

Comparison of the effects of dispersed noble metal (Pd) biomass supported catalysts with typical hydrogenation (Pd/C, Pd/Al₂O₃) and hydrotreatment catalysts (CoMo/Al₂O₃) for in-situ heavy oil upgrading with Toe-to-Heel Air Injection (THAI)

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Full Length Article

Comparison of the effects of dispersed noble metal (Pd) biomass supported catalysts with typical hydrogenation (Pd/C, Pd/Al₂O₃) and hydrotreatment catalysts (CoMo/Al₂O₃) for *in-situ* heavy oil upgrading with Toe-to-Heel Air Injection (THAI)



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HIGHLIGHTS

- The aggregation of bacterial biomass nanoparticles is less than alumina supports.
- The level of upgrading with bio-Pd was comparable to alumina supported Pd.
- Lower coke yield was observed with bio-Pd compared to alumina supported Pd.
- Sulfur and metals reduction with bio-Pd was comparable to Co–Mo/Al₂O₃ catalyst.

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ABSTRACT

Catalyst deactivation due to coke and metals deposition as a result of cracking presents a challenge in heavy oil recovery and upgrading. This is particularly pronounced for *in situ* upgrading techniques, in which pelleted catalyst is packed around the perimeter of the horizontal producer well of the Toe-to-Heel Air Injection (THAI) process. The fixed bed of catalyst is virtually impossible to regenerate in place, promoting investigation of alternative contacting via the dispersion of nanoparticles. The catalysts studied were finely crushed micro-particulates with average size of 2.6 µm and also a catalyst prepared upon a bacterial support. The latter has advantages in terms of ease of preparation of catalysts from recycled metal sources. Heavy oil of API gravity 13.8° and viscosity 1091 mPa s was used as feed and upgrading was performed in a batch reactor at 425 °C, with a catalyst-to-oil ratio of 0.02 (g/g), and at an initial pressure of 20 bar. The activity of the Pd/biomass catalyst was evaluated against a number of other catalysts: Pd/Al₂O₃, Pd/C, Al₂O₃ and Co–Mo/Al₂O₃. By using the Pd/biomass catalyst, the produced oil gravity increased by 7.8° API, and its viscosity was reduced to 7 mPa s. This effect corresponded to an increase in the amount of low-boiling distillate (IBP – 200 °C) from 34.6 vol.% (original feedstock) to 53–62 vol.%, potentially reducing the amount of diluent needed for pipeline transport of bitumen. The coke yields were (wt.%): 13.65 (Al₂O₃), 9.55 (Pd/Al₂O₃), 6.85 (Pd/C) and 3.87 (Pd/biomass). The Pd/biomass catalyst showed significantly reduced coke yield compared to thermal cracking and upgrading using Pd/C and Pd/Al₂O₃ catalysts, which could greatly enhance catalyst survivability in the field.

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1. Introduction

Transportation fuels account for roughly 40% of energy used globally, and 70–80% in advanced economies. Light crude oil

reserves are the main source of these fuels. However, as a consequence of the declining reserves of light oils, attention has shifted to large deposits of untapped heavy oil and bitumen as potential alternatives, as they account for about 70% of world's total 9–13 trillion barrel oil resources [1]. Compared to light crude oil, heavy oil with reservoir viscosity between 100 and 10,000 mPa s and bitumen with reservoir viscosity greater than 100,000 mPa s are

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characterized by high density, high asphaltene content, and high heteroatom (S, N) and metals (V, Ni, Fe) contents under reservoir conditions of temperature 10–20 °C and pressure 5–40 bar [2]. These characteristics confer high cost of production, low market value, and subsequently hamper pipeline transport and ease of refining. Hence, after extraction, significant amounts of diluents are added to the heavy oil to meet density and viscosity specifications as well as facilitating pipeline transportation to refineries. Diluent costs for pipeline transportation and also surface upgrading expense are expected to be substantially reduced.

The concept of simultaneous recovery and *in situ* upgrading of heavy oils by applying thermal energy has received intense attention as it can result in substantial cost, energy and environmental benefits compared to extraction followed by surface upgrading. Thermal and catalytic upgrading can be achieved through the incorporation of a catalytic packing around the perimeter of the horizontal production well and combined with the Toe-to-Heel Air Injection (THAI) process [3–6]. *In situ* catalytic upgrading occurs as the mobilized oil ahead of the combustion front flow across the fixed-bed of catalyst incorporated along the horizontal production well. The thermal energy is delivered to the reservoir by *in situ* combustion to promote pyrolysis and *in situ* catalysis. Thermal conduction is the main heat transfer mechanism in the reservoir rock and coke lay down ahead of the combustion front as fuel [3,7]. However, most of the combustion energy not conducted into the reservoir strata is conveyed ahead of the combustion front and steam front created by heating the water layer ahead of the combustion front [7]. Heating of the reservoir rocks to high temperature (>450 °C) will induce thermal cracking, reduce the *in situ* oil viscosity, and improve its mobility. Cracking of heavy oil molecules generates lighter hydrocarbons and gases. Previous studies by Shah et al. [5] and Hart et al. [6] showed substantial upgrading with 2–7° API gravity increase, 80% viscosity reduction and 40% conversion of fractions with boiling point greater than 343 °C achieved using an *in situ* fixed layer of catalyst which in the field would be packed around the horizontal production well. However it was shown that asphaltenes, coke and metal deposition drastically deactivated the catalyst which impacts adversely on the quality of the produced oil and increases the risk of well plugging and shutdown.

It is believed that finely suspended nanocatalyst in the heavy oil can offer improved contact during upgrading than a fixed layer of catalyst along the perimeter of the horizontal production well, and is less susceptible to deactivation due to the short diffusion path-length with small particles [8]. This approach would also avoid the inconvenience of pre-packing the horizontal well with catalyst pellets prior to starting up, but success requires the transport of the nanoparticles into the mobile oil zone (MOZ) during the THAI process [9,10]. Although rock minerals in the reservoir promote some catalytic cracking, injecting or precipitating nano-sized catalyst ahead of the combustion front could further increase the level of *in situ* catalytic upgrading.

