In situ catalytic upgrading of heavy oil using a pelletized Ni-Mo/Al₂O₃ catalyst in the THAI process

Abarasi Hart a,*, Joseph Wood a,**, Malcolm Greaves b

a School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
b Department of Chemical Engineering, University of Bath, Claverton Down, Bath, BA2 7AY, UK

A R T I C L E   I N F O

Keywords:
Heavy oil
THAI process
In situ upgrading
Pelletized catalyst

A B S T R A C T

Heavy oil and bitumen are difficult crudes to extract and upgrade, with additional transport and refining costs, because of their high viscosity, low API gravity, high asphaltenes, metals (V, Ni), and heteroatoms (N, S). Combining Toe-to-Heel Air Injection (THAI) with its catalytic add-on (CAPRI), a pelletized catalyst is incorporated along the outside of the horizontal producer well for in situ catalytic upgrading. This downhole upgrading process is one means to produce and partially upgrade heavy oil and bitumen with a reduced environmental footprint. In this study, the effectiveness of pelletized hydrodesulfurisation (HDS) Ni-Mo/Al₂O₃ catalyst for downhole catalytic upgrading was investigated at 350–425 °C, 20 bar, and 9 h⁻¹ space velocity. The additional upgrading due to the presence of the catalyst was evaluated in terms of API gravity, viscosity, boiling point distribution, and sulfur and metals removals, before and after the experiment. The results indicate that the viscosity of the upgraded oil reduced by 1.7, 3, and 5 times less than the feed oil (0.49 Pa s) depending on the reaction temperature in the range 350–425 °C. The average increase in API gravity was approximately 2 to 5° while the gasoline yield showed an improvement of 2.5–13 wt.% above that of the original oil. There was also a modest reduction in the sulfur and metals (Ni + V) content of 2–8% and 1.3–9.2% (Ni + V), respectively. However, a possible limiting factor of the process was that rapid catalyst deactivation occurred due to coking.

1. Introduction

Conventional light crude oils have high mobility due to their low viscosity, usually less than 5 cP at reservoirs conditions. On the other hand, unconventional heavy crudes and bitumen have little or no mobility in the reservoir, because of their very high viscosity, which can be several orders of magnitude. Thus, in comparison, heavy crudes are much more difficult to produce and are also more costly to recover and refine. This is chiefly because of their high viscosity, low API gravity, high asphaltenes, heteroatom, and heavy metals content. Heavy reserves are about 4–6 trillion barrels and are therefore of a similar order, or greater, than conventional light oil (Zhang et al., 2012). Canadian production of heavy crude and bitumen has risen to around 2 million Barrels of Oil Per Day (BOPD), Venezuelan extra heavy crude is around 1 million BOPD and long running heavy oil production is approximately 600,000 BOPD, for this to increase in the future will require more advanced production strategies, including advanced Enhanced Oil Recovery (EOR) processes like THAI. Not least, the low quality of heavy oils can be significantly improved via in situ upgrading techniques, using the reservoir as a ‘free’ reactor.

Toe-to-Heel Air Injection (THAI) and its catalytic variant CAPRI, are advanced EOR processes for the recovery and downhole upgrading of heavy oil and bitumen (Greaves and Xia, 2004; Greaves et al., 2012; Xia et al., 2002). The THAI-CAPRI process integrates in situ combustion technology and a horizontal producer well for producing heavy oil, which can then be extended to include pelletized catalytic reactor along the outside of the horizontal well. The latter enables in situ catalytic cracking of the already partially upgraded THAI oil (by thermal cracking), all in the same reservoir arrangement. Xia and Greaves (2001a,b) reported the 3-D physical model studies of catalytic upgrading of Wolf lake heavy oil using THAI-CAPRI. They found that thermal upgrading alone (THAI) achieved about 9° points increase in the API gravity of the produced oil, while the API gravity of the produced oil by incorporating pelletized catalytic CAPRI section increased it by a further 3 to 7° API, with up to 85% recovery of original oil in place (OOIP). This result indicates that it may be possible to design a one-step process for the
conversion of heavy oil to ‘light oil’, using the reservoir as a reactor. As a follow up to this, Shah et al. (2011) reported on the detailed experimental optimization of the THAI-CAPRI process for in situ heavy oil and bitumen recovery and upgrading. They reported that the catalyst deactivated because of coke deposition at high reaction temperature. Thus, reduction in catalyst activity due to coking remains a major challenge to the operability and economics of the THAI-CAPRI process. Hence, the present study evaluates the use of commercial pelleted Ni-Mo/Al₂O₃ catalyst in a THAI-CAPRI process model, to gain more insight into the extent of coke formation and degree of in situ upgrading achievable. Kim et al. (1997) have studied upgrading of bitumen-derived heavy oil using Ni-Mo/Al₂O₃ catalyst over the temperature range 625–685 K, and LHSV of 0.14–0.80 h⁻¹, at 13.7 MPa. Catalyst deactivation was evaluated by measuring the time on-stream change of the upgraded oil API gravity. The API gravity decreased from 16° to 13.5° as the time-on-stream increased from 0 to 500 h. They found that the removal of nitrogen increased remarkably with increasing temperature and residence time, but occurred only slowly when using a Ni-Mo/Al₂O₃ catalyst.

