Metallic bionanocatalysts: potential applications as green catalysts and energy materials

Lynne E. Macaskie,1,4 Iryna P. Mikheenko,1 Jacob B. Omajai,1,4 Alan J. Stephen2 and Joseph Wood2
Schools of 1Biosciences,
2Chemical Engineering, University of Birmingham,
Edgbaston, Birmingham, B15 2TT, UK.

Summary
Microbially generated or supported nanocatalysts have potential applications in green chemistry and environmental application. However, precious (and base) metals biorefined from wastes may be useful for making cheap, low-grade catalysts for clean energy production. The concept of bionanomaterials for energy applications is reviewed with respect to potential fuel cell applications, bio-catalytic upgrading of oils and manufacturing ‘drop-in fuel’ precursors. Cheap, effective biomaterials would facilitate progress towards dual development goals of sustainable consumption and production patterns and help to ensure access to affordable, reliable, sustainable and modern energy.

Introduction
In the late 1990s, bacteria were reported to recover soluble palladium (II) via reduction into cell-bound precious metal (PM) nanoparticles (NPs) (Lloyd et al., 1998) with high catalytic activity (Baxter-Plant et al., 2003). Many authors have reiterated the scope for bio-PM catalysts (e.g. reviews by Deplanche et al., 2011; De Corte et al., 2012; Castro et al., 2014; Kulkarni and Maddapur, 2014; Rai et al., 2015; Singh, 2015; Ashok, 2016). A consultancy report (Catalytic Technology Management, unpublished, 2009) concluded that a ‘me too’ catalyst must be more active than those currently available, cheaper or both. The paradigm bacterial ‘bio-Pd(0)’ has significant potential applications in ‘green chemistry’ and environmental nanotechnology, but the criteria cannot yet be met in full due to high costs of (i) growing dedicated bacteria and (ii) precious metals; (iii) retention of the catalyst for re-use and (iv) potential catalyst poisoning at high reaction temperatures (e.g. by sulfur via degradation of the biomaterial). Waste yeast and bacteria have been successfully reused in ‘second life’ following primary fermentations (Dimitriadis et al., 2007; Orozco et al., 2010; Zhu et al., 2016) while waste precious metals have been bio-reprocessed into active neo-catalysts (e.g. Mabbert et al., 2006; Deplanche et al., 2007; Yong et al., 2010, 2015; Murray et al., 2017a). Metal attrition from cells was negligible, enabling catalyst re-use [e.g. 6 cycles (Bennett et al., 2013)] and also as an immobilized catalyst (Beauregard et al., 2010). The highest ‘green’ potential probably lies in ‘tandem’ one-pot reactions which (e.g.) combine a biotransformation with a bio-Pd-catalysed step [e.g. in an enantioselective deracemization reaction (Foulkes et al., 2011)] although the low Pd loading necessary to permit continued physiological activity may not be optimal for chemical catalysis.

Concerns about nanoparticles in the environment (Valsami-Jones and Lynch, 2015) (biomass will eventually decompose) may restrict pollutant remediation to ex situ applications. Catalyst poisoning is less relevant in a ‘dirty’ process, but this requires cheap, disposable catalyst. A life cycle analysis is needed to determine where bio-metallic catalysts may outcompete traditional comparators, taking into account socio-environmental as well as economic factors.

Bio-precious metal materials are emerging in energy applications (Table 1). Large-scale oil production may justify a once-through catalyst if a low-grade mixed metal ‘dirty’ catalyst can be used. On the other hand, in synthesis of fuel precursors from waste CO2, some bionanoparticles [e.g. structured Pd/Au core shells (Deplanche et al., 2012)] could potentially be used for making (e.g.) formic acid electrochemically (Humphrey et al., 2016). Liu et al. (2016) reported a bio-Pd/Au alloy with electrocatalytic activity, but the thickness of the Pd-shell is critical for product selectivity [e.g. for formate production a Pd-shell of 10 nm is optimal (Humphrey et al., 2016)]; such fine structure control is probably beyond the reach of biosynthetic capability. Moreover,
Table 1. Microbial precious metal nanoparticles and catalysts in energy applications

| Test | Comments | Ref |
|------|----------|----|
| (a) Fuel cells (anodic and cathodic FC electrocatalysts) | Bio-PM catalyst on *Desulfovibrio desulfuricans*. Required sintering to carbonize. Power outputs: commercial Pt FC, 200 mW; commercial Pt FC catalyst 170 mW; Bio-Pt, 170 mW; Bio-Pd, 140 mW*. Metal content was 20 wt% and activated carbon was 80 wt% plus residual biomass component. Loading: 1 mg metal cm$^{-2}$. | 1 |
| Anode (PEMFC) | Bio-Pt catalyst made from waste yeast cells from fermentation, immobilized in polyvinyl alcohol. Activity was half that of commercial Pt on carbon catalyst. Loading 10 mg Pt cm$^{-2}$. | 2 |
| Anode (PEMFC) | Anode as in 1. Power outputs from bio-Pd were: *Rhodobacter sphaeroides* 142 mW; C. metallidurans CH34, 68 mW; *Escherichia coli* MC4100, 29 mW; *E. coli* IC007, 115 mW; *E. coli* IC007 (made from industrial PM waste), 68 mW. Increasing Pd loading onto cells from 5 wt% to 25 wt% doubled power output. | 3 |
| Anode (PEMFC) | Anode as in 1. Power outputs from bio-Pd were: *Rhodobacter sphaeroides* 001 (biodyrogeen-producing), 20 mW and *E. coli* (second life* cells from biodyrogeen process): H701, 28 mW; MC4100, 18 mW; IC007, 56 mW. | 4 |
| Anode (PEMFC) | Bio-Pd on *Shewanella oneidensis* MR-1. Formate was an electron donor in Pd-NP synthesis (NP size 50-10 nm). Pd loading was 20 wt% on cells and 1.28 mg Pd cm$^{-2}$ on anode. Power density was 4.8 mW cm$^{-2}$ for bio-Pd and 5.3 mW cm$^{-2}$ for commercial Pd-catalyst. | 5 |
| Anode (PEMFC) | EPR showed more electronic interactions between bio-Pd and commercial Pd/C; quenching of free radical (FR) of activated carbon was higher with sintered bio-Pd$_{desulfuricans}$ than with bio-Pd$_{E. coli}$. Both bio-Pds gave higher FR quenching than Pd/C catalyst. | 6 |
| Catalyst mix pd/activated carbon in EPR | Pd loading 20 wt% (*E. coli*). Use of formate as an electron donor for Pd(0) formation gave small, well separated NPs with no electrochemical activity. Bio-Pd made under H$_2$ showed proton adsorption/desorption. Similar results obtained using bio-Pd on *Shewanella oneidensis*. | 7 |
| Native cells in rotating disc electrode | Palladium NPs on *D. desulfuricans* (native cells). Pd loading not stated. Concentration gradients involved in extracellular electron transfer processes. Pd-NPs proposed to augment natural electron transport chain. Activity increased by adding formate (live cells only). | 8 |
| Cyclic Voltammetry | Material as in 1. Bio-Pd$_{E. coli}$ at 25 wt% Pd. Commercial anodic catalyst in FC test: Pd$_{E. coli}$, 68 mW; Pd$_{E. coli}$, 68 mW; Pd$_{E. coli}$, 68 mW; Pd$_{E. coli}$, 68 mW. | 9 |
| O-reduction reaction: cyclic voltammetry | Bio-Pd$_{E. coli}$ cleaned in NaOH gave enhanced cyclic voltammetry response, cf. sintered material. Bio-Pd$_{desulfuricans}$ was better when cleaned in phenol–chloroform. Max. current was 25 μA and 25 μA, respectively (glassy carbon rotating disc electrode) | 10 |