A wide variety of water-soluble precursors molybdenum-based (e.g., ammonium molybdates, ammonium heptamolybdate, phosphomolybdic acid, ammonium tetrathiomolybdate) and oil-soluble precursors (e.g., molybdenum naphthenate, molybdenum oleate) has been investigated for *in situ* catalytic upgrading, with the nano-sized unsupported active catalyst being generated *in-situ* during the chemical reaction with the metal precursors added to the heavy oil [11–13]. The metallic precursors used for *in situ* preparation of nano-sized catalyst are similar to those of metal supported pelleted catalysts [12]. The challenges of preparing and stabilizing homogeneous catalyst lie in the boiling point of the metal precursor and thermal stability, which is not the case with a heterogeneous counterpart that offers ease of handling, separation, and thermal stability. However, to maximize the process

economics and suppress coke formation while increasing the level of upgrading, investigating alternative and low-cost catalyst compared to refinery catalyst is necessary. As a potential alternative to traditional homogeneous catalysts, the immobilisation of metallic nanoparticles upon micron-sized bacterial cells leads to a nanoparticle array that has been shown to be active as a catalyst [14]. Palladium based catalysts are known for their high hydrogenation activity, and may suppress coke formation, while biogenic equivalents [14] have been formulated from waste sources for economy and scalability. Noble metal catalysts, including Ru and Pd, have been shown to be effective in the hydrotreatment of bio-oils which are naturally low in sulfur [15,16]. However Ru and Pd were also used as promoters in the hydrodesulfurization of dibenzothiophene on sulfide Ni(Co)Mo/Al₂O₃ catalysts, in order to enhance their hydrogenation function as required for the simultaneous removal of sulfur, nitrogen and aromatics from a gasoil. The use of noble metal catalysts such as bimetallic PtPd on zirconia has also been proposed in the second step of a two-stage process, where the H₂S partial pressure is lower than the primary treatment [17]. It was reported that the sulfur tolerance of such catalysts can be increased by improving the metal dispersion, by using an acidic support, or a second metal like palladium forming a bimetallic catalyst [18], or the combination of the two effects [19].

The use of virgin noble metals for oil upgrading could be potentially expensive leading to uneconomic viability, however there is increasing interest and technology to recover platinum group metals from secondary or waste sources such as urban road dust [20]. Since the introduction of autocatalysts in Europe in the 1980s there has been a clear link between their use and increasing concentrations of platinum group metals (PGMs) in the environment resulting in enhanced levels of these elements occurring in road dust and soils, particularly in urban areas and around major roads [21]. In some urban areas the PGM content is now comparable with that found in low grade primary ores. Murray [22] has developed technology to recover these metals and produce a metal rich concentrate that can either be smelted to recover the PGMs or leached into solution and used to produce new biological based catalysts. Pincock [23] states that 65–75% of the total cost of producing pure PGMs is accrued at the mining stage due to the large energy demand. Recycling is also ecologically advantageous as it reduces the large CO₂ burden associated with primary mining [24], thus using PGMs recovered from secondary waste is both cheaper and less environmentally damaging. In addition to using biorecovered PGMs, waste bacteria left over from another 'primary' fermentation can be used ('second life') to produce the Pd-nanocatalyst [25,26] further reducing the costs of biocatalyst production. Although the metal concentration in these secondary (waste) sources is low the bioreduction process is sensitive enough to recover metal at parts per million (ppm) concentrations, which is often below the economic threshold of traditional recovery methods [27]. A full economic projection is beyond the scope of this work.

The purpose of this study is evaluate the extent of heavy oil upgrading in the presence of bacterially supported nanoparticles of palladium. The test results using bionanoparticles (bioNPs) were compared with those of palladium supported on carbon and alumina, and also with experimental results obtained using alumina and standard refinery catalyst (Co–Mo/Al₂O₃) particles, included for performance evaluations only. Comparisons are made with a control sample of bacterial cells, similarly processed without added metals.

2. Materials and methods

The heavy oil used in this study was a blend of oils produced by the THAI process from eight different wells located at Kerrobert,

Saskatchewan, Canada, and supplied by Touchstone Exploration Inc., Canada. The details of the feedstock properties are summarized in Table 1.

Mechanically, crushing is one of the means of producing nanoparticles [28]. Hence, the pelleted Pd/Al₂O₃, alumina, and Co–Mo/Al₂O₃ refinery catalysts source were crushed using a Tema laboratory Disc Mill model T 750 K (TEMA Machinery Ltd, UK). The size of the catalyst particles after crushing to powder was measured by laser diffraction particle size analyser (Helos-Rodos T4.1, Sympatec, Germany) and the specific surface area was determined by Brunauer–Emmett–Teller (BET) analysis of nitrogen adsorption–desorption using a Micromeritics Analytical Instrument ASAP® 2010 (Table 2). The 5 wt.% Pd/C was purchased from Johnson Matthey, United Kingdom. Philips XL 30 Scanning Electron Microscope (XL 30 ESEM-FEG) was used to examine the surface morphology of the catalysts.

The bio-supported nanoparticles of palladium on bacterial biomass were prepared by reducing a solution of sodium tetrachloropalladate (II) (Na₂PdCl₄) on cells of an anaerobic bacterium (*Desulfovibrio desulfuricans* NCIMB 8307), to make a 5 wt.% bio-Pd (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 µm. The produced Pd/biomass was air-dried and ground into powder (i.e., fresh Pd/biomass). Details of the production procedures of the nanoparticles of Pd supported on bacterial biomass are reported elsewhere [14]. The bacterial-based catalyst was used in an ‘as prepared’ form; the bacteria are killed during the production process such that the produced catalyst support consists of residual biomass rather than live bacteria. A detailed study of the catalyst on the cells was reported previously [29].

The *in situ* catalytic upgrading experiments were carried out in a small stirred batch reactor (100 mL capacity, Baskerville, United Kingdom). The reactions were carried out at a temperature of 425 °C and 10 min reaction time, selected to match the residence time determined in previous fixed-bed investigations [5,6]; detailed experimental conditions are shown in Table 3. The catalyst-to-oil ratio and the agitation used in this study were the optimum values reported by Hart et al. [10]. In order to evaluate the effect of the nanoparticles, another experiment was conducted without nanoparticles to determine the baseline of upgrading with only thermal cracking. A short reaction time (i.e., 10 min) was used to avoid over cracking at reaction temperature above 400 °C, although some additional reaction may occur in the heating and cooling phases. Ortiz-Moreno et al. [11] reported that operating at a temperature above 400 °C a short reaction time enables the evaluation of catalytic effect since thermal effect is dominant above this temperature. Moreover, a longer reaction time does not give a distinguishable effect between thermal cracking upgrading and its catalytic counterpart [11,30]. Therefore, as the reaction

Table 1
Heavy feedstock properties.

