodeoxygenation process at 350 °C for 2 h (43.73 MJ/kg) using 20% catalyst on HTL lignocellulosic bio-oil. Here, a maximum HHV (calculated) of 43 MJ/kg was obtained for the refined oil at 325 °C for 16 h. Overall the Pd/C and bio-Pd/C catalysts showed good performance in terms of deoxygenation and desulfurization under the studied reaction conditions compared to our earlier study [11]; and there is potential to increase the hydrodenitrogenation efficiency of these catalysts by using higher temperature and higher catalytic loading.

Boiling point distribution of the hydrotreated and untreated bio-oils was determined using GC simulated distillation as shown in Fig. 1. The bio-oil composition is reported in four distillate fractions: gasoline (< 185 °C), diesel (185–290 °C), gas oil (290–350 °C), and atmospheric residue (> 350 °C). The untreated bio-oil showed a large fraction of atmospheric residue (71%) containing high molecular weight and high-boiling components, followed by 19% in gas oil range. Gasoline range fraction was only 2% and diesel was 8% in untreated bio-oil. Hydro-treating using commercial Pd/C catalyst at 300 °C increased the gas oil fraction while decreasing the atmospheric residue but did not promote a change in the gasoline and diesel fractions. Increasing the reaction time (and temperature) contributed to increasing the gasoline and diesel fractions and a corresponding decrease in atmospheric residue, indicating that the high molecular weight oil started cracking at longer reaction time and higher temperature (325 °C). Further increasing the temperature will most likely increase cracking and will result in more fuel fractions, as has been shown in earlier studies [11,35,36], where authors were able to obtain up to 78% yields of fuel fractions at 405 °C. Approximately 45% of the upgraded bio-oil at 325 °C for 16 h is now fractionated in the gasoline, diesel, and gas oil fractions, compared to 30% in the bio-oil. High loading of catalyst (10%) at 325 °C did produce more gasoline and diesel, but at the cost of gas oil and no considerable difference was observed in atmospheric residue compared to 5% catalyst loading. The difference between gasoline and diesel yield using

