Effect of Cyclohexane as Hydrogen-donor in Ultradispersed Catalytic Upgrading of Heavy Oil

Hart, Abarasi; Lewis, Charlotte; White, Thomas; Greaves, Malcolm; Wood, Joseph

DOI:
10.1016/j.fuproc.2015.07.016

License:
Creative Commons: Attribution (CC BY)

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):
Hart, A, Lewis, C, White, T, Greaves, M & Wood, J 2015, 'Effect of Cyclohexane as Hydrogen-donor in Ultradispersed Catalytic Upgrading of Heavy Oil', Fuel Processing Technology, vol. 138, pp. 724–733. https://doi.org/10.1016/j.fuproc.2015.07.016

Link to publication on Research at Birmingham portal

Publisher Rights Statement:
Checked October 2015

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

• Users may freely distribute the URL that is used to identify this publication.
• Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
• Users may use extracts from the document in line with the concept of ‘fair dealing’ under the Copyright, Designs and Patents Act 1988 (?)
• Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Download date: 10. Mar. 2020
Effect of cyclohexane as hydrogen-donor in ultradispersed catalytic upgrading of heavy oil

Abarasi Hart \textsuperscript{a}, Charlotte Lewis \textsuperscript{a}, Thomas White \textsuperscript{a}, Malcolm Greaves \textsuperscript{b}, Joseph Wood \textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
\textsuperscript{b} IOR Research Group, Department of Chemical Engineering, University of Bath, BA2 7AY, UK

1. Introduction

The vast reserves of unconventional oil deposits such as heavy oil, bitumen/oilsands, and oil shale could potentially supplement to the declining light oil reserves. However, the challenges imposed by their physical properties such as high viscosity, asphaltenes, metals (e.g., Ni, V, and Fe) and high heteroatom (e.g., S, N, and O) make exploitation difficult and costly \cite{1}. In the light of this, enhanced oil recovery processes such as steam and/or in situ combustion techniques are used to heat up the heavy oil reservoir in order mobilise the oil for production. The Toe-to-Heel Air Injection (THAI) process uses short distance displacement as compared to long distance with conventional in situ combustion (ISC) process \cite{2}. Emplacement of catalyst packing around the horizontal production well (Catalytic upgrading Process In situ, CAPRI) has been developed to augment the THAI process to achieve further upgrading of the produced oil \cite{2,3}.

High temperatures up to 450–700 °C can be achieved in the reservoir during the operation of THAI \cite{4}. The oil may undergo pyrolysis and also upgrading reactions due to the natural catalytic activity of the host rock. Injection of nano-sized catalyst particles ahead of the combustion front will further enhance the upgrading arising from thermal cracking by the THAI process itself. The reactions involving heavy oil taking place on the Toe-to-Heel Air Injection (THAI) process uses short distance displacement as compared to long distance with conventional in situ combustion (ISC) process \cite{2}. Emplacement of catalyst packing around the horizontal production well (Catalytic upgrading Process In situ, CAPRI) has been developed to augment the THAI process to achieve further upgrading of the produced oil \cite{2,3}.

Catalyst deactivation due to coke and metal deposition during in situ catalytic upgrading of heavy oil is potentially a major problem for the implementation of conventional CAPRI \cite{5}. The use of an activated carbon guard bed on top of the catalyst has been reported to reduce coke formation and sustain catalyst lifetime by removal of coke precursors and the addition of hydrogen promotes hydroconversion reactions which are shown to deposit less coke than thermal cracking \cite{3,6,7}. Moreover, in situ hydrogen production from steam via the water–gas-shift reaction has also been investigated as a source of hydrogen to promote hydrocracking and hydrogenation reactions by Hart et al. \cite{7}. It was found that both hydrogen-addition and steam improved API gravity and viscosity of the produced oil and reduced coke formation. However, the pelleted catalyst still experienced pore blockage by macromolecules such as...
asphaltenes and resins [8]. The challenges of packing the horizontal production well with pelleted catalyst and deactivation caused by coke and metal deposition could potentially be decreased by using ultradispersed, once-through nano-sized catalyst. Galarraga and Pereira-Almao [9] reported the use of a trimetallic (Ni–W–Mo) submicronic catalyst for dispersed upgrading at 380 °C in a batch reactor, using a stirrer speed of 500 rpm, and a reaction time of 3–70 h. They found that the produced oil API gravity increased by 6.5° API and the extent of viscosity reduction was 99% relative to the Athabasca bitumen (API gravity 9.5 and viscosity 7680 mPa·s).