Parameter	Value
API gravity (°)	13.8
Viscosity at 20 °C (mPa s)	1091
Density at 15 °C (g cm ⁻³)	0.9737
Sulfur (wt.%)	3.52
Nickel (ppm)	41
Vanadium (ppm)	108
Ni + V (ppm)	149
Asphaltene (wt.%) by nC ₇ H ₁₆	10.4
ASTM D2887 Distillation, °C	
IBP – 200 °C	34.6 vol.%
200 – 343 °C	41.4 vol.%
343 °C – FBP	24.0 vol.%

Table 2

Physical characteristics of particulate catalysts (5 wt.% of Pd).

Catalyst	BET area (m ² /g)	Particle Size (µm)	Total pore volume (cm ³ /g)
Pd/biomass	2.1 ± 0.1 ^a	2.8	0.02
Pd/C	818.7 ± 12	2.2	0.42
Pd/Al ₂ O ₃	237.7 ± 1.5	2.4	0.48
Al ₂ O ₃	115.5 ± 0.3	2.6	0.55
Co–Mo/Al ₂ O ₃	198.4 ± 0.4	2.1	0.43

^a It is not known to what extent the catalyst surface was occluded by residual components of biomass.

Table 3

Experimental conditions.

Parameter	Value
Catalyst weight (g)	0.4
Catalyst-to-oil ratio (w/w)	0.02
Feed oil (g)	20
Stirring speed (rpm)	500
Reaction time (min)	10
Temperature (°C)	425
Start-up pressure (bar)	20

time increases, catalytic upgrading approaches thermal cracking due to the catalyst being encapsulated by precipitated asphaltenes and formed coke, masking the efficacy of the nanoparticles. A typical heat-up, reaction, and cool-down temperature and pressure profile of the stirred batch reactor is presented in Fig. 1. The experiment time was measured from when the internal temperature inside the reactor reached the 425 °C set-point value. The reaction temperature for all experiments was reached within 142 min. Therefore, the nominal 10 min reaction time excludes the heat-up and cool-down times, during which some further reaction may take place.

The products of reaction consist of upgraded liquid oil, gas and coke. The produced gas was analyzed using an Agilent 7890A Refinery Gas Analyser (RGA) with a custom built gas chromatograph (GC) to determine the percent volume composition of hydrogen, light hydrocarbons (C₁–C₅), hydrogen sulfide, and permanent gases (e.g., CO, CO₂).

The following measurements were determined after collecting the upgraded oil; the viscosity was measured with an advanced rheometer AR 1000 (TA Instruments Ltd, United Kingdom), the API gravity was determined using digital Anton Paar DMA 35 portable density meter, and simulated distillation by GC method ASTM

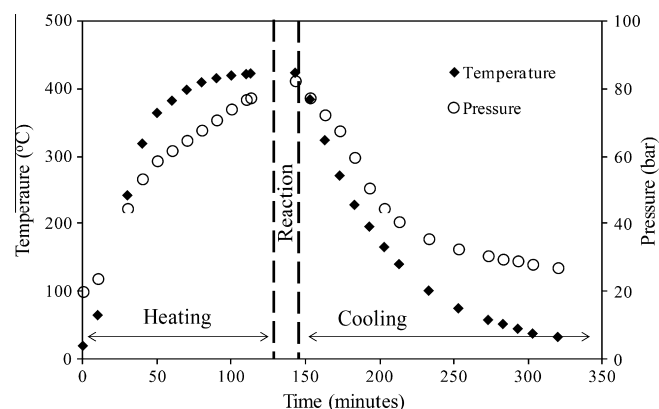


Fig. 1. Internal temperature and pressure as a function of time during start up, reaction and cooling of the stirred batch reactor with Pd/biomass nanoparticles.

D2887 (the calibration mix of the Agilent 6850N GC used in this study contain hydrocarbons from C_5 – C_{40} and subsequently the maximum oven temperature is 280 °C, the method cannot account for some macromolecules such as resins and asphaltene outside this carbon range).

The amount of coke produced from cracking of the heavy oil was determined using thermogravimetric analysis (TGA) of the deposit after upgrading using a NETZSCH-Geratebau GmbH, TG 209 F1 Iris® instrument. The deposit consists of catalyst particles, residual oil, resins and asphaltenes, and coke. Estimation of the coke content was carried out with a ramp temperature increase from 25 to 900 °C at air flow rate of 50 mL min⁻¹. The experimental and analytical methods used in this study are summarized in Fig. 2. More details of the analytical instruments have been reported elsewhere [6,31].

3. Results and discussion

3.1. Product distribution, API gravity, and viscosity

The distribution of liquid (i.e., upgraded oil), gas, and coke products after upgrading was calculated as the yield from the weight of heavy oil fed into the reactor using Eqs. (1) and (2):

$$\text{Yield of product (wt.\%)} = W_i / W_{\text{Feed}} \times 100 \quad (1)$$

$$\text{Gas (wt.\%)} = 100 - \text{liquid yield (wt.\%)} - \text{coke yield (wt.\%)} \quad (2)$$

where W_i is the weight of product i (i.e., gas, upgraded oil and coke) and W_{Feed} is the overall weight of the feed oil.

The amount of coke was determined from the TGA of the recovered deposits in the reactor after the upgraded oil sample was collected. Fig. 3 shows the thermograms or weight loss curves as a function of ramp temperature for n -heptane separated asphaltene, fresh Pd/biomass, and deposits after reaction with 5 wt.% nanoparticles of Pd supported on Al_2O_3 , carbon (C), and bacterial biomass, alumina and Co–Mo/ Al_2O_3 . The burn-off of coke occurs at temperatures beyond that of n -heptane separated asphaltene, because the deposit is a composite of residual oil, polar macromolecules such

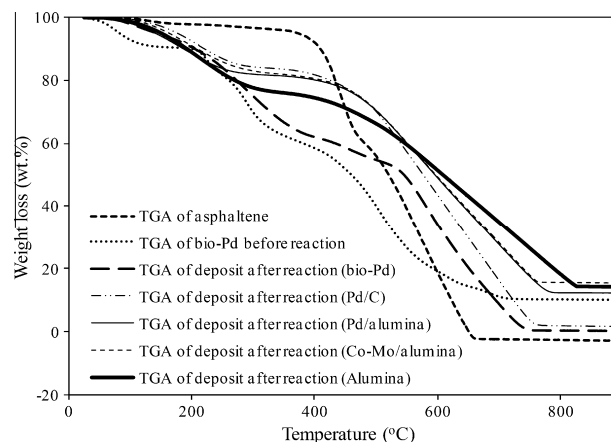


Fig. 3. Thermograms of n -heptane separated asphaltene, fresh Pd/biomass and deposit after reaction with Pd nanoparticles supported on bacterial biomass, carbon and alumina, and alumina and Co–Mo/ Al_2O_3 at 425 °C temperature, 0.02 catalyst/oil, 20 bar pressure, 500 rpm agitation, and 10 min reaction time under nitrogen atmosphere.