The idea of simultaneous recovering and upgrading heavy crude oil in the reservoir, using in situ combustion and catalytic cracking, could have profound economic and environmental benefits, if it can be successfully applied. This is because the thermal energy generated is used to enhance mobility of the crude oil, and at the same time it creates conditions that can enable catalytic cracking reactions to take place in situ to galvanise downhole upgrading (Pereira-Almao, 2012). The reservoir thus serves as a reactor for in situ catalytic reactions, which could drastically decrease the investment required for surface upgrading facilities. However, installing a THAI-CAPRI ‘reactor’ in the reservoir is technically complex, requiring the pelleted catalyst to be ‘gravel packed’ around the outside of the horizontal producer well. The use of fixed-bed technology limits the type of feed and severity of operation, since hydrocarbon and metal deposition will rapidly deactivate the catalyst (Hart et al., 2013; Rezaei et al., 2012; Shah et al., 2011; Fukuyama et al., 2004). The effectiveness of pelleted catalysts under situ reservoir conditions and the extent of coking expected have not been thoroughly evaluated so far.

2. Method and materials

2.1. Feedstock and catalysts

The heavy crude oil used in this study was supplied by Petrobank Energy and Resources Ltd. (now Touchstone Exploration Inc.), from their WHITESANDS THAI Pilot trial at Christina Lake near Conklin, Alberta, Canada. The properties of the feedstock are presented in Table 1.

The catalyst used in this study is a commercial hydrodesulfurisation (HDS) catalyst Ni-Mo/Al₂O₃ quadra-lobed shaped extrudate (Akzo Nobel, The Netherlands). The composition and microstructure characteristics of the catalysts such as specific surface area, pore volume, and pore diameter were determined by Brunauer – Emmett – Teller (BET) technique are presented in Table 2.

2.2. Experimental apparatus

The experiments were performed in a 10 mm ID micro tubular CAPRI reactor assembly, representing a radial section of the annular layer of catalyst surrounding the horizontal production well in the THAI-CAPRI process.

The feed oil and gas (N₂) are mixed together in a separate chamber and then sent to the CAPRI reactor, flowing from top to bottom of the catalyst bed. 3 mm spherical glass beads are placed above and below the catalytic bed to promote radial spreading and gas-oil disengagement. The reactor tube is placed inside a furnace so that the catalyst bed can be heated to reservoir process temperature. The upgraded products, which include light oil and gases were passed to a gas-liquid separator, the flashed gas stream (C₁₂-C₄ light hydrocarbon gases, CO₂, CO, H₂S, and H₂) leaves the gas-liquid separator and is either vented or sent to the refinery gas analyser (RGA) gas chromatography (Agilent 7890A GC) for composition analysis. The main operating conditions of the experiments conducted in this study are listed in Table 3. Further details can be found in Shah et al. (2011), Hart et al. (2013) and Hart (2014).

2.3. Product analysis

The API gravity and viscosity of the produced oil were analysed using a digital Anton Paar DMA 35 portable density meter and Bohlin CVO 50 NF rheometer (Malvern Instruments Ltd, United Kingdom), respectively. The gas products were analysed by an Agilent 7890A gas chromatograph to determine the weight percentage of H₂, CO, CO₂, and C₁-C₅ hydrocarbons. Simulated distillation was performed by gas chromatograph according to ASTM D2887 to analyse the collected liquid samples. A thermogravimetric analyser (TGA) was used to determine amount of coke deposited on the catalyst. Further details of the instrumental techniques used have been reported elsewhere (Hart et al., 2013). The asphaltene content before and after upgrading reactions was determined using n-C₇H₁₆ precipitation in accordance with ASTM D200, and further details can be found in Hart et al. (2014).
3. Result and discussion

In the model CAPRI reactor, the mixture of the gas and vaporised oil flows through the catalyst bed, in which catalytic cracking of the heavier hydrocarbon molecules occurs. This carbon rejection cracking process produces upgraded light oil, but also significant amounts of solid coke, which is deposited on the catalyst surface. The experimental results are presented below:

3.1. Mass balance

The mass balances of the three products (i.e., upgraded oil, gas, and coke) are reported as percentages of the amount heavy oil fed into the CAPRI reactor, which are shown in Table 4. The yield of the products was calculated using the following equations:

\[
\text{Yield (wt.\%)} = \frac{W_i}{W_{\text{Feed}}} \times 100
\]  

Gas (wt. %) = 100 – liquid yield (wt. %) – coke yield (wt. %)

The mass of gas evolved during the upgrading reactions was calculated as the remainder of the mass of the heavy oil fed minus the masses of upgraded oil collected and deposits in reactor. The coke content of the catalyst was determined by thermogravimetric analysis (TGA), after the reactor had been weighed.

Clearly, the coke yield increases while that of the upgraded oil decreases as the reaction temperature increases from 350 to 425 °C. The corresponding increase in gas and coke yield as the reaction temperature increases contributed to the lower yield of upgraded oil at 425 °C. This is attributed to the increased rate of catalytic cracking reaction with temperature. Krumm et al. (2011) and Hart et al. (2013) reported similar trends in the yields of gas, liquid, and coke in catalytic cracking upgrading of heavy oil.