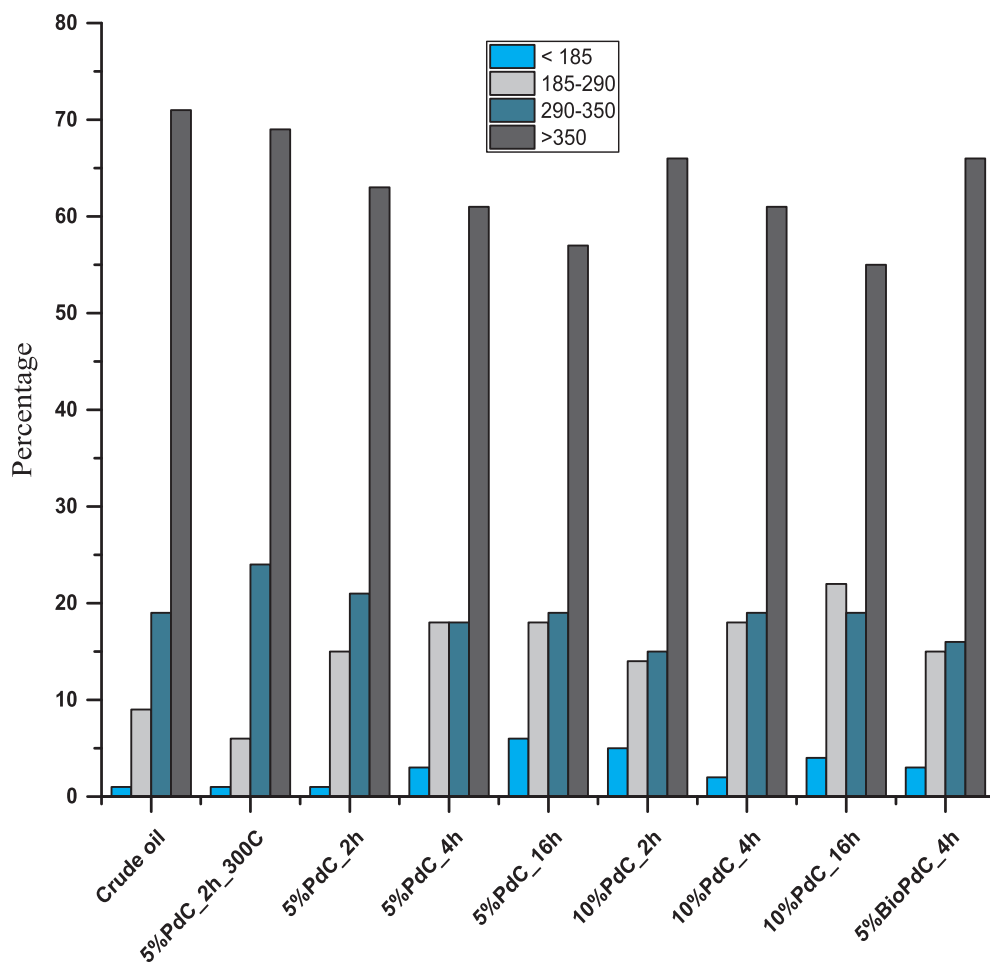


Fig. 1. GC-SimDist Boiling point distribution of untreated and upgraded bio-oils. The first run was conducted at 300 °C, while the remaining runs were carried out at 325 °C.

commercial Pd/C and bio-Pd/C of less than about 2% indicated that bio-Pd/C could replace the commercial catalyst. Intuitively use of a precious metal-based catalyst would be uneconomical. However single-step biorefining of Pd from wastes into new catalysts has been shown in other work, with the biorefining catalyst proving comparable to chemical counterparts in fuel cells [37], in chemical catalysis [38], and in catalytic upgrading of Canadian heavy oil [39], where the economic case was argued [28]. These results show that a high quality fuel can be produced by upgrading HTL bio-oil using a bio-Pd/C that can be prepared from wastes. However, a higher yield at lower temperature and shorter reaction time gave lower fuel conversion while high fuel conversion at higher temperature and longer reaction time gave a poorer yield.

¹H NMR analysis was carried out to investigate the concentrations of alkane and oxygenated components in untreated and upgraded bio-oil (Table 2). Alkenes and heteroatoms with a lone pair of electron such

as oxygen and nitrogen affects oxidative stability, with higher percentages of olefins resulting in lower oxidative stability. The peaks between 0.5 and 2.7 ppm indicated protons attached to alkanes (n- and iso-), which increased from 92% to 97–98% content on upgrading at 325 °C for 16 h. High amounts of aliphatic functionality as observed in untreated bio-oil in this study was observed in our earlier study [31] as well with over 85% of spectral area located in 0.5–2.7 ppm region for algae derived HTL bio-oils. Increase in area% in this region is consistent with increase in HHV values also. Protons from oxygenate (alcohol, ketone, ether, methoxy, etc.) and alkene compounds (chemical shift between 3.3 and 5.6 ppm) were found to be relatively minor for untreated bio-oil and decreased with longer reaction time with maximum reduction of 87% on upgrading the bio-oil for 16 h. It was also observed that higher catalyst loading resulted in lower alkene, oxygenate, and aromatic protons at shorter reaction times of 2 and 4 h. An increase in aromatic-associated protons indicated that Pd/C catalyst favors the

Table 2

¹H NMR of untreated and upgraded bio-oils showing the presence of % proton assigned to each group as determined from the chemical shifts.

Chemical shift	0.5–2.7 ppm	3.3–4.3 ppm	4.5–5.6 ppm	7.5–8.5 ppm
Protons	–CH ₃ , –CH ₂ –, CH, Aromatic CH ₃	CH ₃ O, CH ₂ O, CHO	HC=C–, phenolic H, OH	Aromatic H
Untreated bio-oil	92	2.6	5.2	0.2
5%Pd/C 2 h 300 °C	96.3	1.9	0.7	1.1
10%Pd/C 2 h 325 °C	96	2.3	0.5	1.3
10%Pd/C 4 h 325 °C	96.2	2.3	0.4	1.0
10%Pd/C 16 h 325 °C	97	1.6	0.2	1.2
5%Pd/C 2 h 325 °C	94.9	2.3	0.9	1.9
5%Pd/C 4 h 325 °C	94.1	3.3	0.9	1.7
5%Pd/C 16 h 325 °C	98.3	0.9	0.1	0.6
5%Bio-Pd/C 4 h 325 °C	93.7	3.4	0.6	2.2

aromatization. The hydrotreatment under similar reaction conditions in the presence of Pd/C and bio-Pd/C provided comparable results, with increasing alkanes to 94% and decreasing alkenes and oxygenated compounds by 49%. This further suggests that bio-Pd/C can be substituted easily for commercial Pd/C catalyst.

