



# In-situ catalytic upgrading of heavy oil using dispersed bionanoparticles supported on gram-positive and gram-negative bacteria

Jacob B. Omajali<sup>a,1</sup>, Abarasi Hart<sup>b</sup>, Marc Walker<sup>c</sup>, Joseph Wood<sup>b</sup>, Lynne E. Macaskie<sup>a,\*</sup>

<sup>a</sup> Unit of Functional Bionanomaterials, Institute of Microbiology and Infection, School of Biosciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

<sup>b</sup> School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

<sup>c</sup> Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom

## ARTICLE INFO

### Article history:

Received 9 July 2016

Received in revised form 22 October 2016

Accepted 26 October 2016

Available online 28 October 2016

### Keywords:

Bio-nanoparticles

Coking

Heavy oil

Upgrading

Viscosity

## ABSTRACT

With the continuous depletion of global oil reserves, unconventional alternative oil resources like heavy oil and bitumen have become increasingly attractive. This study investigates the use of bimetallic bionanoparticles (bio-NPs), a potential alternative to commercial catalysts in heavy oil upgrading. The bio-NPs were made by sequential reduction of precious metal (Pd and Pt) ions with hydrogen as the electron donor at 5 wt% and 20 wt% metal loading using bacterial (*Desulfovibrio desulfuricans* and *Bacillus benzeovorans*) cells as support. The bio-NPs were characterized using transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Results of the catalytic upgrading of a feed heavy oil show that the bimetallic bio-NPs produced an increment of  $\sim 2^\circ$  in API (American Petroleum Institute) gravity (*i.e.*  $\sim 9.1^\circ$ ) better than monometallic bio-NPs ( $\sim 7.6^\circ$ ) on average while the API gravity using thermal upgrading was lower ( $6.3^\circ$ ). The API gravity of a commercial Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was  $11.1^\circ$ . However, more coking was produced using the commercial catalyst than with the bio-NPs. The extent of viscosity reduction was: 98.7% (thermal), 99.2% (bio-NPs) and 99.6% (Ni-Mo/Al<sub>2</sub>O<sub>3</sub>) below 1031 mPa s for the feed heavy oil reference (baseline). The potential advantage of using bio-NPs is that the precious metals can be sourced cheaply from waste streams, which could serve as a potential platform for the green synthesis of catalytically active materials using bacteria for *in-situ* catalytic upgrading of heavy oils.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

The world's energy consumption has been projected by the US Energy Information Administration (EIA) to reach approximately  $8.6 \times 10^6$  joules per annum by 2040 [1]. Oil, the world's leading fuel source, supports 32% of global energy consumption, which increased by 2.3% in 2013 [2]. It has been reported that most of the future energy demand will be dominated (95%) by the non-OECD (non-Organization for Economic Cooperation and Development) countries where demand is driven by strong economic growth [2]. As consumption of world energy continues to rise, fossil fuels are

expected to remain the predominant sources of supply, satisfying about 80% of global needs [3] despite major concerns about environmental consequences.

A consequence of the increase in demand and consumption of light crude oil is a global decline in reserves and supply. Therefore, there is a need to supplement short-and-long term needs through less conventional oil resources, like heavy oil and bitumen, whose current production stands at 2–3% (2 million barrels/day, Mb/d) of global supply, with output predicted to reach 7 Mb/d in 2030 [4]. Large deposits of heavy oil and bitumen occur in locations such as Canada (the Alberta Basin) and Venezuela (the Orinoco Belt), which together comprise about 80% of world's remaining oil reserves [5]. Substantial deposits of heavy oil are also located in the Middle East, although owing to its vast light oil reserves, documentation of these reserves tends to be incomplete [6]. Exploitation of these heavy oils forms a major challenge due to their inherent properties *i.e.* high viscosity, low hydrogen content, presence of high molecular weight compounds (resins and asphaltenes) and rich-

\* Corresponding author.

E-mail address: [L.E.Macaskie@bham.ac.uk](mailto:L.E.Macaskie@bham.ac.uk) (L.E. Macaskie).