as resins and asphaltenes, and coke. It can be seen that the $nC_{7H_{16}}$ separated asphaltenes burn-off completely as the temperature increases from 430 to 640 °C. It has been reported for coked catalyst after upgrading that the burn-off beyond that of asphaltenes can be regarded as hard coke [6,32]. Therefore, the portion of the deposit that is coke after reactions with the different particulate catalysts is as follows: Pd/biomass (22.3 wt.%), Pd/C (18.58 wt.%), Pd/ Al_2O_3 (31.6 wt.%), Al_2O_3 (33.8 wt.%) and Co–Mo/ Al_2O_3 (29.8 wt.%). Hence, Pd supported on carbon-based materials produces less coke than with materials containing alumina. The fate of the cells of the Pd/biomass catalyst was not followed during the reaction in oil but it is likely that some pyrolysis had occurred. Upon heating some components of the biomass support may be modified between temperatures of 200 and 700 °C as shown in previous thermogravimetric studies, although the catalytic activity of the Pd nanoparticles remain intact [33]. Previous studies examining the effect of sintering on the biomaterial showed that, in contrast to dried bacterial cells bearing small, well separated metallic nanoparticles, the cellular material was rearranged during heating to give a ‘nesting’ effect around larger metallic nanoparticles (The results can be found in Fig. S1 of the supplementary information section). The carbon material supporting the catalytic particles may have had a protective effect in the present work; sintered biocatalyst material was shown in other work to ‘quench’ unpaired electrons (free radicals) as shown by EPR [34]. A possible moderation of free radical processes may account for the greater activity of the biomaterial-supported catalyst as compared to the chemically-supported catalyst.

It was observed that the deposit completely burns off in the temperature range of 640 to 780 °C. Consequently, the deposit after upgrading with Al_2O_3 (Alumina) showed the highest percentage of coke compared to those of Pd/ Al_2O_3 , Co–Mo/ Al_2O_3 , Pd/biomass and Pd/C catalysts. This can be attributed to the cracking function of the acid sites of the alumina which is not experienced with carbon and bacterial biomass neutral supports. However, the Pd and Co–Mo metals on the alumina supports are known to promote hydrogen-transfer reactions which help to reduce coke formation through the capping of radical coke precursors from the cracking of macromolecules [9,32]. The liberated hydrogen comes from the cleavage of C–H bonds in the hydrocarbon molecules and the abstraction of hydrogen from saturated hydrocarbons to form unsaturated hydrocarbons [9], and its presence has been confirmed in the produced gas composition as shown in Section 3.4.

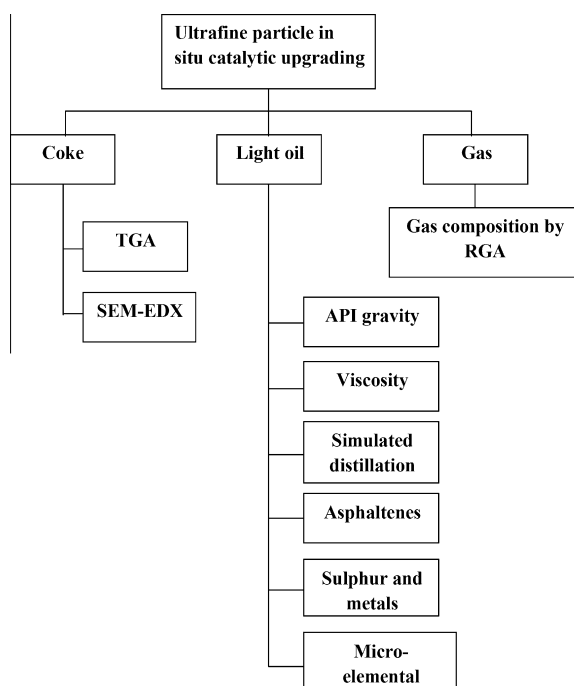


Fig. 2. Experimental and analytical methods.

In Table 4, the product distribution and the extent of API gravity and viscosity improvements after upgrading with thermal cracking, Pd nanoparticles supported on bacterial biomass, carbon and alumina, alumina only, and Co–Mo/Al₂O₃ are presented. The test result of the Co–Mo/Al₂O₃ nanocatalyst is presented for comparison purposes only as a typically used hydrodesulfurisation (HDS) catalyst in the petroleum industry. The reported data are averaged from duplicate experiments. The test using biomass without catalyst was not repeated, but error margins are expected within the same range as the catalytic samples. A more detailed study of the role of the Pd-biomass, confirmed by using more than one bacterial type, will be reported in a subsequent publication [35].

The API gravity of the produced oil after thermal cracking increased from 13.8° for the feed oil to 20.3° API, which represents a 6.5° increase. Comparing the API gravity of the oil produced by non-catalytic upgrading (i.e., thermal cracking) to the produced oil after reactions with 5 wt.% Pd upon different supports under the same experimental conditions, it was observed that this increased further to 21.6° (Pd/biomass), 21.6° (Pd/C) and 22.2° (Pd/Al₂O₃), respectively. An additional 0.6° API was observed for Pd supported on alumina compared with the Pd upon biomass or carbon supports. Though the API gravity increment between thermal cracking and dispersed catalyst upgrading is small, the benefits of introducing catalyst include improved produced oil quality (e.g., reduced impurities), increased yields of fuel distillates, increase yield of desired upgraded oil, and lower yield of undesired coke product. The results for Pd catalysts were also compared with the addition of biomass alone, which showed a small increase in liquid yield and decrease in gas and coke yields relative to thermal cracking, but not as large changes as for Pd/biomass. Such an effect may occur due to the adsorption of hydrocarbon molecules onto biomass particles, and the presence of fine particles which could act as nucleation sites for aggregation of heavy molecules such as asphaltenes [36]. However the augmented liquid yield and further decreases in coke and gas yields with Pd/biomass, evidence that catalytic reactions accompany these physical effects when the noble metal is present. Previous investigations [6] have reported the effects of different hydrogen and hydrogen donor environments upon the reaction and therefore the current study was conducted by filling the reactor with nitrogen and using only hydrogen generated in the course of the reaction since introduction of hydrogen down the well is likely to be infeasible and also introduce additional safety considerations.