Results obtained from Fourier transform infra-red (FT-IR) spectral analysis (Supplementary information Fig. S1) confirmed the NMR data. The FT-IR spectra was dominated by alkane peaks and also had higher heteroatom functional groups ($1750\text{--}1500\text{ cm}^{-1}$) in untreated bio-oil compared to Illinois shale oil (shown in earlier study [31]). The prominent peaks at the $3000\text{--}2840\text{ cm}^{-1}$ wavelengths representing C–H stretching vibrations, 1465 cm^{-1} for CH_2 bending, and 1375 cm^{-1} for CH_3 bending showed the presence of higher concentrations of alkanes. The presence of C=C stretching vibrations at $1640\text{--}1650\text{ cm}^{-1}$ suggested the presence of alkenes, and intensity of this peak decreased as a result of hydrogenation with increasing reaction time reaching lowest value for 16 h. Longer reaction time can be replaced with higher operating pressure with higher reaction temperature, thereby providing increased saturation of bio-oils [35]. The peaks at $1680\text{--}1600\text{ cm}^{-1}$ (C=O stretching) and $1575\text{--}1525\text{ cm}^{-1}$ (N–H bending) associated with amide and amine functional groups [40], were stronger for untreated bio-oil and decreased with increasing reaction time. Minor peak at $1730\text{--}1700\text{ cm}^{-1}$ for C=O stretching of carboxylic acids in untreated bio-oil showed relatively low crude lipid content of algal feedstock [31]. Residual absorbance of this peak even after 16 h reaction time indicated incomplete deoxygenation, which was also observed in results from elemental analysis. Jensen et al. [35] ascribed this incomplete deoxygenation to be caused by insufficient hydrogen. On hydrotreating at higher operating pressures and $350\text{ }^\circ\text{C}$, they showed absence of alcohol or carbonyl absorption, but presence of small peaks due to ethers at 1200 cm^{-1} in the FTIR spectra of hydrotreated bio-oil. Untreated bio-oil shows a strong peak around 1200 cm^{-1} due to C–O stretching of ethers and other oxygenates, which reduced with increasing reaction time. The presence of peaks around $3500\text{--}3300\text{ cm}^{-1}$ indicates the presence of OH groups. The upgrading reactions decrease the concentration of OH groups by removing them in a form of water. The FTIR spectra obtained for 5% bio-Pd/C at 4 h was similar to 5% Pd/C at 4 h showing similar reduction in oxygen, nitrogen and double bond functionalities (Supplementary information Fig. S2).

Table 3 summarizes the GC–MS results of the untreated HTL bio-oil and the hydrotreated bio-oils using Pd/C and bio Pd/C at various temperature, catalyst% and reaction time. The major chemical components are categorized into five groups: hydrocarbons (including straight and branched hydrocarbons); esters, ketones and alcohols (including piperidine and pyrimidinone); organic acids; straight and branched amides, cyclic oxygenates (including phenols, phenol derivatives and fused ring compounds); and N- and O-heterocyclic compounds. It should be noted that each component was categorized in only one group, irrespective of the number of functional groups it contained. In untreated bio-oil, hydrocarbons were minor product, while the major products included complex mixture of numerous