<sup>1</sup> Current address: Department of Biological Sciences, Faculty of Sciences, Thompson Rivers University, 900 McGill Road, V2C 0C8, Kamloops, British Columbia, Canada.

ness in hetero-elements (nitrogen, sulfur and oxygen), as well as high metal contents, especially nickel and vanadium. These properties of heavy oil are thought to be the consequence of subsurface water flows and also microbial activities within a shallow depth of low temperature environments as the oil accumulates over time [7]. Microbial processes introduce changes, especially in the light end of the oil, specifically the hydrocarbon molecules (oxidation of C<sub>6+</sub> components), leading to fluids characterized by high contents of heavy molecules rich in sulfur, nitrogen, oxygen and metals but with decreased API gravity and increased viscosity and acidity [7,8]. Other challenges include environmental concerns such as water management, specifically production water for steam generation, and the control of greenhouse gases and other pollutants during the extra refining required for heavy oils [8].

*In-situ* upgrading technologies such as catalytic thermal conversions in the presence of hydrogen, hydrogen donor solvents and the use of microbial communities generating methane (biodegradation of C<sub>2</sub>–C<sub>5</sub> hydrocarbons) are currently in use but not yet at industrial scale [9] coupled with other emerging technologies [10] which all have environmental advantages because of their ability to trap most of the pollutants generated from heavy oil in the reservoir well. They also reduce the need for surface upgrading, which results in the cleaner production of lower viscosity oil, which is more easily transported without the use of diluents. The THAI-CAPRI (Toe-to-Heel Air Injection coupled with Catalytic Upgrading Process *In-situ*) technology combines thermally enhanced oil recovery with down-hole *in-situ* catalytic upgrading of heavy oil into light fractions [11–13]. This technology, shown for the *in-situ* catalytic upgrading of heavy oil in the presence of steam, hydrogen and methane has demonstrated significant improvements over non-catalytic thermal processes [17].

However commercial cracking catalysts such as noble metals on chemical supports are prohibitively expensive for a large scale once-through technology; an alternative source of cheaper catalyst is therefore essential. One of the options is to utilize regenerated catalysts from treated oils as reported previously [12] which could reduce catalyst cost but the disadvantage is in their low activity. The emergent use of bacteria as new systems for catalyst manufacture [14] provides alternative sources for patterning of metallic nanoparticles (NPs) called bio-nanoparticles (bio-NPs) which are held supported on the cells as micron-sized carriers. Advantages of using bacteria include scalability of NP synthesis, non-toxic reducing agents and supports when compared to strong toxic chemical reductants used in commercial systems and as remediation platforms for precious metal-containing wastes [15]. In addition, the various functional groups (amine, carboxyl, hydroxyl, sulfuryl and phosphoryl) found on bacterial cell surfaces, tend to control and stabilize particle growth [16] via 'bio-patterning' as compared to the use of surfactants and capping agents which introduce artefacts into commercial catalysts. In some cases metallic bio-NPs biorefined from wastes can have higher activity than monometallic bio-NPs [17]. When biomanufactured from an otherwise discarded source such as road dust the concept of a 'once-through' loss into the environment becomes conceptually and economically acceptable and this forms the goal of this investigation. This is because platinum group metals (PGMs – Pd, Pt and Ru) recovered from secondary sources can be bio-converted using bacterial cells (obtainable as wastes from fermentation process and industrial enzyme and drug production) into useful PGM catalysts with various industrial and environmental applications [18]. Recovery from waste streams would reduce the cost of catalyst production and the attendant environmental concerns, especially with regards to the high energy demands required in conventional mining technology. The quantity of PGMs recovered from wastes and through bio-conversion by bacterial cells are usually below current economic standard values but this is regarded as an environmentally sus-

tainable approach with the possibility of future improvement in the process *via* waste upgrading [19]. In addition, the economic reality of using PGM catalysts in catalytic conversion has been highlighted previously [20] and by the authors in a recent paper [21].