Juxtaposing the performance of Pd/biomass catalyst against commonly used hydrodesulfurisation (HDS) catalyst showed that with the typical refinery catalyst (Co–Mo/Al₂O₃), the API gravity of the upgraded oil increased to 23.6°, representing another 2° increase compared with 21.6° (Pd/biomass) and a substantial level of upgrading from 13.8° (feed oil). On the other hand, although the THAI heavy oil viscosity of 1091 mPa s, is considerably lower than the original bitumen viscosity (greater than 1 million mPa S) it was

reduced to 18 mPa s after thermal cracking; catalytic upgrading reduced it further to 10.2 mPa s (Pd/biomass), 4.51 mPa s (Pd/C), and 7.6 mPa s (Pd/Al₂O₃), respectively, after upgrading with Pd nanoparticles on different supports. The further reduction of viscosity observed via using the carbon support is possibly attributed to the adsorption affinity of carbon for the macromolecules [6] and the biomass components could conceivably mimic this function under the conditions used. Achieving this level of viscosity reduction will significantly improve the displacement, sweep efficiency and production of the oil during the recovery process.

The major difference in the 5 wt.% Pd catalysts is the support material. Therefore, the difference in the API gravity and viscosity of the produced oil, as well coke yields, can be attributed to the contribution of the support material. The yield of coke obtained with 5 wt.% of Pd nanoparticles supported on alumina was 9.55 wt.%, with carbon support 6.85 wt.%, and bacterial biomass support 4.93 wt.%, respectively. However, the increased coke yield with Pd/alumina corresponds to the high API gravity increase (8.4°) of the produced oil. Unlike acidic supports such as alumina, neutral support materials restrain coke formation due to lack of acid sites that are responsible for a cracking function [37]. This is reinforced from the experimental results of alumina particles without Pd metal which gave a high API gravity increase of 8.9° and also high coke yield (13.65 wt.%). However, with Co–Mo/Al₂O₃ the highest API gravity increase (9.8°) and lower coke yield compared to alumina particles were observed. This could be attributed to the role of the Co–Mo metals in hydrogen transfer that helps narrow the molecular weight of cracked fragments by capping radicals [10,37]. It was previously shown that the addition of hydrogen gas or a hydrogen source such as methane could increase the level of upgrading occurring compared with an inert environment such as nitrogen gas, and decrease the amount of coke deposit occurring, owing to increased hydrocracking and hydrogenation reactions rather than the carbon rejection that occurs in the absence of hydrogen [9].

Generally, the liquid yield can be improved by minimizing the formation of hydrocarbon gases as well as suppressing coke formation. Hence, the neutral carbon and bacterial biomass supports of Pd could have played an active role in suppressing coke formation, meaning the splitting of C–C and C–heteroatom bonds was enhanced by the strong acid sites of the alumina, thereby yielding large amounts of gas and coke [37,38]. The extent of carbon-rejection during the upgrading reactions therefore is controlled by the metal and support type, with a support of strong acid sites yielding more coke than a neutral support.

3.2. Distillate fractions

The distillation curve of crude oils is an important tool of quality evaluation in the petroleum industry [39]. The distillate fractions for the feed and produced oils after upgrading with the

Table 4

Products distribution, API gravity and viscosity after upgrading with thermal cracking, biomass only, Pd nanoparticles supported on bacterial biomass, carbon and alumina, alumina and Co–Mo/Al₂O₃ at 425 °C temperature, 0.02 catalyst/oil, 20 bar pressure, 500 rpm agitation, and 10 min reaction time under nitrogen atmosphere. [Feed oil: 13.8° API and 1091 mPa s].

Catalyst	ΔAPI (Deg.)	Liquid (wt.%)	Coke (wt.%)	Gas (wt.%)	Viscosity (mPa s)
Biomass alone	6.2	82.6	7.6	9.7	14.8
Pd/biomass	7.8 ± 0.11	87.13 ± 0.10	4.93 ± 0.10	7.94 ± 0.20	10.2 ± 1.1
Pd/C	7.8 ± 0.14	85.9 ± 0.16	6.85 ± 0.12	7.25 ± 0.12	4.51 ± 0.6
Pd/Al ₂ O ₃	8.4 ± 0.20	81.35 ± 0.13	9.55 ± 0.17	9.1 ± 1.02	7.6 ± 0.8
Al ₂ O ₃	8.9 ± 0.21	73.05 ± 0.14	13.65 ± 0.11	13.3 ± 1.20	5.1 ± 1.2
Thermal	6.5 ± 0.32	78.9 ± 0.22	9.8 ± 0.20	11.3 ± 0.42	18 ± 0.3
Co–Mo/Al ₂ O ₃	9.8 ± 0.24	80.8 ± 0.13	12.15 ± 0.11	7.05 ± 0.46	4.4 ± 1.3

Note: ΔAPI gravity = API of upgraded oil – API of feed oil

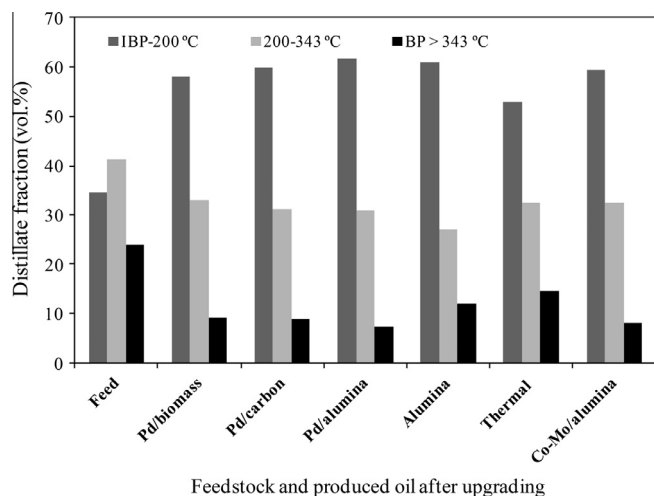


Fig. 4. Amount distilled for feed and produced oils after upgrading with thermal cracking, Pd nanoparticles supported on bacterial biomass, carbon and alumina, alumina and Co-Mo/Al₂O₃ at 425 °C temperature, 0.02 catalyst/oil ratio (g/g), 20 bar pressure, 500 rpm agitation, and 10 min reaction time under nitrogen atmosphere [IBP = Initial Boiling Point].

different nanoparticles and thermal cracking are presented in Fig. 4. The upgraded oils showed significant amounts of product in the naphtha and middle fuel distillates boiling range (IBP – 343 °C) compared to the heavy oil. Notably, nanoparticles of Pd supported on bacterial biomass achieved almost the same level of upgrading as those supported on carbon and alumina and also with a refinery Co-Mo/Al₂O₃ catalyst.