Application | Comments | Ref |
|------------|----------|----|
| (b) Upgrading of 5-hydroxymethyl furfural (5-HMF) into 2,5-dimethyl furan (drop-in fuel) | Pd-based catalyst supported on *Bacillus benzoevo* (Table 3). The conversion was the same as Pd/C catalyst, but selectivity was higher. | 11 |
| (c) Catalytic upgrading of pyrolysis oil Pyrolysis oil algal (Chlorella) | Oil was from algal (Chlorella) slurry. Bio-Pd$_{desulfuricans}$ (5 wt% Pd; biomass; 5 wt% catalyst per reaction) and Pd/C (10 wt% catalyst per reaction: 15 g oil; 4 h; 325°C) had similar activities, O$_2$ and N$_2$ contents were reduced by 65% and 35% respectively. | 12 |
| Pyrolysis oil beechwood | Oil was from beechwood (fast-pyrolyzed 500°C; < 2 h). Catalysts: 5 wt% Pd$_{E. coli}$, 5 wt% Pd/C and commercial Pd/Al$_2$O$_3$ (0.6 g catalyst to 20 g oil). Minimum viscosity was ~0.035 Pas (250°C, 3 h), increasing thereafter. | 13 |
| Pyrolysis oil pine wood | Made from beetle-killed pine trees which were more easily pyrolysed; not tested for upgrading via bio-derived catalysts. | 14 |
| (d) Catalytic upgrading of heavy oils Upgrading of heavy fossil oils from Touchstone (Canada) | Production of bio-magnetite (Fe$_3$O$_4$) by *Geobacter sulfurreducens* that reduces Fe(III) to Fe(II) thence to bio-magnetite. Functionalization of bio-magnetite with Pd(0) onto bio-magnetite. Comparable oil upgrading to commercial alumina-supported catalysts. High liquid yield (90%); less viscous than without catalyst. Coking reduced twofold to fourfold using 9.5 wt% Pd. In situ process proposed by stimulation of natural geomicrobiological system. | 15 |
| Bio-PMs made on cells of *Bacillus benzoevo* and *Desulfovibrio desulfuricans*. Bio-Pd/Pt mix (1:1) was better than Pd alone. Comparable upgrading to commercial catalyst via using 5 wt% and 20 wt% metal loading. Liquid yield was 90%. Coking was reduced by ~20% as compared to using commercial catalyst (Ni/Mo/Al$_2$O$_3$). Extensive catalyst characterization. | 16 |
electrocatalysis does not generate longer chain hydrocarbons and this method may not be readily scalable.

As an alternative, chemical upgrading of CO₂ into hydrocarbon fuels is scalable. Recent advances employ the reverse water gas shift reaction (reduction of CO₂ to CO) in tandem with Fischer–Tropsch chemistry to convert the more reactive CO into hydrocarbons. Consuming CO (a catalyst poison) shifts the equilibrium towards products in the reverse water gas shift reaction, promoting CO₂ consumption. An efficient, abundant, low-cost catalyst(s) must give product selectivity in the desired range (~C₅–8 for gasoline; ~C₉–16 for diesel fuel). Precious metals (Pd, Pt, Ru, Rh) on SiO₂ have been used in the reverse water gas shift reaction, while catalysts for the Fischer–Tropsch process are usually Fe or Co-based, with recent innovations towards one-pot reactions (see e.g. Mattia et al., 2015; Owen et al., 2016; Prieto, 2017) following early work (Dorner et al., 2010) that showed conversion of CO₂ to hydrocarbons (41% conversion and a C₂–C₅⁺ selectivity of 62%) using a doped Fe-based system. The potential for using biogenic catalysts has not been explored although a paradigm hybrid bio-magnetite/Pd(0) catalyst has been reported (Brown et al., 2016). When made from waste, biogenic precious metal catalysts (e.g. Pd/Pt mixtures ~30% Pd) also contained other metals, for example from Degussa processing waste: Al (42%), Ag (6%) and Mg (3%) and from spent automotive catalyst leachate: Fe (14%), Mg (12%) and Al, 27%), i.e. metals that were present in the original solid material (Mabbett et al., 2006; Macaskie et al., 2010). Potentiation of catalytic activity occurred (e.g. more than 10-fold in the case of reduction of Cr(VI) to Cr (III)) using these waste-derived mixed metal catalysts (Macaskie et al., 2010). Hence, exploration of bio-catalyst made from automotive leachate may be warranted for CO₂ valorization, particularly as waste bacteria for use as catalyst support (Orozco et al., 2010; Zhu et al., 2016; Stephen et al., this volume) are readily available from other scalable biotechnology processes. However, selectivity towards specific hydrocarbon products may not be compatible with such economies.