3.2. API gravity and viscosity

The API gravity and viscosity of the produced oil are basic physical benchmarks used in ascertaining the extent of upgrading. The API gravity and viscosity of the produced oil as a function of time-on-stream at 20 bar pressure, 1 mL min⁻¹ oil flow rate, and 350, 400 and 425 °C reaction temperatures are presented in Fig. 1 (a), (b) and (c), respectively. It is clear from Fig. 1a that the API gravity of the produced oil increased by approximately 5° API as the reaction temperature increased from 350 to 425 °C. At 425 °C, the API gravity of the upgraded oil samples using Ni-Mo/Al₂O₃ catalysts increased from 19 to 21° during the initial part of the experiment, but then decreased drastically to about 16° after 200 min, remaining there for the rest of the experiment. It is evident therefore that the API gravity of the produced oil decreases progressively with time-on-stream at all investigated temperatures. This decrease in catalyst activity is attributed to deposition of coke, due to cracking of large hydrocarbon molecules, as also observed by Kim et al. (1997), Xia and Greaves (2001a,b) and Hart et al. (2015).

The viscosity of the produced upgraded oil samples reduced significantly as the reaction temperature increased (Fig. 1b,c). The viscosity decreased from 0.5 Pa s for the feed oil to 0.11 Pa s (350 °C), 0.085 Pa s (400 °C) and 0.022 Pa s (425 °C) during the early hours of the reaction. From 400 min the viscosity remained around 0.4 Pa s (350 °C), 0.2 Pa s (400 °C), and 0.1 Pa s (425 °C) for the rest of the experiment. Notably, the observation of viscosity is a mirror trend of the API gravity with time-on-stream (Fig. 1a,b) and as a function of reaction temperature (Fig. 1c). A similar trend of observation was reported by Hart et al. (2013) in the application of pelletized Co-Mo/Al₂O₃ for heavy oil upgrading using CAPRI process (a detailed comparison is presented in section 3.7). Hart (2014) reported that the average increment in API gravity and viscosity for upgraded oil by thermal cracking alone using 3 mm spherical glass beads for the same feedstock and experimental conditions were 0.7°, 1.1° and 1.7° points and 0.4, 0.3, and 0.2 Pa s, at 350, 400 and 425 °C, respectively. This represents an additional increment of 1.3–4° API and 0.3 to 0.18 Pa s auxiliary decrease in viscosities of upgraded oils upon the incorporation of pelletized Ni-Mo/Al₂O₃ catalyst as the reaction temperature was increased from 350 to 425 °C relative to upgraded oil on by

![Fig. 1.](image-url)
As the reaction temperature increases, the average API gravity of the upgraded oil sample increased while its viscosity decreased in like manner (Fig. 1c). The viscosity of the produced oil at 425 °C is within acceptable pipeline transport range of 0.2 Pa s (Hart, 2013). This indicates that as the reaction temperature increased the heavy molecules cracking increased likewise catalytic cracking by pelletized Ni-Mo/Al₂O₃ catalyst. This improvement occurs as a result of bond scission reactions due to thermal and catalytic cracking, hydrogen-transfer reactions, ring opening, ring closure, desulphurisation, demetallisation, and denitrogenation; cleavage of C–C, C–S, C–N, and C=C bonds (Marafi et al., 2008; Hart, 2014). The cleavage of these bonds is facilitated by the acid sites of the alumina support of the Ni-Mo/Al₂O₃ catalyst (see Table 2), while the metals (i.e., Ni and Mo) promote hydrogen-transfer reactions (Hart et al., 2013). The bond cleavages led to molecular weight reduction in the produced oil which explains the reduction of the viscosity and API gravity increase. However, high reaction temperatures increase the rate of these cracking reactions, and break the chemical structure of the macromolecules like resins and asphaltenes to light hydrocarbons such as saturates and aromatics (Hasan et al., 2010; Chen et al., 2010).

3.3. True boiling point (TBP) distribution

One of the main purposes of upgrading the heavy crude oil is to make it easily refined by conventional refinery methods, and also increase the amount of more valuable light distillates. Fig. 2 shows the results of the simulated distillation of the feed oil and produced upgraded oils using Ni-Mo/Al₂O₃ catalyst for CAPRI at 350, 400, and 425 °C. The TBP curve is a plot of cumulative percentage amount distilled against temperature. The feed oil is characterised by low yields of distillates due to its low API gravity and high content of macromolecules compared to the upgraded oils. It is clear that the curves of the produced oils at 350, 400 and 425 °C reaction temperature shifted to the left at a given temperature compared to that of the feed oil, implying that the produced oil contained light end hydrocarbons with lower boiling point than the feed oil.