different compounds mostly containing oxygen and nitrogen containing compounds (Table 3). The nitrogen containing compounds are ring type structures such as pyrazines, pyrroles and indoles. Long chain hydrocarbons containing both nitrogen and oxygen were also identified, such as hexadecanamide and octadecanamide. The major aim of hydrotreatment is to convert O and N containing heterocompounds to hydrocarbons through hydrodeoxygenation and hydrodenitrogenation, while also saturating the double bonds and hydrocracking high molecular weight compounds. On hydrotreating the aliphatic hydrocarbons increased from 9.4 area% to around 83–88 area% with Pd/C and 54 area% with Bio-Pd/C. Hexadecanenitrile and octadecanenitrile were identified in hydrotreated sample likely due to the conversion of hexadecanamide and octadecanamide upon deoxygenation [11]. Peaks due to pyrazine, pyrrole, and indole compounds present in chromatogram of untreated bio-oil, reduced after 2 h and disappeared completely after 4 h, as shown by area under N and O heterocyclic compounds. Two new low molecular weight hydrocarbons (toluene and ethylbenzene) were identified in hydrotreated samples, as was reported by Biller et al. [11] and Elliott et al. [19]. The hydrotreatment for 4 h resulted in maximum hydrocarbons abundance, while the hydrotreated products obtained from 16 h reaction time resulted in lower hydrocarbons percent compared to 4 h treatments. This attributes to extensive hydrocracking resulting in more gaseous hydrocarbons at longer reaction time. This result is in agreement with the oil yield percentage which gives a lower yield at longer reaction time (Table 1). Hydrotreatment reactions with bio-Pd/C also gave comparable results, as seen with Pd/C under the same conditions, with the exception of a lower hydrocarbon yield (above) and a higher proportion of amides, nitriles and cyclic oxygenates after 4 h.

3.2. Catalyst characterization

The morphologies of the particulate catalysts were studied before and after use in upgradation of HTL bio-oil as shown in Fig. 2. The individual dispersed particles of the bio-Pd/C powder can be seen (Fig. 2a and b). Studies of Omajali et al. [41] have provided detailed characterizations of palladium nanoparticles synthesized by different bacteria including *D. desulfuricans*. It was shown that the type and strain of bacteria may influence the size, location and crystal structure of the metal nanoparticles, in particular whether the metals are located mainly on the surface or the intracellular region of the bacteria. Thus the selection of bacteria used in the process can be used to control the biomanufacturing step. The acidity of the catalyst support can affect the electronic environment of the supported metal on the catalyst. Gram negative bacteria such as *D. desulfuricans* behave in a similar way to a carbonaceous catalyst support, being comprised of an outer layer of carboxyl-rich extracellular materials upon a peptidoglycan layer separated by a phospholipid membrane [24] through which incoming metals can enter the periplasmic compartment which contains the peptidoglycan. The catalytic nanoparticles are laid down in this region. The ability of many microorganisms to biosorb heavy metals could

Table 3
Composition (area %) of untreated and treated bio-oil determined by GC–MS.

Sample	Hydrocarbons	Esters, ketones and alcohols	Organic acids	Straight and branched amides, nitrile, cyclic oxygenates	N- and O-heterocyclic compounds
Crude-oil	9.4	38.0	11.3	21.5	19.8
5%Pd/C 2 h 300 °C	43.5	10.9	0.9	44.1	4.7
10%Pd/C 2 h 325 °C	48.7	3.9	1.5	44.7	1.1
10%Pd/C 4 h 325 °C	88.4	1.7	0.0	6.2	0.0
10%Pd/C 16 h 325 °C	64.8	2.6	0.0	32.6	0.0
5%Pd/C 2 h 325 °C	41.8	4.6	1.6	55.3	1.0
5%Pd/C 4 h 325 °C	82.6	4.7	0.0	12.7	0.0
5%Pd/C 16 h 325 °C	56.7	4.4	1.1	35.7	2.1
5%Bio-Pd/C 4 h 325 °C	53.5	3.4	2.8	37.7	2.7