In contrast to CO₂-valorization, ‘proof-of-principle’ application of biogenic catalysts has been shown in four key areas of energy and fuels (Table 1).

### Fuel cell electrocatalysts

Fuel cells comprise an anode [where fuel, e.g. H₂, is split catalytically to give electrons (current) and protons], a cathode (where protons combine with O₂ in air to give water) (Krayshterg and Ein-Eli, 2014) and an electrolyte that allows passage of positive ions between them (Kurubakaran et al., 2009). The polymer electrolyte fuel cell (PEM fuel cell) uses purified hydrogen at low temperatures (80°C) with rapid start up (Mehta and Cooper, 2003). PEM fuel cells are applicable for use in (e.g.)

---

Table 1. (Continued)

| Test | Comments | Ref |
|------|----------|----|
| Catalyst (Bio-Pd/Pt; 2.5 wt% Pd/2.5 wt% Pt) was made on B. benzevorans and E. coli. The former showed ~30% reduced coking. It was discussed that the catalyst may reduce V(V) to a V-species that does not promote free radical reactions leading to coking. These higher inorganic phosphate content of the Gram-positive cell wall (teichoic acids) may sorb Ni²⁺ (although the cells become carbonized to become part of the fuel). Similar results were obtained using metals sourced from simulated road dust waste leachates | 17 |
| Upgrade waste glycerol | Bio-Au(0) nanocatalyst from jewellery waste was shown to oxidize glycerol to glycerate Application to biodiesel waste glycerol is not yet shown. Glycerate is a substrate for bio- | 19 |
| Photocatalytic water splitting to make H₂ | Noble metals are used to split water to make H₂_2 (Bio-PMs are not yet tested) | 20 |
| | Optically active ZnS was made using mine drainage treatment bioprocess off- gas (H₂S) | 21 |
| | CuS has been separated from other metals in biogenic metal recovery from waste | 22 |
| | CuS/ZnS hybrid (chemically made) was used in photocatalytic water splitting | 23 |
| | CdS quantum dots were made with bacteria and cysteine (Cd is more toxic than Zn; an energy application was not reported). | 24 |
| | Biogenic metal selenides were made ex-situ (reduction of selenite by Veilonella atypica) | 25 |
| | CdSe can be made by Fusarium oxysporum (intracellularly; metabolic process) | 26 |
| | CdSe-hydrogenase hybrids/artificial hydrogenases are reported for water splitting | 20 |

1. Yong et al. (2007). 2. Dimitriadis et al. (2007). 3. Yong et al. (2010). 4. Orozco et al. (2010). 5. Ogi et al. (2011). 6. Carvalho et al. (2009). 7. Courtney et al. (2016). 8. Wu et al. (2011). 9. Stephen, A.J. unpublished data. 10. Williams (2015). 11. Omajali (2015). 12. Kunwar et al. (2017). 13. Dellami et al. (unpublished). 14. Luo et al. (2017). 15. Brown et al. (2016). 16. Omajali et al. (2017). 17. Murray et al. (2015). 18. Pakhare and Spivey (2014). 19. Deplanche et al. (2007). 20. Ran et al. (2014). 21. Murray et al. (2017b). 22. Nancuccho and Johnson (2012). 23. Zhang et al. (2011). 24. Yang et al. (2015). 25. Fellowes et al. (2013). 26. Yamaguchi et al. (2016).
vehicles (Hannan et al., 2014) or larger ‘stacks’ for domestic power (Staffell et al., 2015). Durability targets (internationally) are 5000 h and 40 000 h of operation for automotive and stationary fuel cells, respectively (Rice et al., 2015). The US Department of Defence installed 5 kW PEM fuel cell systems in ~40 military bases (cost of > $100 000 per system) but, with an operational lifespan of only 500 h, the systems required overhauling annually (Staffell et al., 2015). The cost of precious metal catalysts is restrictive; other catalysts are under development but the power to weight ratio is key, especially for portable and aerospace applications. Substitution of fuel cell Pt-electrocatalysts (0.2–0.8 mg cm$^{-2}$) would use lighter, equivalently performing (but robust against the high local acidity) metals like Pd (e.g. Meng et al., 2015; Gómez et al., 2016), particularly in the cathodic reduction of O$_2$ (He et al., 2005) which is rate-limiting. Reducing Pt costs/loadings could also be achieved by optimizing Pt nanoparticles (via size control and increased uniformity), or by developing alloys (Zhu et al., 2015). Developments towards microbially derived fuel cell catalysts are shown in Table 1. The anodic reaction is well reported, and the challenge is now to develop an efficient cathodic oxygen reduction catalyst; electrochemical test data are shown in Table 2.

2,5-dimethyl furan (DMF) production from 5-hydroxymethyl furfural (5-HMF)

Carbohydrates form ~75% of the annual renewable biomass (Schmidt and Dauenhauer, 2007). In thermochemical hydrolysis [e.g. of fermentation feedstocks: Orozco 2011], 5-hydroxymethyl furfural is produced via breakdown of hexoses in cellulose and starch hydrolysates (Román-Leshkov et al., 2007; van Putten et al., 2013). 5-hydroxymethyl furfural is a precursor to 2, 5-dimethyl furan (DMF), a ‘drop-in’ fuel for conventional engines (Zhorg et al., 2010). DMF contains comparable energy to gasoline (Davis et al., 2011) (energy contents are 31.5 MJ l$^{-1}$ and 35 MJ l$^{-1}$ respectively). DMF is also more advantageous than ethanol because of its higher gravimetric energy density (about 40%), higher boiling point and insolubility in water; hence, it is a potential alternative biofuel (Tian et al., 2011).