For example, at a boiling point (BP) of 200 °C the cumulative percentage yield for reaction temperatures 350, 400, and 425 °C were 15 vol.%, 22 vol.% and 23 vol.% respectively, relative to the feed oil of 10 vol.%. At BP of 200 °C, thermally upgraded oil at the same temperatures were 10 vol.%, 16 vol.% and 18 vol.% respectively (Hart, 2014). This shows a further improvement towards naphtha and middle distillates fraction upon the incorporation catalytic upgrading process. Conversely, the same 10 vol.% yield of distillate at 200 °C for the feed oil was obtained at lower temperatures about 165–170 °C for the produced upgraded oils depending on the reaction temperature, which explains the shift of curves to the left. This result is consistent with the reported result by Fujimoto et al. (2009) on the recovery of lighter oil by cracking heavy oil using zirconia-alumina-iron oxide catalyst in a steam environment. This is indicative of catalytic upgrading occurrence because the large hydrocarbon components have been broken into lighter molecules which resulted in the high yield of distillates, high API gravity and lower viscosity observed in the produced oil relative to the feed oil.

3.4. Asphaltenes, sulfur and metals content

The asphaltene content of the heavy oil contributes very significantly to its high viscosity, low API gravity and low fuel distillate fractions. The sulfur and metals impurities are mostly concentrated in the macromolecules of the resins and asphaltenes. Hence, their reduction is an essential goal of in situ catalytic upgrading, in order to improve API gravity and viscosity of the oil. Table 5 shows the asphaltene, sulfur and metals content of the feed and upgraded oils.

Clearly, as the reaction temperature increases from 350 to 425 °C the conversion of asphaltene to low molecular weight components was favoured. The asphaltene content decreased respectively by 29% (350 °C), 36.7% (400 °C), and 43.4% (425 °C) to 11.3 wt.% contained in the feed oil. This reduction could have contributed to the increased API gravity and decreased viscosity of produced upgraded oils shown in Fig. 1a–c.

At reaction temperature of 350 °C the sulfur and (Ni + V) metals removal was small compared to 400 °C in which 5.3% (sulfur) and 3% (Ni + V metals) decrease was observed. Whilst at 425 °C 7.9% (sulfur) and 9.2% (Ni + V metals) removal was observed for the collected upgraded oil sample. The removal of sulfur and metals is consistent with the conversion of the asphaltene. This shows that reaction temperature plays a significant role in cracking the macromolecules such as resins and asphaltenes that incorporate the sulfur and metals in order for them to be removed. Also, the pore diameter of Ni-Mo/Al₂O₃ catalyst (34 nm) caused diffusion limitation and restricted access of the macromolecules to the active sites, thereby inhibiting their cracking. However, the low removal of sulfur and metals observed at 350 °C can be attributed to visbreaking as the major means of upgrading. A similar observation has been reported for pelletized Co-Mo/Al₂O₃ catalyst at the same experimental conditions (Hart et al., 2013). However, significant amount of iron was removed after catalytic upgrading with Ni-Mo/Al₂O₃ catalyst. It has been reported that the removed metals are mostly deposited on the catalyst as metallic sulphides (e.g. M₂Sₓ, where; M is V, Ni, Fe, etc.) (Rezaei et al., 2012; Leyva et al., 2007). In the light of this, the conversion of high-boiling species into low-boiling fractions led to boiling point shift to the left of the feed oil TBP curve due to the following reactions:

- cracking of C-C bonds in the heavy oil
- cracking of C-S and C-N (i.e., C-hetero-atoms bonds) and
- metals removal

Gray (1994) has pointed out that the decreased heteroatom content of the produced oil could also contribute to its low-boiling range compared

Table 5: Asphaltenes, sulfur and metals content before and after reactions.

| Impurities | Heavy oil | After reaction (350 °C) | After reaction (400 °C) | After reaction (425 °C) |
|------------|-----------|------------------------|------------------------|------------------------|
| Asphaltenes (wt.%) | 11.30 | 8.02 | 7.15 | 6.40 |
| Sulfur (wt.%) | 3.8 | 3.7 | 3.6 | 3.5 |
| Nickel (ppm) | 56 | 56 | 54 | 51 |
| Vanadium (ppm) | 150 | 148 | 146 | 136 |
| Ni + V (ppm) | 206 | 202 | 200 | 187 |
| Iron (ppm) | 36 | 18 | 5 | 3 |

*Note Sulfur and metals content was performed by Intertek Laboratories Sunbury Technology Centre, UK, using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).
to the original heavy oil. While some of the sulfur is removed through sulfidation of catalyst and lost in the produced gas. The heavy metals form a considerable part of the coke deposited, but this is locked in the reservoir.

3.5. Spent catalyst coke content

The cross section of coked pelletized Ni-Mo/Al₂O₃ catalyst bed in the reactor after upgrading reactions is shown in Fig. 3. It can be observed that the catalyst pellets are now agglomerated because of deposited asphaltenes and coke. It is very obvious that this causes serious plugging of the catalyst bed.

The TGA of the spent catalysts was carried out using about 10.4 mg samples weight of recovered Ni-Mo/Al₂O₃ catalyst after upgrading reactions to determine their coke content. The coke content of the spent catalyst is an indicator of the extent of deactivation due to coke deposition from cracked hydrocarbons during the 25 h time-on-stream operation. Fig. 4 shows the thermograms of weight loss curves (TGA) as a function of ramp temperature for the recovered Ni-Mo/Al₂O₃ catalyst after reaction is presented. Also shown in Fig. 4, is the derivative of the weight loss curve (DTG) during the thermal burn-off in air atmosphere in order to interpret the different regions. It has been reported that the burn-off observed above 600 °C, the deposits on the spent catalysts are defined as coke (Barman et al., 1997; Douda et al., 2004; Trejo et al., 2010; Alvarez et al., 2011; Murugan et al., 2011; Hart et al., 2013).