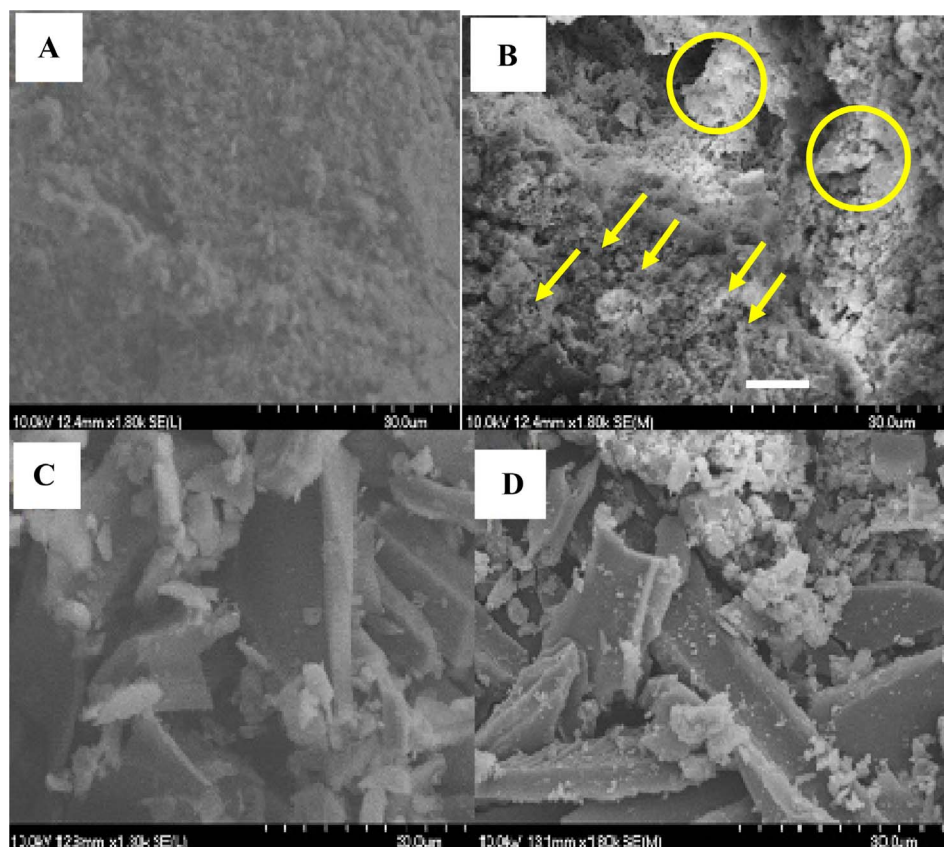


Fig. 2. SEM images of (a) fresh bio-Pd/C (b) reclaimed bio-Pd/C (c) fresh Pd/C (d) Reclaimed Pd/C. Scale: White bar shown in (a) is 10 μm . Individual bacterial cells are visible in (a). Catalyst was recovered from the reaction mixture after the hydrotreatment reaction at 325 $^{\circ}\text{C}$. Small 'donut' structures are apparent in the recovered bio-Pd/C (arrowed) and dense deposits assumed to be coke (circled).

potentially open up a route for in-situ production of active catalysts from recycled materials such as metal processing wastes. Indeed, this approach was described in the application of such biorecycled neo-catalysts to the upgrading of heavy fossil oils [39]. Major differences were not observed in the morphological images in this study before and after the reactions but the post-reaction bio-catalyst appeared to be denser, with some discrete 'donut' structures visible (Fig. 2b, arrowed). This may be caused by degradation of the bio-Pd/C structures which released the Pd metal into a 'melt' and also formed a coke around it. This may indicate that the bacterial support becomes damaged by the high temperatures encountered in the reaction and the metals behave similarly to a homogeneous dispersed catalyst. However, other work using EPR has shown that, after sintering to carbonise the biomass and mixing the biomaterial with additional activated carbon, free radicals were exchanged between the Pd-bionanoparticles and the carbon matrix; the bio-Pd (but not Pd on carbon commercial catalyst) quenched the free radicals of the activated carbon [42]. We hypothesize that the residual biomatrix becomes carbonized during the oil upgrading reaction and this neo-carbon/Pd hybrid 'diverts' free radicals away from the processes that lead to coking; i.e. providing an additional role as a free radical 'sink'. This difference was not observed in the images of Pd/C obtained before and after the reactions although some densification was apparent in the metallic clusters on the support. No differentiation was made between catalyst and coke deposits; the reaction temperature of 325 $^{\circ}\text{C}$ is mild enough to cause coking or damage to the Pd/C catalyst.

XRD analysis of Pd/C, bio-Pd/C, reclaimed Pd/C and reclaimed bio-Pd/C provided additional information regarding long-range order and average metal crystallite size [43], as shown in Fig. 3. The lack of sharp, pronounced peaks in XRD pattern of fresh Pd/C and bio-Pd/C showed that the Pd metal was highly dispersed as small crystallites whereas distinct peaks observed in the reclaimed Pd/C and reclaimed bio-Pd/C were attributed to larger crystallites. In comparison to Pd/C, bio-Pd/C displayed a broad XRD peak near 40 $^{\circ}$ (2θ value) suggesting larger

crystallites in bio-Pd/C compared to Pd/C. These data is in agreement with the visual data of Fig. 2. Re-use of the reclaimed catalysts in subsequent reactions was not evaluated.