Various catalytic applications have been developed to achieve good yield and selectivity to 2, 5-dimethyl furan. Most have focused on commercial heterogeneous mono and bimetallic catalysts based on (e.g.) Ru, Pd, Pt, Au, Cu (Tong et al., 2011; Hansen et al., 2012; Nishimura et al., 2014; Zu et al., 2014; Luo et al., 2015) which are costly. A bacterial platform would provide a cheaper, sustainable source of supported precious metal catalyst, possibly using metals biorefined from waste sources. As the first step, conversion of 5-HMF to DMF using a bio-Pd-based catalyst and a Pd/carbon catalyst was compared (Omajali, 2015), with better selectivity to DMF observed using the biomaterial (Table 3). Nishimura et al. (2014) showed application of a Pd/Au bimetallic/C catalyst and hence the use of bio-Pd/Au (Deplanche et al., 2012; Hosseinkhani et al., 2012; Liu et al., 2016) is worth evaluating in this application.

Table 2. Activity of bio-Pt catalyst on Escherichia coli and Desulfovibrio desulfuricans compared to commercial TKK fuel cell catalyst.

| Material/treatment                  | Specific activity (mA cm$^{-2}$) | Mass activity (mA mg Pt$^{-1}$) | No. electrons transferred per O$_2$ |
|-------------------------------------|----------------------------------|----------------------------------|------------------------------------|
| Bio-Pt$_{E. coli}$(NaOH)            | 0.68 ± 0.15                      | 75 ± 17                          | 3.78 ± 0.23                       |
| Bio-Pt$_{D. desulfuricans}$(phenol-chloroform) | 1.43 ± 0.28                      | 304 ± 53                         | 3.84 ± 0.12                       |
| TKK catalyst                        | 0.45 ± 0.02                      | 374 ± 4                          | 3.68 ± 0.07                       |

Taken from Williams (2015). Pt loading was 5 wt% of the biomass. Bio-Pt$_{E. coli}$ was cleaned using NaOH. Bio-Pt$_{D. desulfuricans}$ was cleaned using phenol–chloroform. As with the anodic and cathodic tests in the PEM fuel cell (Table 1), the E. coli biomass was ~25% as active (mass activity) as that from D. desulfuricans and had ~half the specific activity (mA cm$^{-2}$). However, growth of E. coli is readily scalable and it makes active bio-metal catalyst when used in ‘second life’ following an independent primary fermentation (Orozco et al., 2010; Zhu et al., 2016). In contrast to E. coli, D. desulfuricans cells are obligately anaerobic, growth is less readily scalable, and they produce H$_2$S, a powerful catalyst poison that requires more extensive washing of the cells prior to use. However, a metal bioremediation process that couples excess biogenic H$_2$S (used for minewater clean-up with respect to heavy metals (Hedrich and Johnson, 2014)) also produces waste biomass of a sulfate-reducing bacterial consortium which may find a ‘second life’ use as a bio-metallic catalyst for fuel cell application, mitigating waste disposal costs.

© 2017 The Authors. Microbial Biotechnology published by John Wiley & Sons Ltd and Society for Applied Microbiology, Microbial Biotechnology, 10, 1171–1180
and theoretical chemistry can play an important role in understanding the competing reactions on the surface of, for example, Pt (111) faces (Liu et al., 2017). However commercial precious metal catalysts would be uneconomic; moreover, fuel cell electrocatalysts (above) will compete in parallel for limited global resources. The energy demand of winning precious metals from primary ores (e.g. 14 t of CO$_2$ is emitted per kg of Pt produced: Anon 2008) is a major consideration; carbon-neutral fuel needs, in itself, to produce a low carbon footprint.

Catalytic deoxygenation reactions include dehydration, hydrogenolysis, hydrogenation, decarbonylation and decarboxylation (Fig. S1, Table S1). For fuels in the diesel range, C-C coupling reactions can be achieved through routes such as aldol-condensation, ketonization, oligomerization and hydroxalkylation, but hydrodeoxygenation is currently considered the most effective method for bio-oil upgrading, improving the effective H/C ratio and leading to hydrocarbons.

To date, several classes of catalysts are reported for hydrodeoxygenation. In addition to precious metal catalysts, other metals (Fe, Ni and Cu) have shown good selectivities in hydrogenation and hydrogenolysis reactions. However, high hydrogen pressures can lead to complete hydrogenation of double bonds (Bykova et al., 2012). Industrial catalysts based on Co-Mo and Ni can provide good hydrodeoxygenation performance, but these deactivate rapidly due to coke formation and water poisoning (Badawi et al., 2011).

The acidic, corrosive biofuels also limit catalyst lifetime and compromise the process economics. Work has focused on upgrading of biocrude oils using various catalysts (e.g. Co-Mo, Ni-Mo Pd/C (e.g. Biller et al., 2015; Si et al., 2017)). Of these, Pd (which is a noble metal and hence is dissolution tolerant) is promising. 5-hydroxymethylfurfural is made within in the product oil (Dang et al., 2016), enabling possible catalytic conversion into 2,5-dimethyl furan into a second fuel stream.

Despite the high costs, precious metal-based catalysts are favoured for bio-oil upgrading (see reviews: Watson, 2014; Pandey et al., 2015; Cheng et al., 2016; Lee et al., 2016; Nam et al., 2017; Femoso et al., 2017); bio-manufactured catalyst should now be added to the portfolio (Table 1). Bio-reprocessed precious metal waste has not yet been tested as a cheap metal source (c.f. below). The upgrading efficiency, product spectrum and cost savings are being factored into ongoing research via life cycle analysis, towards the dual development goals of sustainable consumption and production patterns for affordable, reliable, sustainable (non-fossil) energy.