The coke content of spent Ni-Mo/Al₂O₃ catalyst increased in the order 37.2, 46.5, and 48.9 wt.%, respectively for 25 h time-on-stream operation as the reaction temperature increase from 350 to 425 °C. The deposited coke from cracking heavy hydrocarbon molecules greatly impacted on the pelleted catalyst activity with time-on-stream. Its impact can be seen in the sharp decrease in API gravity and increased viscosity with time-on-stream at 200 min, due to initial coke deposited on the catalyst surface (Fig. 1a–b). It can also be observed in Fig. 4 that the coke formed at 350 °C started burn-off at lower temperature compared to coke deposited on the spent catalysts at 400 °C and 425 °C. Beside catalyst and reactor fouling and clogging, coke build-up on the catalyst bed is one of the main routes for deactivation; shorten lifespan, pressure drop increase and possible shutdown (Ali et al., 2006).

The nitrogen sorption isotherm of the catalyst before and after reaction at 425 °C is shown in Fig. 5. While the hysteresis loop of the fresh catalyst indicates the meso-pore structure of type IV, the spent catalyst shows massive deposits leading to a huge hysteresis loop.

The remarkably lower volume of nitrogen sorption of the spent catalyst relative to its fresh counterpart at the same relative pressure, represent a loss in porosity and surface area. About 99.6% of the 195 m² g⁻¹ surface area (fresh Ni-Mo/Al₂O₃) has been lost due to asphaltene and coke deposits, which reafirms the coke content of the spent catalyst presented in Fig. 4 for reaction at 425 °C. This could have altered the catalyst microstructure, textural properties and activity. Abi-Halabi et al. (1991) stated that the coke deposit starts from smaller pores while narrowing large pores throat, before eventually plugging them. A similar observation has been reported in the literature (Ancheyta et al., 2002; Rana et al., 2008; Hart et al., 2013).

The above trend is in line with the published work of Hart et al. (2013) and Meng et al. (2007) on coking behaviour and catalyst deactivation for catalytic pyrolysis of heavy oil. The high content of coke in the spent catalyst at 425 °C compared to 350 and 400 °C shows that the deactivation rate due to coke deposition is dominant at high temperatures. However, considering the level of upgrading obtained at 425 °C (Figs. 1–2), a trade-off is required between upgrading and coke formation. Alternatively, other means of decreasing coke formation while maintaining the level of upgrading at 425 °C should be considered in future investigation. Nonetheless, Shah et al. (2011) found that 425 °C is

---

Fig. 3. Photograph of coked Ni-Mo/Al₂O₃ catalyst of the CAPRI reactor cross-section after upgrading at temperature 425 °C, gas-to-oil ratio 500 mL mL⁻¹, and pressure 20 barg (Reactor tube internal diameter 10 mm).

Fig. 4. Thermogram of spent Ni-Mo/Al₂O₃ catalyst after reaction at reaction temperatures of 350, 400, and 425 °C, pressure 20 bar, 500 mL min⁻¹ gas flow, and 1 mL min⁻¹ oil flow rate conditions.
Eventually catalyst bed blockage leading to shut down.

...continuous deposition of coke and macromolecules such as asphaltenes resulting in constriction and blockage (Hart et al., 2013; 2015). The activity was caused by coke and metal deposited in the pelletized catalyst (Zhao et al., 2001; Meng et al., 2007; Ming et al., 2007). The deposited condensation reactions leading to increase of coke content and coke yield components becomes dominant and subsequently promote their dimerisation or oligomerisation reactions, and dehydrogenation (i.e., the aliphatic structures to form aromatics, polymerisation and condensation cracking of side chains from aromatic hydrocarbons, condensation of...

3.6. Produced gas composition

The produced gas composition is presented in Table 6. The gas composition for thermal cracking alone at 425 °C has been reported in Hart et al. (2013). It can be observed that the amount of gas produced increases as the reaction temperature increases from 400 to 425 °C. Since the aliphatic hydrocarbon gases have higher hydrogen-to-carbon ratio, it implies that their high production will lead to a corresponding carbon rejection in order to balance the elemental hydrocarbon distribution between the gas, coke and upgraded oil phases. The increased aliphatic hydrocarbon gas and hydrogen as temperature increased from 400 to 425 °C correlate with coke yield with reaction temperature reported in section 3.6.

The hydrogen in the gas is a product from cracking of hydrocarbons, ring opening and dehydrogenation of aliphatic hydrocarbons to olefins, which can be seen in Table 6. With the aid of the Ni-Mo/Al2O3 catalyst, this hydrogen gas could support hydrogen-transfer reactions if the reaction pressure at a given temperature is favourable. Also produced is hydrogen sulphide which is an indication of hydrodesulphurisation (HDS) reaction aided by the in situ generated hydrogen from the hydrocarbons by the Ni and Mo metals on the catalyst. The HDS increases with temperature rise. Consequently, during the THAI-CAPRI process these gases could enhance the pressure within the reservoir and also promote miscible displacement at the formation matrix which would facilitate recovery.