Dispersed catalysts such as iron-containing ‘red mud’, a waste product created during the processing of bauxite for aluminium production in the Bayer process, have been shown to be effective for upgrading heavy oils [10]. Moreover nano-sized catalysts have a high surface to volume ratio, low intraparticle mass transfer resistance and thus may be more resistant to deactivation than pelleted catalysts [9,11]. Ultrafine (micron) scale particles may also offer some of these advantages whilst being cheaper to produce, not requiring specialist preparation and easier to handle, for example not being absorbed easily through the skin. The combination of such catalysts with in situ upgrading in CAPRI would require the catalyst to be conveyed or pumped as slurry into the reservoir and thus enabling the catalyst to contact the oil in a once-through manner. This would also reduce the residence time in contact with the oil, and catalyst. The catalyst, which does eventually deactivate, could nevertheless easily be replenished. The combustion zone in the THAI-CAPRI process can reach temperatures of 450–700 °C, so that reservoir water and water from combustion reactions are available to generate steam. The resulting steam bank flooding and hot water are displaced towards the immobile cold bitumen [4,12,13]. The in-situ generated hydrogen via water–gas-shift is not adequate to moderate the population of free radicals formed during heavy oil pyrolysis, hence an external source of hydrogen is required, particularly as the water gas shift reaction is not very active at the temperatures of ~400 °C in the well. The addition of gaseous hydrogen from external source can however prove challenging and dangerous to introduce into an oil reservoir. Alternatively, hydrogen can be generated in situ by injecting a suitable donor solvent. In the light of this, a hydrogen-donor solvent such as cyclohexane, tetralin, and decalin, for example can be injected to supplement the produced hydrogen from hydrocarbons and steam. The use of hydrogen-donor solvents such tetralin, decalin, and cyclohexane for coal/oil shale liquefaction and thermal/catalytic upgrading of heavy oil vacuum residues have been extensively recognised in the literature [14–18].

A study of fixed-bed of pelleted catalyst and ultradispersed catalyst for in situ catalytic upgrading of heavy oil with CAPRI was reported by Hart et al. [19]. Their results showed that dispersed catalyst had a better upgrading performance than fixed-bed of pelleted catalyst. Moreover, the ultradispersed catalyst produced oil with properties that approach conventional light oil characteristics [19]. However, it is challenging to simultaneously increase the amount and quality (API) of upgraded liquid product and also suppress coke yield. Heavy oil is hydrogen-deficient; hence carbon-rejection and/or hydrogen-addition are the two main routes of upgrading. Hydrogen helps to stabilise generated free radicals that are formed during cracking reactions, to narrow the molecular weight distribution of the product. It has been reported that the dehydrogenation of cycloalkanes such as cyclohexane, methylcyclohexane, and decalin can provide an effective hydrogen supply to carbons sourced during catalytic upgrading [16,18,20]. Dehydrogenation of cyclohexane (CH) could liberate hydrogen for hydrocracking and hydrogenation reactions, if the partial pressure of hydrogen is high enough. In this work, the in situ generation of hydrogen and application of ultradispersed particle slurry are investigated with a view to suppressing the formation of free radicals and subsequently improve the API gravity and viscosity, enhance the yield of liquid product and suppress coke formation. The effect of cyclohexane as hydrogen-donor solvent was investigated, whilst the cyclohexane-to-oil ratio was optimised by varying the amount of cyclohexane using ultradispersed Ni–Mo/Al2O3 catalyst. The aims of the work are to improve liquid yield, fuel distillate products, API gravity and lower viscosity of the produced oil whilst suppressing coke formation.

2. Materials and methods

The feed oil was supplied by Touchstone Exploration Inc., from the THAI field operation at Kerrobert, Saskatchewan, Canada. The elemental composition and properties of the feed oil are shown in Table 1. The cyclohexane was purchased from Fisher Scientific UK Limited with 99% purity, boiling point (BP), 80.7 °C and density, 0.78 g·cm−3.

The ultrafine particles of Ni–Mo/Al2O3 were produced by mechanically crushing pelleted Ni–Mo/Al2O3 catalyst (1.2 mm diameter × 1.8–5 mm length, 17.4 wt.% (Mo) and 1.8 wt.% (Ni), supplied by AkzoNobel, Netherlands) using a Tema laboratory disc mill model T 750 K (TEMA Machinery Ltd, UK). The size of the ultrafine particles after crushing was measured by a laser diffraction particle size analyser (Helos-Rodos T4.1, Sympatec, Germany) and a Micromeritics Analytical Instrument ASAP® 2010 was used to measure their surface area. Properties of the ultrafine Ni–Mo/Al2O3 catalyst are presented in Table 2. The number and strength of the acid sites based on the adsorption–desorption of tert-butyllamine (\(\text{CH}_3\text{CH}_2\text{NH}_2\)) were determined using temperature programmed desorption (TPD) of the fresh Ni–Mo/Al2O3 catalyst with a Micromeritics AutoChem II 2920 analyser.

