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Comparison of the effects of dispersed noble metal (Pd) biomass supported catalysts with typical hydrogenation (Pd/C, Pd/Al_2O_3) and hydrotreatment catalysts (CoMo/Al_2O_3) 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/Al_2O_3 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/Al_2O_3, Pd/C, Al_2O_3 and Co–Mo/Al_2O_3. 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 (Al_2O_3), 9.55 (Pd/Al_2O_3), 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/Al_2O_3 catalysts, which could greatly enhance catalyst survivability in the field.

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/Al_2O_3 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 H_2S 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 CO_2 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/Al_2O_3) 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,