Though the use of alumina shows a high level of upgrading in terms of API gravity increment, viscosity reduction and yield of naphtha fraction (IBP – 200 °C), its residue fraction (>343 °C) is high compared to using Pd supported on bacterial biomass, alumina, and carbon. This implies that despite carbon-rejection being the dominant route to the upgrading, hydrogen can be readily adsorbed onto the Pd, Co and Mo surface where it becomes incorporated into a free radical reaction to form a stable hydrocarbon molecule. Although, the amount hydrogen adsorbed on the metals surface will be higher when the pressure is high. It is thought that the acid sites of alumina promoted cracking activity resulting in high production of naphtha fraction and coke [40,41]. This explains the high coke content found in the deposit after reactions with alumina (see Fig. 3). In the reaction environment cracking occurs as the C–C, C–H, and C-heteroatom bonds produce radicals that take part in the abstraction of hydrogen, radical intermediate rearrangement, radical termination, and/or another β -scission propagation step to form other active hydrocarbon chains with products that cover a range of lower molecular weight hydrocarbons than the starting molecule. Moreover, when a radical reacts with another radical through an addition-reaction, an adduct of

larger molecular size will be formed [39,42]. This adduct radical intermediate can undergo cracking, hydrogen-abstraction, or radical termination to a larger molecule which leads to the formation of high boiling point molecules. However, radical termination is favoured in the absence of metals such as Pd and Co-Mo, which is the probable reason for the high yield of residue fraction (BP > 343 °C) after upgrading with alumina particles and thermal cracking compared to the use of Pd nanoparticles supported on bacterial biomass, carbon, alumina and Co-Mo/Al₂O₃ catalyst (Fig. 4).

3.3. Asphaltene, sulfur and metals content

Asphaltenes are the heaviest component of heavy crude oil. Their aggregation and deposition can cause many operational problems; they are associated with heavy metals such as Ni and V and heteroatoms like sulfur and nitrogen, which readily deactivate refining catalyst. Table 5 shows the asphaltene, metals and sulfur content of feedstock and produced oils after upgrading by thermal cracking and with Pd/biomass and Co-Mo/Al₂O₃ particles. Most of the sulfur and metals are associated with the rejected coke after upgrading, however, thermal cracking without nanoparticles reduced respectively the sulfur and metals (Ni + V) content of the produced oil to 2.93 wt.% and 44 ppm relative to 3.52 wt.% and 149 ppm for the feedstock. However, the addition Pd/biomass and Co-Mo/Al₂O₃ particles further promote desulfurization and demetalisation compared to thermal cracking only (Table 5). The performance of the novel Pd nanoparticles supported on bacterial biomass (Pd/biomass) evaluated against that of a standard HDS and hydrodemetalisation (HDM) catalyst (Co-Mo/Al₂O₃) has shown that the two catalysts performed similarly (Table 5). It is also clear that thermal reaction is the predominant considering the difference in sulfur and metals (Ni + V) reduction between thermal cracking only and catalytic upgrading by either the Pd/biomass and Co-Mo/Al₂O₃ particles. Although most of the metals are retained in the produced coke, the further reduction in sulfur and metals (Ni + V) noticed with the addition of catalyst is attributed to the sulfidation of the metals (Pd, Co and Mo) on the particles [10].

After upgrading the asphaltene content of the produced oil decreased by 64–70% relative to 10.4 wt.% for the heavy oil feedstock. This significant decrease contributed to the increase in API gravity and improved viscosity of the produced oils as observed in Table 4. Furthermore, the sulfur content of produced oil with Co-Mo/Al₂O₃ and Pd/biomass under the same conditions was reduced by 24.4% and 29.8%, respectively, relative to 3.52 wt.% of the heavy oil feedstock. An additional 5.4% sulfur content reduction can be noticed upon the use of Pd/biomass. A decrease in the metals content was observed after upgrading; the (Ni + V) content was reduced by 82.55% (Co-Mo/Al₂O₃) and 80.54% (Pd/biomass) below 149 ppm in the heavy oil feedstock after upgrading. Other metal impurities such as iron, boron, and aluminum were also reduced

Table 5

Asphaltene, metals and sulfur content of feedstock and produced oil after upgrading by thermal cracking and using nanoparticulate catalyst of Co-Mo/Al₂O₃ and Pd/biomass at reaction temperature of 425 °C, nitrogen reaction media, agitation of 500 rpm, and 10 min of reaction time.

Impurities	Feedstock	Produced oil (Co-Mo/Al ₂ O ₃)	Produced oil (Pd/biomass)	Produced oil (thermal cracking)
Asphaltene (wt.%)	10.4	3.45	3.74	5.8
Aluminum (ppm)	2	<1	1	<1
Boron (ppm)	6	5	4	5
Iron (ppm)	5	<1	<1	<1
Nickel (ppm)	41	8	10	11
Vanadium (ppm)	108	18	19	33
Ni + V (ppm)	149	26	29	44
Sulfur (wt.%)	3.52	2.66	2.47	2.93

after upgrading (Table 5), indicating improved quality and potential commercial value compared to the original heavy oil. It is concluded that Pd nanoparticles supported on bacterial biomass could achieve a similar level of sulfur and metal reduction as well as yields of fuel distillates in the upgraded oil, as does a typical HDS catalyst. The possibility of sulfur poisoning of the catalyst is discussed in the following section.