Process variables, such as temperature, pressure, gas-to-oil ratio, catalyst-to-oil ratio and residence time used in this study were optimised values obtained from previous studies in the fixed-bed CAPRI reactor [3,5,19]. The effect of cyclohexane (CH) as a hydrogen-donor solvent for ultradispersed catalytic upgrading was tested using a stirred batch reactor (100 mL capacity), Baskerville UK. The experimental setup is shown in Fig. 1. The batch reactor enabled the screening of an economical quantity of catalyst and oil whilst separating the effects of the catalyst from possible flow problems of conveying a viscous oil and catalyst slurry, as may occur in the fixed bed. Separate studies are being carried out to evaluate how the catalyst could be contacted with oil in the reservoir. The reactions were carried out at a temperature of 425 °C, catalyst-to-oil ratio 0.02 (g·g−1), agitation 500 rpm and 10 minute reaction time, as determined in previous fixed-bed and ultradispersed catalyst investigations [5,19]. The reactor was pressurised to an initial pressure of 17.5 bar (nitrogen or hydrogen), which increased to 65–70 bar with the rising temperature and gas production due to cracking reactions. The reactor pressure decreased to 24–25 bar upon cooling the reactor to room temperature. The high pressures generated indicate that the process is suitable for reservoir depths of greater than 75 m. Once the desired temperature of 425 °C is reached, 10 minute reaction time was allowed to match the residence time reported by Shah et al. [5] in a fixed-bed operation. The experimental conditions are summarised in Table 3. A detailed description of the experimental procedure has been reported elsewhere [19]. To evaluate the effect of

| Table 1 | Properties heavy oil. |
|---------|----------------------|
| Parameter | Value |
| API gravity (°) | 14.8 |
| Viscosity at 20 °C (mPa·s) | 840 |
| Sulphur (wt.%) | 3.52 |
| Nickel (ppm) | 41 |
| Vanadium (ppm) | 108 |
| Ni + V (ppm) | 149 |
| Asphaltene (wt.%) | 11.1 |

| Elemental analysis | |
|-------------------|---|
| C | 88.82 wt.% |
| H | 10.17 wt.% |
| N | 0.57 wt.% |
| H/C | 0.114 |

Please cite this article as: A. Hart, et al., Effect of cyclohexane as hydrogen-donor in ultradispersed catalytic upgrading of heavy oil, Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.07.016
the ultrafine Ni–Mo/Al2O3 catalyst, a thermal cracking experiment was performed without catalyst. Additionally, an experiment with hydrogen gas (instead of nitrogen) was performed for comparison with the hydrogen-donor cyclohexane experiment at the same conditions.

After the upgrading reactions were completed, three products consisting of upgraded oil (liquid), non-condensable gas and coke were quantified. For the upgraded liquid product the following measurements were made: viscosity (Advanced rheometer AR 1000, TA Instruments Ltd, United Kingdom), API gravity (Anton Paar DMA 35 portable density meter), and true boiling point (TBP) distribution by Agilent 6850 N gas chromatography (GC) based on ASTM D2887 method (the calibration mix of the GC contain hydrocarbons from C5 to C40 and also the maximum oven temperature is 280 °C, hence the macromolecules such as resins and asphaltenes outside this carbon range cannot be accounted for). The column details are as follows: DB-HT 5 m length, 0.53 mm internal diameter, and film thickness capillary is 0.15 μm. The GC was fitted with a Programmed Temperature Vaporisation (PTV) injector which rapidly heats the sample to 360 °C to vaporise the sample before introduction to the column. The asphaltene content before and after the upgrading reactions was determined through precipitation using n-heptane in the ratio oil/n-heptane of 1:40 (g·mL−1). The produced coke was determined using thermogravimetric analysis (TGA) (NETZSCH-Geratebau GmbH, TG 209 F1 Iris®) of the deposit left in the reactor after the liquid portion has been collected. The analysis was performed with a ramp temperature increase from 25 to 900 °C under air flow of 50 mL·min−1. A detailed description of these analytical instruments has been reported elsewhere [3,6,7]. The products are grouped into coke, liquid and non-condensable gas yields after the upgrading reaction and are calculated by the following Eqs. (1) and (2):

\[
\text{Yield of product (wt.%) = \frac{\text{weight of product}}{\text{weight of feed oil}} \times 100} \quad (1)
\]

\[
\text{weight of feed oil} - \frac{\text{weight of autoclave content after reaction}}{100}. \quad (2)
\]

The experiments were performed in triplicate to check repeatability, and the values reported are the average values.

3. Results and discussion

The monitored temperature and pressure profiles during heating, reaction and cooling are presented. The data showing the extent of upgrading of the heavy oil and the effect of cyclohexane (CH) as hydrogen–donor solvent in comparison to the use of hydrogen is evaluated in terms of API gravity increase, viscosity reduction, asphaltene reduction and yield of distillate. Additionally, the effects upon the extent of coke deposit of adding hydrogen and cyclohexane relative to only thermal cracking and addition of ultradispersed catalyst without hydrogen donor are also presented and discussed in the following sections.

3.1. Temperature and pressure profile

The starting point of the experiments occurred when the internal temperature inside the reactor reached its set-point value of 425 °C, although some additional, small amount, of upgrading may also occur during the initial start-up and final shutdown of the reactor. The reaction temperature for all experiments was reached within 124 min. The internal temperature and pressure profiles inside the stirred batch reactor during heat-up, reaction, and cool-down for thermal cracking, ultradispersed catalytic cracking, and the addition of different ratios of cyclohexane in the presence of ultradispersed catalyst are presented in Fig. 2.