### Upgrading of fossil oils

The hydrogen economy and carbon-neutral biofuels lag behind the timeline for change articulated by the Stern Review (Stern, 2006). Hence, cleaner production of fossil fuels is vital as these will remain the predominant short-term sources of supply (~80% of global needs; Anon 2014). With globally declining light crude oil reserves, heavy oil and bitumen use will increase from 2 to 7 million barrels day$^{-1}$ by 2030 (Anon 2015). Oil sands production emits more greenhouse gas and uses more water than conventional light oil production (Findlay, 2016) and additional refining is also required (Huc, 2011). Heavy oil exploitation is complicated by the high viscosity, low hydrogen content and high amounts of resins and asphaltenes. (Bio)geochemical processes evolved the hydrocarbons, leading to materials with high contents of heavy molecules rich in sulfur, nitrogen, oxygen and metals (e.g. Ni, V), with high viscosity and acidity (Head et al., 2003; Huc, 2011). Technologies for heavy oil upgrading have been reviewed (Heraud et al., 2011; Castañeda et al., 2014). Upgrading in situ gives a cleaner production of less viscous oil, which is more easily transported without the use of diluents (Shah et al., 2010). The THAI-CAPRI (Toe-to-Heel Air Injection coupled with Catalytic Upgrading Process In situ) technology combines thermally enhanced oil recovery with down-hole catalytic upgrading of heavy oil into light fractions (Greaves and Xia, 2004; Hart et al., 2014). This catalytic upgrading, using steam, hydrogen and methane, showed significant improvements over non-catalytic thermal processes (Hart et al., 2014). Conventional cracking catalysts such as supported noble metals are prohibitively expensive; one economic option could utilize regenerated catalysts from treated oils but these have lower activity (Hart et al., 2014).

The future is uncertain. Healing (2015) questioned the economics of the THAI process, Findlay (2016) discussed this in view of wider issues (regulation, cost and price uncertainties), and Nduagu et al. (2017) discussed

**Table 3.** Pd-catalyst-mediated upgrading of 5-hydroxymethyl furfural into 2,5-dimethyl furan.

| Catalyst and H-donor | 5-HMF conversion (%) | DMF yield (%) |
|----------------------|----------------------|--------------|
| 5 wt% Pd/carbon (formic acid) | 97.5 | 26.5 ± 2.0 |
| Bio-Pd-based (5 wt% metal; formic acid) | 96.8 | 49.8 ± 0.6 |
| 5 wt% Pd/carbon (2-propanol) | 94.5 | 32.6 ± 1.8 |
| Bio-Pd-based (5 wt% metal; 2-propanol) | 94.5 | 42.6 ± 1.2 |

Taken from Omajali (2015). Bio-catalyst was prepared on cells of *Bacillus benzeovorans*. *Bacillus* was selected because this genus is grown at large scale for commercial production of enzymes; a cost-benefit analysis for ‘second life’ production of catalyst as compared to other current routes for disposal of waste biomass is required.
the wider issues of oil sands processes in terms of performances and economics including greenhouse gas emissions and other environmental impacts. Meanwhile, emerging researches include modelling of the THAI-CAPRI process (Ado et al., 2017) and the successful use of bio-nanoparticle catalysts sourced from wastes (Table 1). Application of nanoparticles in enhanced oil recovery has been reviewed (Negin et al., 2016; Sun et al., 2017). While bio-nanoparticles are held immobilized on bacterial cells, thermal degradation would evolve them in association with biomass-carbon. Environmental concerns about nanoparticles have been expressed (see earlier), but it is also argued that naturally occurring nanoparticles are ubiquitous in the environment (Montano et al., 2014) while evidence for natural biogeochemical cycling of platinum has been reported (Reith et al., 2016).

Conclusions and future scope

As far as we are aware, this is the first overview of the potential for biogenic catalysts in various energy applications within the ‘whole energy mix picture’. The concept of using microbial technologies to make materials for application to sustainable energy-generating processes (as compared to energy and waste savings via use in ‘green chemistry’) is a new direction. Palladium occurs in spent nuclear fuels (one ton of spent nuclear fuel contains > 2 kg of Pd or 10% of global requirements: Bourg and Poinssot, 2017). Even though radiation-resistant bacteria are well known, and the ability of microorganisms to discriminate between isotopes of essential metals (Fe, Mo) has been reported (Wasyleńki et al., 2007), separation of the active $^{107}$Pd (half-life 6.5 m yrs; 15% of the Pd inventory) from the stable isotopes (85%) is probably beyond the reach of 21st-century biotechnology. Moreover, while biorecovery of precious metals from aggressive solutions (using pre-palladized cells, via chemical catalysis using Pd-bionanoparticle ‘seeds’) has been shown (Murray et al., 2017a), the metal composition of the neo-catalyst reflects the metallic composition of the waste (Macaskie et al., 2010), and hence, selective biorecovery of Pd against higher active radionuclide contaminants would be prohibitively difficult.

Photochemical water splitting to make clean hydrogen is a well-established solar technology, best achieved traditionally using noble metal catalysts (Ran et al., 2014). As potential alternatives, various biogenic, optically active, materials have been made (metal sulfides, selenides; Table 1) but as far as we are aware these have not yet been tested in this application. Biotechnologically, hydrogenase-metal selenide hybrids show potential (Ran et al., 2014). Economic attractiveness is boosted by the potential fabrication of such materials from metallic or H$_2$S wastes (Nancucheo and Johnson, 2012; Murray et al., 2017b) but, given that the elements are abundant and cheap, the main driver may be waste valorization and mitigation of disposal costs, while incorporation of even a small amount of metal impurity may affect the optical property, and hence, neo-material from metallic waste may not be a useful option.

For biofuels, an unexpected ‘biotechnology’ has added value towards pine wood-derived pyrolysis oil. Very large areas of pine forest in the USA have been killed by beetles, producing very dry, porous wood. This enables the use of larger wood chips (Luo et al., 2017), reducing comminution costs and energy use. It would be interesting to apply novel biogenic catalysts to pyrolysis oil obtained from this material.

Acknowledgements

This work was funded by NERC (Grant No. NE/L014076/1 to LEM) and EPSRC (studentship to AJS) within the CDT ‘Fuel Cells and Their Fuels’.

Conflict of interest

None declared.

References

Ado, M. R., Greaves, M., and Rigby, S. P. (2017) Dynamic simulation of the toe-to-heel air injection heavy oil recovery process. Energy Fuels 31: 1276–1284.

Anon (2008) Resource efficiency KTN, material security – ensuring resource availability for the UK economy.

Anon (2014) World Energy Outlook. Paris, France: International Energy Agency (IEA). ISBN: 978 9264 12413 4.