3.4. Produced gas composition

The composition of produced gas during upgrading is shown in Table 6. Clearly, thermal upgrading produced higher concentration of hydrocarbon gases compared to catalytic upgrading by nanoparticles, which is consistent with the high yield of gas shown in the mass balance (see Table 4). The significant differences in gas composition from thermal and catalytic upgrading present further evidence for catalytic reactions occurring, rather than just a physical effect of the nanoparticles upon coke deposit. The presence of hydrogen in the gas could promote hydrogenation and hydrocracking reactions, therefore, the metals (i.e., Co–Mo, and Pd) could have contributed to promoting hydrogenation of cracked active hydrocarbon fragments and coke precursors to form small chain hydrocarbons which is not experienced in the thermal cracking counterpart where a high yield of coke was observed (see Table 4). The produced gases for upgrading via Pd/C and Pd/Al₂O₃ showed similar composition to that presented in Table 6 (not shown). The use of Pd/biomass and Co–Mo/Al₂O₃ produced more olefins than thermal cracking. This confirms that the catalytic upgrading reaction occurred with Pd/biomass. It is noteworthy that the reaction carried out with the latter produced less hydrogen sulfide compared to micro Co–Mo/Al₂O₃. This can be as a result of the synergistic interaction of Co–Mo with hydrogen-transfer reactions and C–S bond compared to the monometallic Pd/biomass. This is confirmed by the negligible hydrogen sulfide observed for thermal cracking of the heavy oil. Additionally, some of the sulfur was removed for the sulfidation of the metallic catalysts component during reaction as well as coke deposition. It is known that sulfur and sulfur-containing species (e.g. H₂S, RSH, RSSR) have been reported to have poisoning effects on heterogeneous metal catalysts [43] when adsorbed onto the metal surface. However, bacterial cells intrinsically contain quantities of sulfur within ubiquitous glutathione molecules [44] as well as sulfhydryl groups of amino acids; indeed, Pd–was co-localized with S in cellular Pd-nanoparticles, as shown via elemental mapping of ‘palladised’ cells of *D. desulfuricans* [45]. Other reports have shown that sulfur may also act as an activity promoter or selectivity modifier of metal catalysts when present at certain concentrations [46,47]. With respect to palladium the effects of strong adsorbates such as sulfur have been discussed in the palladium–hydrogen system with respect to the adsorbate interactions and atomic arrangements on the faces of the palladium metal surface ((210), (110) and (111)) [48] but it is not known which Pd-surface is specifically involved with the bio-material; indeed the biomatrix could be

regarded in this respect as a ‘partial poisoning’ agent by virtue of its interaction with the Pd NP which is held tightly within it. In addition, Dunleavy [43] reported that, based on practical experience, the addition of H₂S and other sulfur species of concentrations <10 ppb can prolong the life of PGM (platinum group metals) catalyst. For instance, various studies have been highlighted by McCue and Anderson [47] where sulfur at various concentrations played crucial roles in enhancing reactivity/selectivity of heterogeneous PGM catalysts. Kritzing et al. [49] found that industrial Fischer Tropsch catalysts contain 0.002–0.003% sulfur after two years of operation which is considerably lower than the cross over point between promotion and deactivation identified by McCue and Anderson [47] to lie at between 0.4 and 0.5 wt.% sulfur. In this study, analysis of oil residues after reactions shows that the concentration of hydrogen sulfide gas produced was within the industrial limit (0.0003–0.002, Table 6), meaning that hydrogen sulfide at this low concentration may have played a promotional effect rather than poisoning. The high sulfur concentration found in the produced oil (Table 5) could easily have reacted with the various inherent heavy metals of which some would have been deposited as low concentrations with hydrogen sulfide gas in the original oil or produced after reaction (Table 6). Although the native oil contains potentially inhibitory sulfur species it may be assumed that these could be present in non-available forms due to binding to other metals already present in the oil; however the bio-derived and chemical catalyst performed comparably.

3.5. SEM of catalysts

The morphologies of the particulate catalysts were studied before and after reactions with heavy oil. Fig. 5 shows a photomicrograph of the catalysts before and after reaction, the latter depicting particles encapsulated with deposits of asphaltene and coke. The magnification of air-dried and ground bio-Pd powder is 5000× to enhance clarity of the bacterial cells (Fig. 5a).

The individual dispersed particles of the Pd/biomass powder can be observed (Fig. 5a), and this is an important attribute of the nanoparticles required for transport into the reservoir for *in situ* catalytic upgrading in order to avoid aggregation that could cause plugging of reservoir formation. The SEM of the deposit (i.e., composite of particles, asphaltene and coke) after reaction shows abundant spheroids with a shape factor of approximately one and micro-size ranging from 1 to 4 μm (see Fig. 5b). The micro-sized globules are almost identical in size and compact with an amorphous ground mass. It is suggested that the structure of the Pd/biomass ruptured to release the Pd metals during reaction due to high sulfur, reaction temperature and stress from agitation. Hence, each fragment becomes a potential nucleus for precipitated asphaltene and formed coke leading to the formation of globules. The fresh Pd/C does not form agglomerates, however; after reaction the Pd/C particles were encapsulated with coke and asphaltene as can be observed in Fig. 5c and d. Unlike the Pd/biomass and Pd/C, it can be seen that the particles of Co–Mo/Al₂O₃ and Pd/Al₂O₃ (Fig. 5e and g) show the potential to aggregate and agglomerate to larger granules. This tendency increases the chances of formation plugging during dispersion into the reservoir. After reaction with Co–Mo/Al₂O₃, the residual particles and coke aggregate show an amorphous mass background with varying holes and a sponge microstructure (Fig. 5f). Notably, some of the particles are distributed within the coke deposit. Similarly, the encapsulation of the Pd/C catalyst particles can be observed from the deposit after reaction with small sized globules of about 5 μm (Fig. 5d).

Comparing Fig. 5b (Pd/biomass catalyst) with the corresponding Fig. 5f (Co–Mo/Al₂O₃), a clear difference can be seen in the morphology of the produced coke. Whilst the produced coke of the former is in the form of globules (Fig. 5b), the coke formed upon

Table 6

Typical produced gas composition after upgrading with thermal cracking, Pd/biomass, and Co–Mo/Al₂O₃ at 425 °C temperature, 0.02 catalyst/oil ratio (g/g), 20 bar pressure, 500 rpm agitation, and 10 min reaction time under nitrogen atmosphere.