The use of *Desulfovibrio desulfuricans* (Gram-negative) and *Bacillus* sp. (Gram-positive) bacteria has been widely examined in the context of bio-NPs catalyst production [22–24]. However, the production of hydrogen sulfide (normally a strong catalyst poison) by the former, coupled with the problem of production at scale, would make *Bacillus* more preferable but on the other hand, sulfidation of metals by sulfur often leads to activation of catalyst [25]. In spite of various reports about the poisoning effects of sulfur-containing species on precious metal catalysts [26,27], the adsorption of sulfur onto the surface of heterogeneous metal catalyst (including PGM catalysts) at very low concentrations was reported to influence various catalytic properties such as promotion of activity and enhancement of selectivity [27,28] and sometimes prolongs the life-span of PGM catalysts [26]. Interestingly, recent work [29,30] has shown *via* high resolution transmission electron microscopy and elemental mapping the ability of palladium nanoparticles to co-localize with bacterial sulfhydryl groups, an effect which may result in partial poisoning or elongation of the life-span of a PGM catalyst. *Bacillus* spp. are produced in large quantities *via* e.g. the commercial manufacturing of enzymes and hence waste biomass could provide a sustainable source for the synthesis of new catalytic materials.

Various precious metals (e.g. Pd, Pt and Au) have been reductively precipitated into bio-NPs by various strains of Gram-negative and Gram-positive bacteria and utilized in a range of catalytic reactions of industrial importance, with activities comparable to commercial catalysts [31,32]. Some of these important reactions of bio-NPs made *via* reduction at the expense of either hydrogen or formate include the reductive dechlorination of polychlorinated biphenyls [33,34], chromium VI reduction [15,35] and dehalogenation of dichlofenac [36]. Similar synthetic approaches have been used to produce bio-NPs with relevance in the pharmaceutical industries particularly in Heck-coupling and Suzuki reactions [32,24] while Zhu et al. [37] demonstrated their applications in selective hydrogenation of 2-pentyne and soy bean oil. In addition, bio-NPs synthesized from the plant, *Arabidopsis* was used as a heterogeneous catalyst in a Suzuki reaction [38] while bio-NPs made from fungal mycelia degraded 4-nitrophenol [39]. More recently, a silver bio-NP nanocluster with luminescent properties was developed with the ability to bind to tumor cells [40]. Meanwhile there are no reports on the use of bimetallic bio-NPs for *in-situ* catalytic upgrading of heavy oil prior to this study; metallic mixtures would be the unavoidable characteristic of a bio-catalyst made from a waste with little or no metal selectivity in the biorecovery step [14]. It was reported that bimetallic bio-NPs are more catalytically active in various reactions than their monometallic counterparts [36], attributed to the synergistic effects of the two metals, which has also been shown in chemical synthesis [41]. For example, a bio-Pd/Au core-shell bimetallic catalyst synthesized using *E-coli* was shown to be comparable to a commercial catalyst in the selective oxidation of benzyl alcohol [42] while De Corte et al. [36] synthesized Pd/Au bimetallic using *S. oneidensis* MR-1 to make a better dechlorination catalyst of dichlofenac than monometallic bio-Pd.

This study evaluates the potential for use of bio-NPs for the upgrading of heavy oil and compares the efficacy of the bio-NPs synthesised on *Desulfovibrio desulfuricans* (bio-Pd<sub>Dd</sub>) with counterparts synthesised on *Bacillus benzeovorans* (bio-Pd<sub>Bb</sub>). Other catalytic tests have shown some strain-dependent differences using monometallic NPs following differences shown between Gram-negative and Gram-positive supports [23]. Hence, the second aim, prerequisite to the biomanufacturing of active bimetallic Pd/Pt NPs from wastes [43] is to compare bimetallic bio-NPs of two

Download English Version:

<https://daneshyari.com/en/article/6454582>

Download Persian Version:

<https://daneshyari.com/article/6454582>

[Daneshyari.com](https://daneshyari.com)