Anon (2015) Total oil and gas. Reserves for the future. URL http://www.total.com/en/energies-expertise/oil-gas/exploration-production/strategic-sectors/heavy-oil/challenges/reserves-future. Accessed 05/05/2015.

Ashok, B. (2016) Smart bio-palladium nanomaterials synthesised by green method. J Nanomed Res 3: 1–3. https://doi.org/10.15406/jnmr.2016.03.00060

Badawi, M., Paul, J. F., Cristol, S., Payen, E., Romero, Y., Richard, F., et al. (2011) Effect of water on the stability of Mo and CoMo hydrodeoxygenation catalysts: a combined experimental and DFT study. J Catal 282: 155–164.

Baxter-Plant, V., Mikheenko, I. P., and Macaskie, L. E. (2003) Sulphate-reducing bacteria, palladium and the reductive dehalogenation of chlorinated aromatic compounds. Biodegradation 14: 83–90.

Beauregard, D. A., Yong, P., Macaskie, L. E., and Johns, M. L. (2010) Using non-invasive magnetic resonance imaging (MRI) to assess the reduction of Cr(VI) using a biofilm–palladium catalyst. Biotechnol Bioeng 107: 11–20.

Bennett, J. A., Mikheenko, I. P., Deplanche, K., Shannon, I. P., Wood, J., and Macaskie, L. E. (2013) Nanoparticles of
using novel modular bioreactors. *Environ Sci Technol* 48: 12206–12212.

Heraud, J.P., Kemp, A. and J.F. Argiller, J.F. (2011) In-situ upgrading of heavy oil and bitumen. In *Heavy Crude Oils: From Geology to Upgrading*. Alain-Yves, H. (ed.). Paris: Editions Technip, pp. 388–402. ISBN: 978-2-7108-0890-9.

Hosseinkhani, B., Sobjerg, L. S., Rotaru, A. E., Emhiazi, G., Skydstrup, T., and Meyer, R. L. (2012) Microbially supported synthesis of catalytically active bimetallic Pd-Au nanoparticles. *Biotechnol Bioeng* 109: 45–52.

Huber, G. W., Iborra, S., and Corma, A. (2006) Synthesis of transportation fuels from biomass: chemistry, catalysis and engineering. *Chem Rev* 106: 4044–4098.

Huc, Y. (2011) Geological origin of heavy oil. In *Heavy Crude Oil: From Geology to Upgrading*. Alain-Yves, H. (ed.). Paris: Editions Technip, pp. 25–31. ISBN: 978-2-7108-0890-9.

Humphrey, J. L., Plana, D., Celorio, V., Sadasivan, S., Tooze, R., Rodriguez, P., and Ferrin, D. J. (2016) Electrochemical reduction of carbon dioxide at gold-palladium core–shell nanoparticles: product distribution versus shell thickness. *ChemCatChem* 8: 952–960.

Kirubakaran, A., Jain, S., and Nema, R. K. (2009) A review on fuel cell technologies and power electronic interface. *Renew Sust Energ Rev* 13: 2430–2440.

Kraysberg, A., and Ein-Eli, Y. (2014) Review of advanced materials for proton exchange membrane fuel cells. *Energy Fuels* 28: 7303–7330.

Kulkarni, N., and Maddapur, U. (2014) Biosynthesis of metal nanoparticles: a review. *J Nanotechnol* 2014: 1–8.

Kunwar, B., Deilarni, S. D., Macaskie, L. E., Wood, J., Biller, P., and Sharma, B. K. (2017) Nanoparticles of palladium supported on bacterial biomass for hydroprocessing bio-oil from continuous hydrothermal liquefaction (NTL) of algae. *Fuel* [In press].

Lee, H., Kim, C., Yu, M. J., Ko, C. H., Jeon, J.-K., Park, S. H., et al. (2016) Catalytic hydrodeoxygenation of bio-oil model compounds over Pt/HY catalyst. *Sci Rep* 6: 28765. https://doi.org/10.1038/srep28765.

Liu, J., Zheng, Y., Hong, Z., Cai, K., Zhao, F., and Han, H. (2016) Microbial synthesis of highly dispersed PdAu alloy for enhanced electrocatalysis. *Sci Adv* 2: e1600858. http://advances.sciencemag.org/content/2/9/e1600858.

Liu, D., Li, G., Yang, F., Wang, H., Han, J., Zhu, X., and Ge, Q. (2017) Competition and cooperation of hydrogenation and deoxygenation reactions during hydrodeoxygenation of phenol on Pt (111). *J Phys Chem C* 121: 12249–12260.

Lloyd, J. R., Yong, P., and Macaskie, L. E. (1998) Enzymatic recovery of elemental palladium by using sulfate-reducing bacteria. *Appl Environ Microbiol* 64: 4607–4609.

Luo, J., Arroyo-Ramirez, L., Gorte, R. J., Tzoulaki, D., and Vlachos, D. G. (2015) Hydrodeoxygenation of HMF Over P/C in a continuous flow reactor. *AIChE J* 61: 590–597.

Luo, G., Chandler, D. S., Anjos, L. C. A., Eng, R. J., Jia, P., and Resende, F. L. P. (2017) Pyrolysis of whole wood chips and rods in a novel ablative reactor. *Fuel* 194: 229–338.

Mabbett, A. N., Sanyahunumbi, D., Yong, P., and Macaskie, L. E. (2006) Biorecovered precious metals from industrial wastes. Single step conversion of a mixed metal liquid waste to a bionorganick catalyst with environmental applications. *Environ Sci Technol* 40: 1015–1021.

Macaskie, L. E., Mkhheenko, I. P., Yong, P., Deplanche, K., Murray, A. J., Paterson-Beedle, M., et al. (2010) Today’s wastes, tomorrow’s materials for environmental protection. *Hydrometallurgy* 104: 483–487.

Mattia, D., Jones, M. D., O’Byrne, J. P., Griffiths, O. G., Owen, R. E., Sackville, E., et al. (2015) Towards carbon-neutral CO2 conversion to hydrocarbons. *ChemSusChem* 8: 4064–4072.