3.7. Ni-Mo versus Co-Mo on alumina support

Alumina (Al2O3) supported molybdenum oxide catalysts promoted with nickel, cobalt, or tungsten are mostly used in the refinery for HDS and hydrodemetallisation (HDM). In our previous study, Co-Mo/Al2O3 catalyst was reported (Hart et al., 2013). Both catalysts shared the same shape, similar pellet length and diameter. However, Co-Mo catalyst has larger surface area and bigger pore diameter compared to that of the Ni-Mo catalyst (214.1 vs. 195.4 m2 g−1 and 64 vs. 34 nm). The performance of both catalysts was evaluated based here on the bases of changes in API gravity, viscosity, asphaltenes content, metal and sulfur removal, and the conversion of boiling-fractions higher than 343 °C into low-boiling fractions.

In the study with Co-Mo/Al2O3 catalyst, it was found that significant conversion of 343 °C + hydrocarbons into low-boiling fractions was 25–45% against 22–36% for Ni-Mo/Al2O3 catalyst reported here. The upgraded oil with Co-Mo has a higher percentage of naphtha and middle...
distillate fractions than Ni-Mo counterpart (Hart, 2014). At 425 °C and the same experimental conditions no difference was observed in the average API gravity and absolute viscosity of the produced oil (Co-Mo: 0.094 Pa s, 18° API and Ni-Mo: 0.089 Pa s, 18° API), compared to the original feed oil (0.5 Pa s and 13° API). However, for the conversion of asphaltenes, Co-Mo/Al2O3 catalyst also reduced the asphaltene content of the feed oil from 11.3 to 5.7 wt% compared to 6.8 wt% for Ni-Mo/Al2O3 catalyst. This is because of its large surface area and pore size provides by the Co-Mo/Al2O3 to give access to the macromolecules such as resins and asphaltenes in the oil to active site while the high acid strength enhanced the cracking activity for them to be converted into low molecular weight fractions compared to small pore and moderate acid sites Ni-Mo catalyst reported here (Stanislaus et al., 1996; Mouli et al., 2011; Boahene et al., 2011). In terms of desulfurisation and demetallation, it was found that with Co-Mo/Al2O3 5.3% and 12.2% decrease was observed for sulfur and Ni + V while 8% and 9.2% was achieved with Ni-Mo counterpart relative to 3.8 wt% (sulfur) and 206 ppm (Ni + V) for feed oil. Hence, Ni-Mo performed slightly better in desulfurisation reactions whereas Co-Mo/Al2O3 was slightly better for demetallisation reactions. This can be attributed to the promotional functions of the Ni and Co metals in addition to the Mo.

In the 3D combustion cell experiments reported by Xia and Greaves (2001a,b) and Greaves et al. (2004), it was found that the oil API gravity and viscosity improved remarkably in the THAI phase (from 10.5 to 17.8° API and 24.4 to 0.22 Pa s), which further increased in the CAPRI phase (23.1° API and minimum 0.025 Pa s). The sulfur and metals content decreased respectively 5.8 to 4.3 wt% and 268 to 20 ppm (Ni + V). The 3D combustion cell achieved up to ~20° API (Athabasca bitumen) and ~26° API (Wolf Lake heavy oil) with the catalyst less affected by high coke deposition as observed in micro tubular CAPRI reactor reported here, because the combustion zone reached almost down to the horizontal producer well. Therefore, the catalyst could have been regenerated slightly by burn off of deposited coke due to advancing combustion front (Greaves et al., 2004). However, it could be challenging in the reservoir, because it would burn out the well.

4. Conclusions and future outlook

The laboratory scale investigation of the CAPRI reactor model section of THAI process for heavy oil recovery and in situ upgrading was carried out using pelleted Ni-Mo/Al2O3 catalyst. The results have provided insight into how further upgrading might be achieved using a CAPRI reactor section in the THAI process and also how catalyst deactivation could be reduced. The upgraded oil produced was characterised in terms of its API gravity, viscosity, and also simulated distillation by GC. The improvement in API gravity was ~2-5° points and the viscosity was reduced to 0.11–0.02 Pa s compared to the original feed oil values of 13 API and 0.5 Pa s, over a temperature range of 350–425 °C. However, a large amount of coke (37–49 wt%) was deposited on the catalyst during a 25 h operation. Consequently, the Ni-Mo/Al2O3 catalyst had only a short operating life, since virtually its entire surface area and pore volume were blocked by coke. In situ regeneration of the deactivated pelleted catalyst, which is incorporated (gravel packed) along the outside of the horizontal producer well of the THAI-CAPRI reservoir process would be challenging. An alternative contacting pattern is therefore required, so that injected nanoparticles, together with steam and/or hydrogen donor solvents, could incite coke suppression while enhancing upgrading.

Note

The authors declare no competing financial interest.

Data access

Data sets from the above work are available via epapers.bham.ac.uk.