The thermogravimetric profile for fresh and reclaimed catalysts is shown in Fig. 4. Rapid weight loss, also called onset temperature, due to oxidation of carbon started at 392 $^{\circ}\text{C}$ for fresh Pd/C whereas reclaimed Pd/C showed a rapid weight loss starting at a lower temperature of 330 $^{\circ}\text{C}$. Unlike Pd/C, the rapid weight loss for fresh bio-Pd/C started at 230 $^{\circ}\text{C}$. Smooth TG curves were obtained for Pd/C and reclaimed Pd/C catalysts showing single-stage degradation ascribed to highly homogeneous material. The TG curve for bio-Pd/C and reclaimed bio-Pd/C showed degradation happening in 2–3 stages showing heterogeneous material. The decomposition of carbon was complete at approx. at 750 $^{\circ}\text{C}$ for all fresh and reclaimed catalysts except for reclaimed bio-Pd/C in which no measurable weight loss was observed after 500 $^{\circ}\text{C}$ and even at 900 $^{\circ}\text{C}$, a very high residual mass was noted ($\sim 65\%$). One of the reasons for small weight loss in the reclaimed bio-Pd/C catalyst might be due to the decomposition of bacterial carbon at reaction temperature during the hydroprocessing, which is also visible from decomposition of bio-Pd/C starting at much lower temperature of 230 $^{\circ}\text{C}$ compared to Pd/C (392 $^{\circ}\text{C}$), as seen in Fig. 4.

Elemental analysis (Supplemental information Table S1) showed the decrease in carbon percent in reclaimed catalyst compared to fresh catalysts, supporting TGA results. Accordingly, the Pd content of the reclaimed bio-Pd catalyst (determined using ICP-MS) increased by threefold as compared to fresh catalyst. This subsequent increase in the metal content after the reaction with bio-Pd/C can be attributed to possible decomposition of bacterial carbon during the hydroprocessing. These elemental composition results are in agreement with the TGA analysis. However, such a carbon support decomposition was not observed with commercial fresh and reclaimed Pd/C catalysts.