Mehta, V., and Cooper, J. S. (2003) Review and analysis of PEM fuel cell design and manufacturing. *J Power Sources* 114: 32–53.

Meng, H., Zeng, D., and Xie, F. (2015) Recent development of Pd-based electrocatalysts for proton exchange membrane fuel cells. *Catalysts* 5: 1221–1274.

Montano, M. D., Gregory, A. F., Lowry, V., von der Cammer, F., Blue, D. J., and Ranville, J. F. (2014) Current status and future direction for examining engineered nanoparticles in natural systems. *Environ Chem* 11: 351–366.

Murray, A. J., Omajali, J. B., Del Mastio, Y., Hart, A., Wood, J., and Macaskie, L. E. (2015) Potential for conversion of waste platinum group metals from road dust into biocatalysts for cracking heavy oil. *Adv Mat Res* 1130: 623–626.

Murray, A. J., Zhu, J., Wood, J., and Macaskie, L. E. (2017a) A novel biorefinery: biorecovery of precious metals from spent automotive catalyst leachates into new catalysts effective in metal reduction and in the hydrogenation of 2-pentene. *Mins Erg* [In press].

Murray, A. J., Roussel, J., Rolley, J., Johnson, D. B., and Macaskie, L. E. (2017b) Biosynthesis of zinc sulfide quantum dots using waste off-gas from metal bioremediation process. *RSC Adv* 7: 21484–21491.

Nam, H., Kim, C., Capareda, S. C., and Adhikan, S. (2017) Catalytic upgrading of fractionated microalgal-bio-oil (Nannochloropsis oculata) using a noble metal (Pd/C) catalyst. *Algal Res* 24: 188–198.

Nanuccheo, I., and Johnson, D. B. (2012) Selective removal of transition metals from acidic mine waters by novel consortia of acidophilic sulfidogenic bacteria. *Microbial Biotechnol* 5: 34–44.

Nduagwu, E., Sow, A., Umeozor, E., and Millington, D. (2017) Economic potentials and efficiencies of oil sands operations: processes and technologies. Calgary, Alberta, Canada: Canadian Energy Research Institute.

Negin, C., Ali, S., and Xie, Q. (2016) Applications of nanotechnology for enhancing oil recovery: a review. *Petroleum* 2: 324–333.

Nishimura, S., Ikeda, N., and Ebitani, K. (2014) Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2, 5-dimethylfuran (DMF) under atmospheric hydrogen pressure over carbon supported PdAu bimetallic catalyst. *Catal Today* 232: 89–98.

Ogi, T., Honda, R., Tamaoki, K., Saitoh, N., and Konishi, Y. (2011) Direct room temperature synthesis of a highly dispersed palladium nanoparticle catalyst and its electrical properties in a fuel cell. *Powder Technol* 205: 143–148.

Omajali, J.B. (2015) Novel bionanocatalysts for green chemistry applications. PhD Thesis. Birmingham, UK: University of Birmingham.
Omajali, J. B., Hart, A., Walker, M., Wood, J., and Macaskie, L. E. (2017) *In situ* catalytic upgrading of heavy oil using dispersed bio-nanoparticles supported on Gram-positive and Gram-negative bacteria. *Appl Catal B Environ* **203**: 807–819.

Orozco, R. L., Redwood, M. D., Yong, P., Caidelari, L., Sargent, F., and Macaskie, L. E. (2010) Towards an integrated system for bio-energy: hydrogen production by *Escherichia coli* and use of palladium-coated waste cells for electricity generation in a fuel cell. *Biotechnol Lett* **32**: 1837–1845.

Orozco, R. L. (2011) Hydrogen production from Biomass by Integrating Thermochemical and Biological Processes. PhD Thesis. Birmingham, UK: University of Birmingham.

Owen, R. E., Pawel Plucinski, P., Mattia, D., Laura Torrente-Murcianoc, L., Valeska, P., Ting, V. P., and Jones, M. D. (2016) Effect of support of Co-Na-Mo catalysts on the direct conversion of CO2 to hydrocarbons. *J CO2 Utiliz* **16**: 97–103.

Pakhare, D., and Spivey, J. (2014) A review of dry (CO2) reforming of methane over noble metal catalysts. *Chem Soc Rev* **43**: 7813–7837.

Pandey, A., Bhaskar, T., Stöcker, M., and Sukumaran, R. (eds) (2015) *Thermochemical Conversion of Biomass*. Amsterdam: Elsevier.

Prieto, G. (2017) Carbon dioxide hydrogenates into higher hydrocarbons and oxygenates: thermodynamic and kinetic bounds and progress with homogeneous and heterogeneous catalysts. *ChemSusChem* **10**: 1956–1970.

van Putten, R. J., van der Waal, J. C., de Jong, E., Rasendra, C. B., Heeres, H. J., and de Vries, J. G. (2013) Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. *Chem Rev* **113**: 1499–1597.

Rai, M., Maliszewska, I., Ingle, A., Gupta, I., and Yadav, A. (2015) Diversity of Microbes in Synthesis of Metal Nanoparticles. In *Bio-Nanoparticles: Biosynthesis and Sustainable Biotechnology Applications*. Singh, O. V. (ed). Hoboken, NJ: John Wiley & Sons, pp. 1–30.

Ran, J., Zhang, J., Yu, J., Jaroniec, M., and Qiao, S. Z. (2014) Cocatalysts based on noble metals required for reasonable activity in most semiconductor-based photocatalytic systems. *Chem Soc Rev* **43**: 7787–7812.

Reith, F., Zammit, C. M., Shar, S. S., Etschmann, B., Bottrill, R., Southam, G., et al. (2016) Biological role in the transformation of platinum-group mineral grains. *Nat Geosci* **9**: 294–298.

Rice, C. A., Urchaga, P., Pistono, A. O., McFerrin, B. W., McComb, B. T., and Hu, J. (2015) Platinum dissolution in fuel cell electrodes: enhanced degradation from surface area assessment in automotive stress tests. *J Electrochem Soc* **162**: F1175–F1180.