Gas	Co–Mo/Al ₂ O ₃ (vol.%)	Pd/biomass (vol.%)	Thermal (vol.%)
n(C ₁ –C ₅)	7.73	6.34	10.3
i(C ₄ –C ₆)	0.34	0.87	0.48
Olefin (C ₂ –C ₄)	0.61	0.45	0.34
CO ₂	0.33	0.38	0.12
CO	0.1	0.16	0.11
H ₂ S	0.002	0.001	0.0003
H ₂	1.67	1.15	1.47

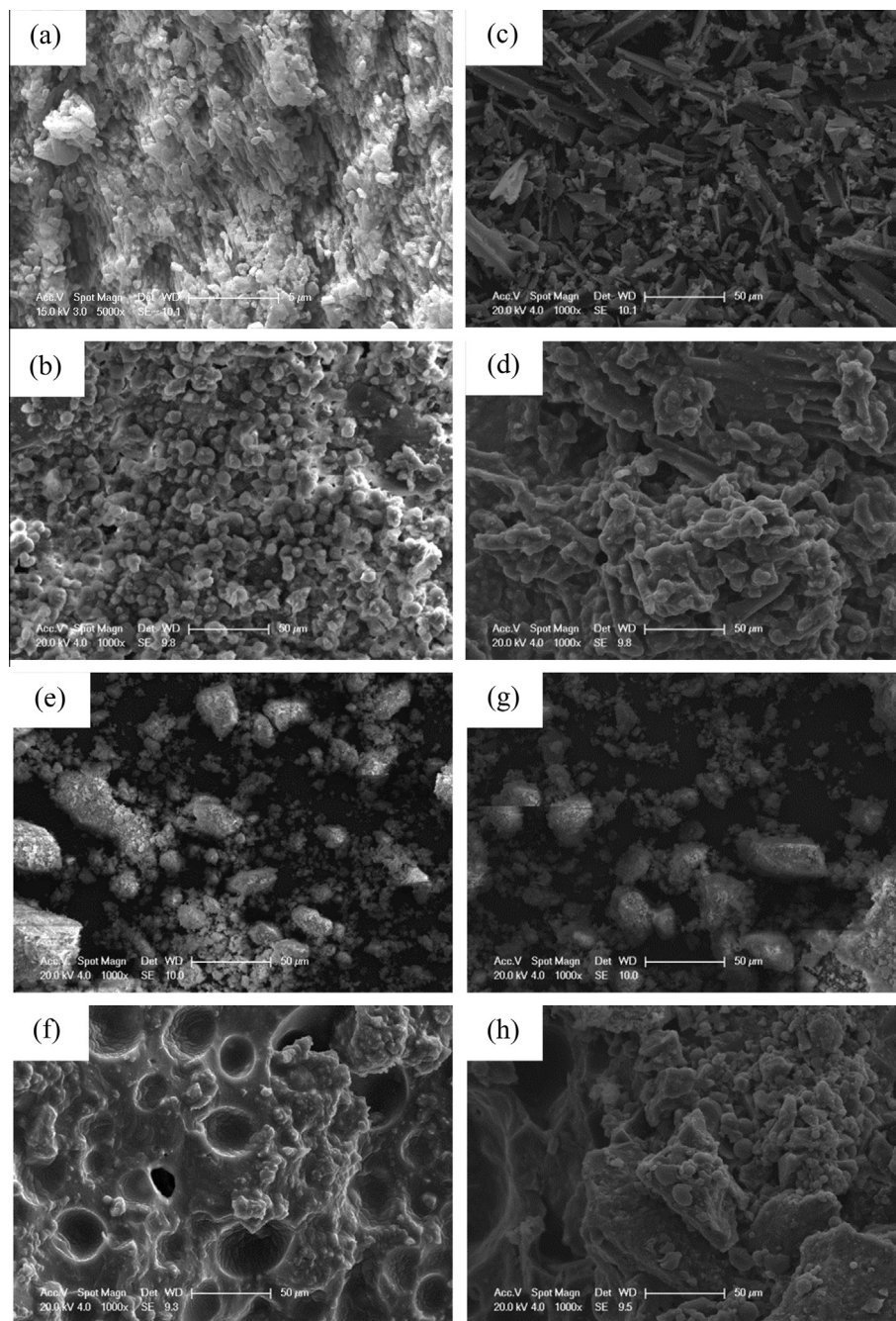


Fig. 5. SEM photomicrographs of (a) fresh Pd/biomass, (b) coked Pd/biomass, (c) fresh Pd/C, (d) coked Pd/C, (e) fresh Co-Mo/Al₂O₃, (f) coked Co-Mo/Al₂O₃, (g) fresh Pd/Al₂O₃ and (h) coked Pd/Al₂O₃. [Note the magnification of (a) is 5000× to enhance clarity of the bacterial cells].

the latter is sponge-like (Fig. 5e). These observations suggest that agglomeration of some particles with asphaltenes and coke occurred during the heavy oil upgrading reactions, forming aggregates which did not occur with biomass-supported material. The encapsulation of the catalyst particles by asphaltenes and coke could have impeded the catalytic performance and activity. It is worth noting that the metals and sulfur contaminants removed from the feedstock after reaction are included in the aggregate. Del-Bianco et al. [50] observed that the encapsulated aggregate could act as supplementary catalyst material in their micrometallic-coke form, as exchange of molecules such as active hydrogen, methyl, ethyl and others with the bulk oil-phase continues.

4. Conclusion

In situ catalytic upgrading with nanoparticles in the THAI process was tested in a batch reactor at temperature of 425 °C, using a short residence time of 10 min. Nanoparticles of palladium (5 wt.%) supported on bacterial biomass, carbon, and alumina were compared with typical refinery Co-Mo/Al₂O₃ catalyst. The API gravity of the upgraded oil increased by ~8–10°, viscosity decreased in the range 5–14 mPa s relative to 1091 mPa s (heavy oil) and also a significant improvement in naphtha fractions was observed. Though the API gravity increment and viscosity reduction between produced oil by thermal cracking and upgrading with Pd/biomass is marginal, upgrading with Pd/biomass shows a

benefit in terms of lower yield of coke 4.93 wt.% against 9.8 wt.% (thermal), lower yield of residue fraction (bp > 343 °C) 9 vol.% against 14.4 vol.% (thermal) relative to 24 vol.% (feed oil) and also improved quality of produced oil with approximately 30% and 81% reduction in sulfur and Ni + V contents. The results of the simulated distillation, viscosity reduction, asphaltene, sulfur and metals content after upgrading showed that the alternative Pd/biomass nanoparticles have the potential of achieving a similar level of upgrading as obtainable with typical HDS catalyst particles such as Co–Mo/Al₂O₃ as well as Pd supported on carbon and alumina, respectively. Since effective Pd-biocatalyst can be biorefined from wastes such as road dust and electronic scraps with comparable activity to that reported here these findings warrant an in-depth cost-benefit analysis [35]. Application of nanoparticulate catalysts down-well is challenging owing to the requirement to transport nanoparticles through porous media. Associated studies in this project have investigated the statistics of highly heterogeneous flow fields confined to three-dimensional porous media, with the aim to present a basis for analyzing this problem [51].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2016.04.064>.

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