It can be observed that the temperature–pressure profiles follow a similar trend for all the experiments. However, the maximum pressure during thermal cracking periods was significantly higher than that of the catalytic cracking counterpart. Since the initial pressures were the same, the only reason is an increase in gas formation during thermal cracking. A similar observation of the high yield of gas during thermal cracking, compared with catalytic upgrading was reported by Sawarkar et al. [21] for residue upgrading in a stirred batch reactor. In the ultradispersed Ni–Mo/Al2O3 catalyst experiment, in addition to decreasing the activation energy, it is postulated that the fine particles were able to abstract some radicals such as methyl, ethyl, as well as other light hydrocarbons, from the gas-phase into the liquid-phase to quench cracked active hydrocarbon chains [19]. Hence, the amount of gas decreases, so a pressure decrease is also observed.

The addition of cyclohexane (CH) to the ultradispersed Ni–Mo/Al2O3 catalyst displayed an increase in the pressure beyond the maximum experienced during the thermal and catalytic cracking. The dehydrogenation of cyclohexane (CH) is an endothermic reaction and the chemical equilibrium is favourable at high temperatures [16]. The boiling point (BP) of CH is 80.7 °C, which corresponds to a pressure of about 19 bar, therefore the evaporation of the liquid CH occurs during the heating
to 425 °C to form vapour-phase reactant. This can be noticed in Fig. 2 as the pressure under added CH over the temperature range 80.7 °C to 425 °C was progressively higher than that without CH addition. As the temperature increases beyond 80.7 °C rapid volume expansion occurs (see Fig. 2) as a result of phase change within the slurry medium. This phase change occurs as noted between 150 and 400 °C, in Fig. 2. The release of hydrogen and the formation C1–C5 due to ring opening contributed to the increased pressure observed upon the addition of CH [22]. This is confirmed from the increased pressure noticed with increasing CH-to-oil ratio. The increased pressure however increases the partial pressure of the liberated hydrogen to favour hydrocracking and hydrogenation reactions. The maximum pressure of the ultradispersed experiment under hydrogen atmosphere is significantly lower than that carried out under nitrogen atmosphere with or without CH because of the consumption of hydrogen for hydrocracking and hydrogenation reactions.

3.2. Coke, gas and liquid yields

The heavy oil/bitmen upgrading reactions take place in a three phase gas–liquid–solid environment on the surface of the ultradispersed catalyst. It is very likely in this situation that solid carbonaceous (coke) deposits will be produced [21]. The coke can deactivate active sites and lower catalyst performance; hence the amount of liquid product obtainable is decreased. The ultrafine particles of Ni–Mo/Al2O3 were encapsulated with residual oil, asphaltenes, deposited metals such as vanadium, nickel and iron, and coke after upgrading reactions [8]. So, it is challenging to separate the spent catalyst and recycle it after reaction. It has been reported that the Ni–Mo metals in the catalyst ended as metallic sulphides after reaction due to the high sulphur content of the heavy oil [6,8]. Hence, TGA was used to quantify the amount of coke in the composite deposit after reaction. The portion of the feed oil converted to coke was determined from TGA of the deposit (which includes residual oil, asphaltene, metals and coke).

![Fig. 2. Temperature and pressure profile during heating, reaction and cooling for the experiments carried under nitrogen and hydrogen atmospheres at 425 °C, CTO 0.02 (g·g\(^{-1}\)), initial pressure 17.5 bar, agitation 500 rpm, reaction time from set point 10 min, and CH:oil ratio 0 to 0.06 (g·g\(^{-1}\)).](image)

![Fig. 3. TGA of deposits after thermal cracking and ultradispersed catalytic upgrading under nitrogen and hydrogen atmospheres at 425 °C, CTO 0.02 (g·g\(^{-1}\)), initial pressure 17.5 bar, agitation 500 rpm, reaction time from set point 10 min, and CH:oil ratio 0 to 0.08 (g·g\(^{-1}\)).](image)
asphaltenes, catalyst particles and coke) left in the reactor after the upgraded oil has been collected. The thermogram is shown in Fig. 3. The weight loss from 25 to 278 °C represents devolatilisation of residual oil in the deposits. The weight loss from 278 °C to final ‘burn-off’ temperature represents the ‘burn-off’ of soft (278–521 °C) and hard coke (521 °C–final temperature) from rejected carbon due to cracked hydrocarbons. The observed temperatures for the complete burn-off coke are presented in Table 4.

From Table 4, it can be seen that the deposited coke after catalytic upgrading burns-off approximately 100 °C lower than the deposit produced by thermal cracking. This indicates that the coke produced by thermal cracking is harder and more condensed than that produced by catalytic upgrading. It can also be observed that the burn-off temperature of the coke produced after ultradispersed catalytic upgrading decreases as the CH:oil ratio increases, from 0.01 to 0.08 (g·g⁻¹). This suggests that the extent of polymerisation and condensation of macro-molecules such as resins and asphaltenes was suppressed as the cyclohexane (CH)–to-oil ratio increases. The observation can be attributed to increased release of hydrogen from the dehydrogenation of cyclohexane. This notion is re-enforced as the burn-off temperature of the coke produced after catalytic upgrading under hydrogen atmosphere is lower than that obtained under nitrogen gas environment and the use of cyclohexane.