Acknowledgement

This work was supported by the Petroleum Technology Development Fund (PTDF), Nigeria and EPSRC (Grant nos. EP/E057977/1 and EP/J008303/1), United Kingdom. The authors also wish to thank Petrobank Energy and Resources, Ltd. (now Touchstone Exploration Inc.), Canada, for supplying the heavy crude oil used in this study. The sulfur and metals analysis was performed by Intertek Laboratories Sunbury Technology Centre, UK, using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

References

Ahs-Halabi, M., Stanislaus, A., Trimim, D.L., 1991. Coke formation on catalysts during the hydroprocessing of heavy oils. Appl. Catal. 72, 193–215.
Ali, A.F., Hauser, A., Abdullah, A.H., Al-adwani, A., 2006. Accelerated solvent extraction of spent hydrotreating catalysts: a study on oil and coke fractions. Energy Fuel 20, 45–53.
Alvarez, E., Marroquin, G., Trejo, F., Centeno, G., Ancheyta, J., Diaz, A.J.I., 2011. Pyrolysis kinetics of atmospheric residue and its SARA fractions. Fuel 90, 3602–3607.
Ancheyta, J., Betancourt, G., Marroquin, G., Centeno, G., Castaneda, L.C., Alonso, F., Munoz, J.A., Gomez, T.M., Rayo, P., 2002. Hydroprocessing of Maya heavy crude oil in two reaction stages. Appl. Catal. A Gen. 233, 159–170.
Barman, N.B., Starlos, L., Kusnher, J.D., 1997. Simultaneous determination of oil and coke contents in spent hydrotreating catalyst by thermogravimetry. Energy Fuel 11 (3), 593–595.
Boahene, E.P., Kapil, K.S., Ayaj, K.D., John, A., 2011. Application of different pore diameter SBA-15 supports for heavy gas oil hydrotreatment using FeW catalyst. Appl. Catal. A Gen. 402, 51–60.
Chen, Y., He, J., Wang, Y., Li, P., 2010. GC-MS used in study on the mechanism of viscosity reduction of heavy oil through aquathermolysis catalysed by aromatic sulphinic H3PMo12O40. Energy 35, 3454–3460.
Douglas, J., Linnos, M.E., Alvarez, R., Lopez Franco, C., Montoya de la Fuente, J.A., 2004. Pyrolysis applied to the study of a Maya asphaltenes. J. Anal. Appl. Pyrol. 71, 601–612.
Fukuyama, H., Terai, S., Uchida, M., Cano, L.J., Ancheyta, J., 2004. Active carbon catalyst for heavy oil upgrading. Catal. Today 98, 207–215.
Fumoto, E., Matsumura, A., Sato, S., Takahashibi, T., 2009. Recovery of lighter fuels by cracking heavy oil with zirconia-alumina-iron oxide catalysts in a steam atmosphere. Energy Fuel 23, 1388–1394.
Gray, R.M., 1994. Heavy Oil and Residue Properties and Composition, in Upgrading Petroleum Residue and Heavy Oils. Marcel Dekker, Inc., New York, NY, pp. 1–40.
Gray, R.M., Zhao, Y., McKnight, C.M., 2000. Coke and mineral removal from bitumen hydroconversion catalysts. Fuel 79, 285–294.
Greaves, M., Dong, L.L., Rigby, S.P., 2012. Simulation study of the toe-to-heel air injection three-dimensional combustion cell experiment and effects in the mobile oil zone. Energy Fuel 26, 1656–1669.
Greaves, M., Xia, T.X., 2004. Downhole upgrading of Wolf Lake oil using THAI-CAPRI processes-tracer tests. Prep. Pap.-Am. Chem. Soc. Div. Fuel Chem. 49 (3), 69–72.
Greaves, M., Xia, T.X., Imbus, S., Nero, V., 2004. THAI-CAPRI process: tracing downhole upgrading of heavy oil. 5th Canadian International Petroleum Conference (55th Annual Technical Meeting), Calgary, Alberta, Canada, June 8–10.
Hart, A., 2013. A review of technologies for transporting heavy crude oil and bitumen via pipeline. J. Petrol. Explor. Prod. Technol. http://dx.doi.org/10.1186/1320-0139-6-9.
Hart, A., 2014. Advanced Studies of Catalytic Upgrading of Heavy Oils. PhD Thesis. University of Birmingham.
Hart, A., Greaves, M., Wood, J., 2015. A comparative study of fixed-bed and dispersed catalytic upgrading of heavy crude oil using CAPRI. Chem. Eng. J. 282, 213–223.
Hart, A., Leeke, G., Greaves, M., Wood, J., 2014a. Downhole heavy crude oil upgrading using CAPRI effect of steam upon upgrading and coke formation. Energy Fuel 28 (3), 1811–1819.
Hart, A., Shah, A., Leeke, G., Greaves, M., Wood, J., 2013. Optimization of the CAPRI processes for heavy oil up-grading: effect of hydrogen and guard bed. Ind. Eng. Chem. Res. 52 (44), 15394–15406.
Hart, A., Leeke, G., Greaves, M., Wood, J., 2014b. Downhole heavy crude oil upgrading using CAPRI effect of steam upon upgrading and coke formation. Energy Fuel 28 (3), 1811–1819.
Hasan, W.S., Ghannam, T.M., Esmail, N., 2010. Heavy crude oil viscosity reduction and rheology for pipeline transportation. Fuel 89, 1095–1100.
Kim, J.W., Longstaff, C.D., Hansen, V.F., 1997. Upgrading of bitumen-derived heavy oils over a commercial HDN catalyst. Fuel 76 (12), 1145–1150.
Krumm, L.R., Deo, M., Petrick, M., 2011. Direct thermal and catalytic Treatment of Paraffinic crude oils and heavy fractions. Energy Fuel 26, 2663–2671.
Levy, C., Rana, S.M., Trejo, F., Ancheyta, J., 2007. On the use of acid-base-supported catalysts for hydroprocessing of heavy petroleum. Ind. Eng. Chem. Res. 46, 7448–7466.
Marafi, A., Kam, E., Stanislaus, A., 2008. A kinetic study on non-catalytic reactions in hydroprocessing Boscian crude oil. Fuel 87, 2131–2140.
Meng, X., Xu, C., Gan, J., 2007. Cokeing behaviour and catalyst deactivation for catalytic pyrolysis of heavy oil. Fuel 86, 1720–1726.
Ming, L., Wang, J., Deng, W., Que, G., 2007. Effects of Fe/carbon black, Ni/carbon black catalysts on hydrocracking reaction of residual oil. J. Fuel Chem. Technol. 35 (5), 558–562.