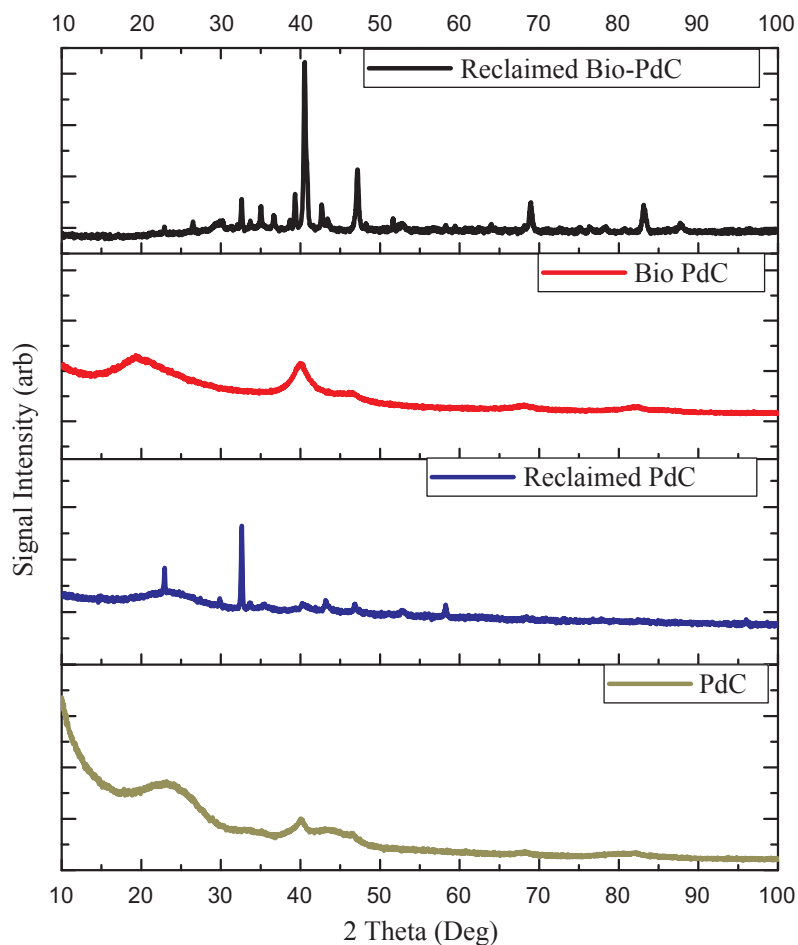


Fig. 3. X ray powder diffraction patterns of commercial Pd/C as received, bio-Pd/C, reclaimed Pd/C and reclaimed bio-Pd/C after the hydrotreatment reaction.

4. Conclusions

The hydroprocessing of bio-oil obtained from hydrothermal liquefaction of algae was successfully shown using bio-Pd/C catalyst and

compared with commercial Pd/C catalyst. Bio-Pd/C resulted in similar catalytic activities as commercial Pd/C. Both bio-Pd/C and commercial Pd/C were able to decrease the O, N and S content by approx. 72%, 52% and 93% and improved the HHV from 35 MJ/kg to 41 MJ/kg

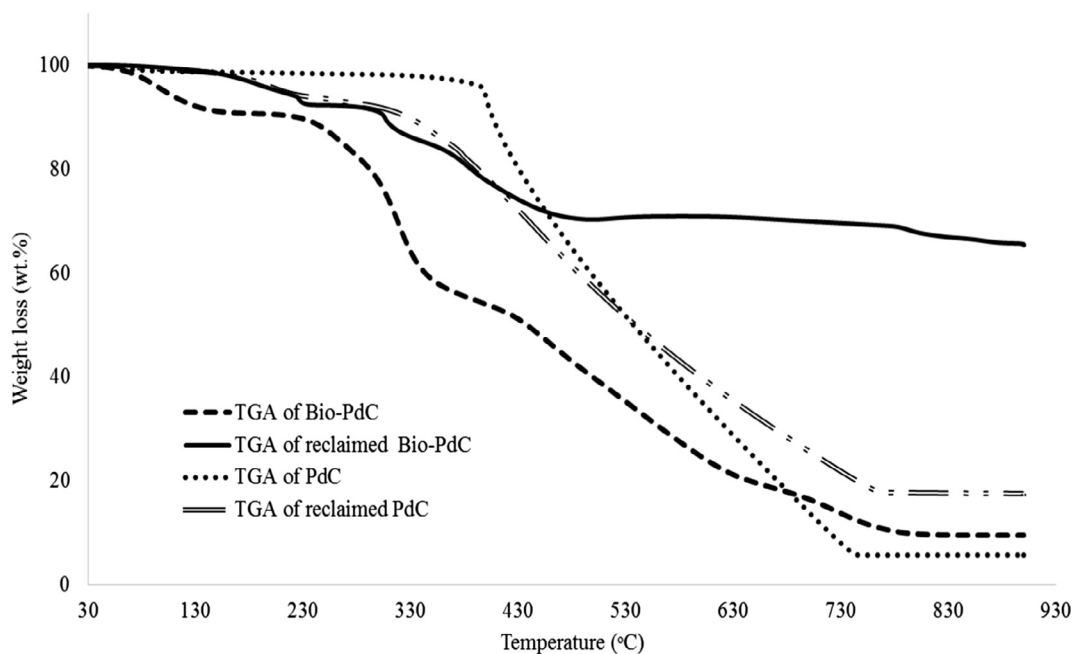


Fig. 4. Thermogravimetric curves of fresh and reclaimed bio-Pd/C and Pd/C.

under similar reaction conditions. However, carbon in bio-Pd/C possibly decomposed during the upgrading process, potentially reducing the reusability of the catalyst. However since bio-Pd/C can be bio-refined from low-grade waste sources and used in oil upgrading [39] a ‘once through’ process is acceptable, particularly since the catalyst can be retained for onward commercial reprocessing, effectively realizing a ‘second life’ per unit of primary resource mined. In addition, since the bacteria to make bio-Pd can be sourced as spent biomass from a previous bioprocess [44,45] this reduces waste disposal costs while realizing benefit as additional carbon neutral fuel.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2017.08.007>.

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