Table 5 displays the mass balance of gas, liquid and coke after thermal cracking and ultradispersed catalytic upgrading under nitrogen, hydrogen atmosphere and cyclohexane solvent. It can be observed that there is greater production of non-condensable gas and coke, and less liquid products with thermal cracking than ultradispersed catalytic upgrading. Fig. 4 shows the relation between CH-to-feed oil ratio and coke and upgraded oil yields after reaction. With thermal cracking 13.35 wt.% (gas) and 7.95 wt.% (coke) were produced, whilst ultradispersed catalytic under nitrogen atmosphere produced 11.5 wt.% (gas) and 4.67 wt.% (coke). This represents, respectively, 13.5% (gas) and 41.3% (coke) reduction with ultradispersed catalyst relative to thermal cracking. This confirmed the higher pressure observed during thermal cracking compared to ultradispersed catalytic upgrading (see Fig. 2). Hence, the catalyst suppresses undesired coking reactions and subsequently increases conversion of heavy molecular weight hydrocarbons to light products.

Under a hydrogen atmosphere, the gas and coke produced decreased by respectively 21.7% and 65.5%, relative to that achieved with thermal upgrading. In comparison to upgrading under a nitrogen atmosphere, there was 9.5% and 41.2% further reduction in gas and coke yields. This confirmed the previous well-established findings of the role of hydrogen in suppressing coking formation, also observed by Hart et al. [3,6], and also a similar decrease in gas and coke yields under hydrogen atmosphere has been reported in the literature [23, 24]. Under nitrogen atmosphere, the catalytic upgrading is mainly a carbon rejection process, in which the hydrogen within the hydrocarbons is redistributed among the cracked fragments, resulting in light fractions (distillates) and deposits with lower hydrogen/carbon atomic ratio (coke). However, for hydrogen-addition combined with ultradispersed catalytic process, the complex molecules such as resins and asphaltenes (i.e., the less volatile fractions) or macromolecular weight radicals formed during the reaction, being less mobile, are readily adsorbed by the catalyst particles and become saturated by hydrogenation via carbonium ion mechanisms. Hence, a balance between fuel distillates and coke production in ultradispersed catalytic upgrading becomes necessary.

It was observed that the addition of cyclohexane (CH) hydrogen-donor solvent reduces coke compared to the amount of coke produced upon upgrading under nitrogen (see Fig. 4). Quantitatively, the coke decreased by 6.2% to 45.4% as the CH:oil ratio increased from 0.01 to 0.08 (g·g⁻¹) relative to 4.67 wt.% of coke observed without CH in ultradispersed catalytic upgrading under nitrogen environment (see Table 5 and Fig. 4). Correspondingly, the amount of upgraded oil increases in mirror trend with the decrease in amount of coke as the CH:oil ratio increased from 0 to 0.08 (see Table 5 and Fig. 4). This observation suggests that adding CH solvent makes it possible to increase the yield of upgraded oil whilst suppressing coke formation. The improvement can be attributed to the release of hydrogen during reaction due to dehydrogenation of CH, and subsequently, under high pressure, hydrocracking and hydrogenation reactions are promoted. The ability of the cracked hydrocarbon radicals to undergo addition-reaction to form adducts with larger molecular weight than the starting hydrocarbon has been reported by Gray and McCaffrey [25]. Under an inert environment such as nitrogen these reactions are favoured [8]. This addition-reaction between hydrocarbon radicals produces bigger molecules, which decreases the yield of low-boiling components and the produced oil is characterised by low-API gravity and high viscosity (upgrading under N₂: 21.2 °API and 10.5 mPa·s; upgrading under H₂: 21.7 °API and 6.1 mPa·s, see Section 3.3). The dehydrogenation of CH produces hydrogen and benzene (i.e., aromatic hydrocarbon). The aromatic hydrocarbons are known coke precursors during the upgrading reaction, whereas the dissociation of hydrogen produces the lightest and the fastest diffusing active species (H⁺), which help to suppress the addition-reactions between hydrocarbon free radicals, hydrogenate olefins and aromatics to form stable hydrocarbon molecules. This is the

| Deposit burn-off temperatures. | Burn-off temperature (°C) |
|--------------------------------|---------------------------|
| Deposit from experiment        |                           |
| Thermal cracking + N₂         | 890.4                     |
| Ultradispersed + N₂           | 785.4                     |
| Ultradispersed + H₂           | 674.2                     |
| Ultradispersed + N₂ + CH:oil (0.01) | 792.0                 |
| Ultradispersed + N₂ + CH:oil (0.02) | 761.0                 |
| Ultradispersed + N₂ + CH:oil (0.04) | 746.0                 |
| Ultradispersed + N₂ + CH:oil (0.06) | 727.3                 |
| Ultradispersed + N₂ + CH:oil (0.08) | 719.8                 |