Rinaldi, R., and Schuth, F. (2009) Design of solid acid catalyst for the conversion of biomass. *Energy Environ Sci* **2**: 610–626.

Román-Leshkov, Y., Barrett, C. J., Liu, Z. Y., and Dumesic, J. A. (2007) Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **447**: 982–985.

Schmidt, L. D., and Dauenhauer, P. J. (2007) Hybrid routes to biofuels. *Nature* **447**: 914–915.

Shah, A., Fishwick, R., Wood, J., Leeke, G., Rigby, S., and Greaves, M. (2010) A review of novel techniques for heavy oil and bitumen extraction and upgrading. *Energy Environ Sci* **3**: 700–714.

Si, Z., Zhang, X., Wang, C., Ma, L., and Ding, R. (2017) An overview on catalytic hydrodeoxygennation of pyrolysis oil and its model compounds. *Catalysts* **7**: 169–191.

Singh, O. V. (ed) (2015) *Bio-nanoparticles: Biosynthesis and Sustainable Biotechnological Implications*. Hoboken: John Wiley and Sons.

Staffeill, I., Brett, D. J. L., Brandon, N. J., and Hawkes, A. D. (2015) *Domestic Microgeneration: Renewable and Distributed Energy Technologies*. London, UK: Routledge, Taylor & Francis.

Stern, N. (2006) *The Economics of Climate Change*. Cambridge, UK: Cambridge University Press.

Sun, X., Zhang, Y., Chen, G., and Gai, Z. (2017) Application of nanoparticles in enhanced oil recovery: a critical review of recent progress. *Energies* **10**: 245–378.

Tian, G., Daniel, R. and Xu, H. (2011) DMF – a new biofuel candidate, biofuel production: recent developments and prospects. In *Biofuel Production: Recent Developments and Prospects*. Dos Santos Bernardes, M.A. (ed.). InTech, pp. 487–520. ISBN: 978-953-307-478-8.

Tong, X., Ma, Y., and Li, Y. (2011) Biomass into chemicals: conversion of sugars to furan derivatives by catalytic processes. *Appl Catal A Gen* **385**: 1–13.

Valsami-Jones, E., and Lynch, I. (2015) How safe are nanomaterials? *Science* **350**: 388–389.

Wasylenyk, L. E., Anbar, A. D., Liermann, L. J., Mathur, R., Gordon, G. W., and Brantley, S. L. (2007) Isotope fractionation during microbial metal uptake measured by MC-ICP-MS. *J Analyst Atom Spectrum* **22**: 905–910.

Watson, M. J. (2014) Platinum group metal catalysed hydrodeoxygennation of model bio-oil compounds. *Johnson Matthey Technol Rev* **58**: 1656–1661.

Williams, A. R. (2015) Biogenic precious metal-based nanocatalysts for enhanced oxygen reduction. PhD Thesis. Birmingham, UK: University of Birmingham.

Wu, X., Zhao, F., Rahunen, N., Varcoe, J. R., Avignone-Rossa, C., Thumser, A. E., and Slade, R. C. T. (2011) A role for microbial palladium nanoparticles in extracellular electron transfer. *Ang Chemie* **123**: 447–450.

Yamaguchi, T., Tsuruda, Y., Furukawa, T., Yoshimura, E., and Suzuki, M. (2016) Synthesis of CdSe quantum dots using Fusarium oxysporum. *Materials* **9**: 855–867.

Yang, Z., Lu, L., Berard, V. F., He, Q., Kiely, C. J., Berger, B. W., and McIntosh, S. (2015) Biomanufacturing of CdS quantum dots. *Green Chem* **17**: 3775–3782.

Yong, P., Paterson-Beedle, M., Mikheenko, I. P., and Macaskie, L. E. (2007) From bio-mineralisation to fuel cells: biomannurification of Pt and Pd nanocrystals for fuel cell electrode catalyst. *Biotechnol Lett* **29**: 539–544.

Yong, P., Mikheenko, I. P., Deplanche, K., Redwood, M. D., and Macaskie, L. E. (2010) Biorefining of precious metals from wastes: an answer to manufacturing of cheap nanocatalysts for fuel cells and power generation via an integrated biorefinery? *Biotechnol Lett* **32**: 1821–1828.

Yong, P., Liu, W., Zhang, Z., Johns, M. L., and Macaskie, L. E. (2015) One step bioconversion of waste precious...
metals into *Serratia* biofilm-immobilised catalyst for Cr(VI) reduction. *Biotechnol Lett* 37: 2181–2191.

Zhang, J., Yu, J. G., Zhang, M., Li, Q., and Gong, J. R. (2011) Visible light photocatalytic H$_2$-production activity of CuS/ZnS porous nanosheets based on photoinduced interfacial charge transfer. *Nano Lett* 11: 4774–4779.

Zheng, S., Daniel, R., Xu, H., Zhang, J., Turner, D., Wyszynski, M. L., and Richards, P. (2010) Combustion and emission of 2,5-dimethylfuran in a direct-injection spark-ignition engine. *Energy Fuels* 24: 2891–2899.

Zhu, F., Kim, J., Tsao, K.-C., Zhang, J., and Yang, H. (2015) Recent development in the preparation of nanoparticles as fuel cell catalysts. *Curr Opin Chem Eng* 8: 89–97.

Zhu, J., Wood, J., Deplanche, K., Mikheenko, I. P., and Macaskie, L. E. (2016) Selective hydrogenation using palladium bioinorganic catalyst. *Appl Catal B Environ* 199: 108–122.

Zu, Y. H., Yang, P. P., Wang, J. J., Liu, X. H., Ren, J. W., Lu, G. Z., and Wang, Y. Q. (2014) Efficient production of the liquid fuel 2, 5-dimethylfuran from 5-hydroxymethylfurfural over Ru/Co$_3$O$_4$ catalyst. *Appl Catal B Environ* 146: 244–248.

**Supporting information**

Additional Supporting Information may be found online in the supporting information tab for this article:

**Fig. S1.** Major reactions occurring during bio-oil hydrodeoxygenation.

**Table S1.** Comparison of 5 wt% Pd on carbon catalyst and 5 wt% bio-Pd.