Mouli, C.K., Kapil, S., Ajay, D., John, A., 2011. Effect of pore diameter of Ni-Mo/Al-SBA-15 catalysts on the hydrotreating of heavy gas oil. Appl. Catal. A Gen. 404, 21–29.

Murugan, P., Thilakavathi, M., Mahinpey, N., Dong, M., 2011. Pyrolysis kinetics of Athabasca bitumen using a TGA under the influence of reservoir sand. Can. J. Chem. Eng. 90, 315–319.

Pereira-Almao, P., 2012. In situ upgrading of bitumen and heavy oils via nanocatalysis. Can. J. Chem. Eng. 90, 320–329.

Rana, S.M., Anchevita, J., Maity, S.K., Rayo, P., 2008. Heavy crude oil hydroprocessing: a zeolite-based CoMo catalyst and its spent catalyst characterisation. Catal. Today 130, 411–420.

Rezaei, H., Ardakani, J.S., Smith, J.K., 2012. Comparison of MoS2 catalysts prepared from Mo-micelle and Mo-octoate precursors for hydroconversion of Cold Lake vacuum residue: catalyst activity, coke properties and catalyst recycle. Energy Fuel 26, 2768–2778.

Shah, A., Fishwick, R.P., Leeke, G.A., Wood, J., Rigby, S.P., Greaves, M., 2011. Experimental optimisation of catalytic process in situ for heavy-oil and bitumen upgrading. J. Can. Petrol. Technol. 50 (11–12), 33–47.

Speight, J.G., 1998. The chemistry and physics of coking. Korean J. Chem. Eng. 15 (1), 1–6.

Speight, J.G., 2011. The Refinery of the Future. Gulf Professional Publishing, London, pp. 81–116.

Stanislaus, A., Abis-Halabi, M., Khan, Z., 1996. Influence of catalyst pore size on asphaltenes conversion and coke-like sediments formation during catalytic hydrocracking of Kuwait vacuum residues. Stud. Surf. Sci. Catal. 100, 189–197.

Trejo, F., Rana, S.M., Anchevita, J., 2010. Thermogravimetric determination of coke from asphaltenes, resins and sediments and coking kinetics of heavy crude asphaltenes. Catal. Today 150, 272–278.

Xia, T.X., Greaves, M., 2001a. Down-hole upgrading of Athabasca Tar sand bitumen using THAI-SARA analysis. In: Presented at SPE International Thermal Operations and Heavy Oil Symposium, Margarita Island, Venezuela, March 12. SPE, p. 69693.

Xia, T.X., Greaves M., 2001b. 3-D physical model studies of downhole catalytic upgrading of Wolf Lake heavy oil using THAI Paper 2001-17 Presented at the Petroleum Society’s Canadian International Petroleum Conference 2001, Calgary, Alberta, Canada, June 12–14.

Xia, T.M., Greaves, M., Werfilli, W.S., and Rathbone, R.P., 2002. Downhole conversion of Lloydminster heavy oil using THAI-CAPRI process. SPE/PS-CIM/CHOA International Thermal Operations and Heavy Oil Symposium and International Horizontal Well Technology Conference, Calgary, Alberta, Canada, 4–7 November 2002.

Zhang, H.Q., Sarica, C., Pereya, E., 2012. Review of high-viscosity oil multiphase pipe flow. Energy Fuel 26 (7), 3979–3985.

Zhang, X., Shaw, M.I., 2006. Impact of multiphase behaviour on coke deposition in heavy oils hydroprocessing catalysts. Energy Fuel 20, 473–480.

Zhao, Y., Gray, R.M., Chung, K.H., 2001. Molar kinetics and selectivity in cracking of Athabasca asphaltenes. Energy Fuel 15, 751–755.