| Table 5 |
|---------|
| The yields of liquid (i.e., upgraded oils), gas and coke after thermal and ultradispersed catalytic upgrading. |
| Experiment | Liquid (wt.%) | Gas (wt.%) | Coke (wt.%) |
|-----------|--------------|------------|------------|
| Thermal cracking + N₂ | 78.71 ± 0.11 | 13.35 ± 0.54 | 7.95 ± 0.43 |
| Ultradispersed + N₂ | 83.79 ± 0.17 | 11.55 ± 0.19 | 4.67 ± 0.36 |
| Ultradispersed + H₂ | 86.81 ± 0.47 | 10.45 ± 0.49 | 2.74 ± 0.03 |
| Ultradispersed + N₂ + CH:oil (0.01) | 86.97 ± 1.38 | 8.66 ± 1.02 | 4.38 ± 0.29 |
| Ultradispersed + N₂ + CH:oil (0.02) | 87.05 ± 1.23 | 8.93 ± 1.85 | 4.02 ± 0.13 |
| Ultradispersed + N₂ + CH:oil (0.04) | 87.94 ± 0.38 | 8.64 ± 0.22 | 3.43 ± 0.16 |
| Ultradispersed + N₂ + CH:oil (0.06) | 88.25 ± 1.28 | 8.56 ± 1.11 | 3.20 ± 0.18 |
| Ultradispersed + N₂ + CH:oil (0.08) | 88.76 ± 1.11 | 8.69 ± 1.20 | 2.55 ± 0.13 |

Please cite this article as: A. Hart et al., Effect of cyclohexane as hydrogen-donor in ultradispersed catalytic upgrading of heavy oil, Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.07.016

Fig. 4. Effect of CH:feed oil ratio on coke and upgraded oil yields.
reason for the lower amount of coke observed under hydrogen atmosphere compared to the used of CH solvent, whereas higher amount of upgraded oil was produced with CH (see Table 5). However, lower gas yields in the presence of CH compared to thermal cracking reaffirmed that the increased pressure with increasing CH:oil ratio during reaction can be attributed to evaporation, thermal expansion and phase-change of cyclohexane (see Fig. 2). It was noted that there is a strong correlation between coke yield and CH:oil ratio ($R^2$ value = 0.98 as shown in Fig. 4 based on regression analysis). Thus from the regression equation shown in Fig. 4, it can be deduced that CH:oil ratio of approximately 0.073 g·g$^{-1}$ is required to achieve a similar reduction of coke yield compared with hydrogen gas. The amount of cyclohexane required, represents 6.8 wt.% of the feed oil mixture.

High temperature contributes mainly to condensation of free radicals and abstraction of hydrogen to form coke [19,23,24], and is favoured by thermal cracking. However, in the presence of dispersed Ni–Mo/Al2O3 catalyst hydrogen; methyl and ethyl transfer reactions were activated on the active sites of the ultrafine particles and react with the cracked fragments. This helps to suppress the condensation of hydrocarbon free radicals due to thermal cracking; hence the yields of large molecular weight hydrocarbons and coke are reduced [19]. Hence, coke inducing period and colloidal stability of the reaction medium is improved and prolonged in the presence of hydrogen and cyclohexane [23,24].

The composition of the produced gas was determined using Refinery Gas Analyser (RGA) by gas chromatograph in selected experiments and presented in Table 6 for thermal cracking and ultradispersed catalytic upgrading under nitrogen and hydrogen. The produced gas upon the addition of cyclohexane was not analysed. However, it can be observed that thermal cracking produced more normal alkane gases than ultradispersed catalytic upgrading. This is consistent with the material balance presented in Table 5, Fig. 2 and also with the observation of Sawarkar et al. [21]. The isomers iC$_5$-C$_6$ and olefins (C$_3$-C$_4$) were produced more with ultradispersed catalytic upgrading under nitrogen atmosphere than thermal counterpart. This is an indication of the dominance of catalytic cracking promoted by the Ni–Mo/Al2O3 particles. In the reservoir, the hydrocarbon gases can miscibly displace oil and provide recovery through gas drive mechanism.

Ultradispersed upgrading under hydrogen atmosphere produced 0.44 vol.% olefin gases whilst 1.07 vol.% of the same was produced when upgrading was carried out under nitrogen atmosphere. This represents a 0.63 vol.% decrease of olefin gases under hydrogen atmosphere. This shows that under hydrogen atmosphere, the ultradispersed Ni–Mo/Al2O3 catalyst promotes hydrogenation of olefins and aromatic hydrocarbons. The bimetallic Ni–Mo is responsible for the hydrogenation function which helps to moderate free radicals and coke precursors produced from cracking of heavy oil and subsequently lower coke yields for ultradispersed catalytic upgrading. In the presence of hydrogen both hydrocracking and hydrogenation occur concurrently. The extent of sulphur removal resulting in the release of hydrogen sulphide under hydrogen atmosphere is 1.3 times more than experienced under nitrogen atmosphere. Hence, the level of hydrodesulphurisation (HDS) function of the Ni–Mo/Al2O3 catalyst is greatly enhanced in the presence of hydrogen.

### 3.3. API gravity, viscosity and asphaltene

The API gravity [defined as $(141.5 / \text{specific gravity of oil}) – 131.5$] is used to classify crude oil into light, medium, heavy or extra-heavy oil. Crude with API gravity less than 20° and viscosity greater than 100 mPa·s is regarded as heavy oil [26]. On the other hand, heavy oil differs from light oils by their high viscosity at reservoir conditions, hence upgrading is necessary to improve fluidity for pipeline transportation. Table 7 shows the API gravity, viscosity and the asphaltene content of the feed and upgraded oil samples. Clearly, all the upgraded oil samples are lighter than the feed oil. However, thermal cracking only increases the API gravity by 4.37°, but the ultradispersed Ni–Mo/Al2O3 particles increases it to 6.4° relative to the feed oil under nitrogen atmosphere. This represents approximately 2° further improvement in API gravity with ultradispersed catalyst compared with only thermal cracking. The additional gain of 2° API with catalyst is significant as it may represent a premium of $\$2–3 for each barrel of oil produced [3], and more also with ultradispersed catalyst more upgraded oil and less coke are produced relative to thermal cracking only and the upgraded oil possesses better quality (discussed in Section 3.5) and yields more fuel distillates (discussed in Section 3.4).

Under hydrogen atmosphere the API gravity increased to 21.65° compared to 21.2° (nitrogen). This represents a gain of 0.42° for ultradispersed catalytic upgrading under hydrogen atmosphere. A similar observation was reported by Hart et al. [6]. Furthermore, under hydrogen atmosphere hydrocracking and hydrogenation reactions are favoured. The function of the Ni–Mo/Al2O3 catalyst is to promote these reactions which leads to smaller molecular weight products, as the aluminia promote cracking of macromolecules whilst the Ni–Mo metals transfer active hydrogen to the cracked fragments to form a smaller stable molecule following the carbonium ion mechanism. The extent of hydrogenation can be noticed in the lower olefins and the higher amount of hydrogen sulphide in the produced gas when ultradispersed catalytic upgrading was carried under hydrogen atmosphere compared to nitrogen atmosphere (see Table 6). Testing the effect of cyclohexane (CH) on ultradispersed catalytic upgrading under nitrogen atmosphere, it was observed that API gravity increases by an additional 0.45 to 1.14° as the CH:oil ratio increases from 0.01 to 0.08 g·g$^{-1}$ compared to the 21.2° achieved with ultradispersed catalytic upgrading under nitrogen gas atmosphere. The re-condensing effect of the cyclohexane and/or from benzene can be seen to be negligible as the reaction was carried at high temperature (425 °C), the boiling point of cyclohexane is 80.7 °C, only a small amount of CH (0.2–1.2 g) was used, and the changes in API gravity and viscosity of the produced oil after reaction varies narrowly. In addition to hydrogen supply, other light hydrocarbon gases such as C$_4$–C$_5$ are formed as a result of ring opening [27]. Notably, upgrading with CH:oil ratio of 0.04 g·g$^{-1}$ under nitrogen atmosphere had a similar effect to adding hydrogen. The results presented in Tables 5 and 6 show that the trend in the

### Table 6

Produced gas composition for thermal cracking and ultradispersed catalytic upgrading under N$_2$ and H$_2$.

| Gas       | Thermal cracking (vol.%) | Ni–Mo under N$_2$ (vol.%) | Ni–Mo under H$_2$ (vol.%) |
|-----------|--------------------------|---------------------------|---------------------------|
| n(C$_3$–C$_5$) | 16.23                    | 10.48                     | 13.17                     |
| iC$_4$–C$_5$ | 0.63                     | 0.94                      | 1.25                      |
| Olefin (C$_3$–C$_4$) | 0.55                     | 1.07                      | 0.44                      |
| CO        | 0.20                     | 0.23                      | 0.13                      |
| C$_2$H$_4$ | 0.01                     | 0.01                      | 0.007                     |
| C$_2$H$_6$ | 1.52                     | 1.61                      | 78.61                     |
| H$_2$S     | 0.0001                   | 0.002                     | 0.0026                    |

| Sample               | API gravity (°) | Viscosity (mPa·s) | Asphaltene (wt.%) |
|----------------------|----------------|-----------------|------------------|
| Feed oil             | 14.8           | 840             | 11.1             |
| Thermal cracking + N$_2$ | 19.17 ± 0.40   | 13.83 ± 1.5     | 7.3 ± 0.3        |
| Ultradispersed + N$_2$ | 21.20 ± 0.26   | 10.52 ± 2.1     | 6.7 ± 0.3        |
| Ultradispersed + H$_2$ | 21.65 ± 0.37   | 6.14 ± 1.3      | 5.6 ± 0.1        |
| Ultradispersed + N$_2$ + CH (0.01) | 21.51 ± 0.12   | 9.39 ± 0.5      | 6.8 ± 0.1        |
| Ultradispersed + N$_2$ + CH (0.02) | 21.54 ± 0.33   | 9.43 ± 1.5      | 6.2 ± 0.1        |
| Ultradispersed + N$_2$ + CH (0.04) | 22.00 ± 0.24   | 6.33 ± 1.0      | 5.8 ± 0.2        |
| Ultradispersed + N$_2$ + CH (0.06) | 22.33 ± 0.10   | 6.75 ± 1.3      | 5.8 ± 0.2        |
| Ultradispersed + N$_2$ + CH (0.08) | 22.31 ± 0.21   | 5.84 ± 1.2      | 5.7 ± 0.1        |

Please cite this article as: A. Hart, et al., Effect of cyclohexane as hydrogen-donor in ultradispersed catalytic upgrading of heavy oil, Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.07.016
amount of coke and API gravity after upgrading is consistent with the report of Dim et al. [18]. The slight increase in API gravity with increasing CH:oil ratio whilst suppressing coke formation suggests that significant carbon-rejection in the upgrading reaction is required for a remarkable API gravity rise. Therefore limiting the coke deposit is not consistent with a large rise in API gravity.

The fluidity of the upgraded oil samples improved as their viscosities were significantly lower compared to the feed oil viscosity of 840 mPa·s (Table 7). The upgraded oil samples have viscosities less than 100 mPa·s, which is necessary for a pipeline transport. Notably the viscosity of the produced oil by ultradispersed catalytic upgrading is 3.3 mPa·s lower than that produced with thermal cracking. However, the viscosity of the upgraded oils are approximately the same and within the same error margin. It is well known that bond breaking is temperature dependent, therefore, since the experimental conditions are the same, it was concluded that the hydrogen and cyclohexane contributed majorly to upgrading chemistry [19]. A similar observation has been reported by Hart et al. [3] for catalytic upgrading under hydrogen and nitrogen atmosphere [29]. Fig. 5 shows the TBP curves for the feed and upgraded oil samples after upgrading with thermal cracking and ultradispersed Ni–Mo/Al₂O₃ catalyst under nitrogen, hydrogen, and cyclohexane solvent, respectively. Table 8 summarises the distillate fractions into naphtha (IBP – 200 °C), middle distillate (200–343 °C) and residue (>343 °C). The shift to left of the temperature–volumetric yield curve of the upgraded oils relative to the feed oil curve, indicates improved low-boiling components (see Fig. 5). A significant improvement in the upgraded oils relative to the feed heavy oil can be noticed between 240 and 440 °C of the TBP curves. This increase in light hydrocarbon components in the upgraded oils is the reason for the increased API gravity and lower viscosity observed in Table 6 relative to the feed oil.

It can be noticed that the feed oil contains a low proportion of fuel constituents (with boiling point (BP) below 343 °C) compared to the upgraded oil. The True Boiling Point (TBP) distribution according to the ASTM D-2887 standard is a method for crude oil characterisation. It provides a good approximation of the expected separation by distillation in the refinery [29]. The TBP curves of feed and upgraded oil after thermal cracking and ultradispersed catalytic upgrading under nitrogen and hydrogen atmospheres at 425 °C, CTO 0.02 (g·g⁻¹), initial pressure 17.5 bar, agitation 500 rpm, reaction time from set point 10 min, and CH:oil ratio 0 to 0.08 (g·g⁻¹) are shown in Fig. 5.

Table 8

| Sample                        | Distillation fractions (vol%) |
|-------------------------------|-------------------------------|
|                               | IBP – 200 °C | 200–343 °C | >343 °C |
| Feed                          | 42            | 44.80      | 50.50   |
| Thermal cracking + N₂         | 4.5           | 50.83      | 44.17   |
| Ultradispersed + N₂ + H₂      | 6.2           | 50.13      | 43.17   |
| Ultradispersed + N₂ + CH:oil (0.01) | 5.2     | 50.13      | 43.17   |
| Ultradispersed + N₂ + CH:oil (0.02) | 6.8     | 53.86      | 38.84   |
| Ultradispersed + N₂ + CH:oil (0.04) | 7.8     | 54.86      | 36.84   |
| Ultradispersed + N₂ + CH:oil (0.08) | 15.3    | 52.40      | 31.80   |

The True Boiling Point (TBP) distribution

The True Boiling Point (TBP) distribution according to the ASTM D-2887 standard is a method for crude oil characterisation. It provides a good approximation of the expected separation by distillation in the refinery [29]. Fig. 5 shows the TBP curves for the feed and upgraded oil samples after upgrading with thermal cracking and ultradispersed Ni–Mo/Al₂O₃ catalyst under nitrogen, hydrogen, and cyclohexane solvent, respectively. Table 8 summarises the distillate fractions into naphtha (IBP – 200 °C), middle distillate (200–343 °C) and residue (>343 °C). The shift to left of the temperature–volumetric yield curve of the upgraded oils relative to the feed oil curve, indicates improved low-boiling components (see Fig. 5). A significant improvement in the upgraded oils relative to the feed heavy oil can be noticed between 240 and 440 °C of the TBP curves. This increase in light hydrocarbon components in the upgraded oils is the reason for the increased API gravity and lower viscosity observed in Table 6 relative to the feed oil.

It can be noticed that the feed oil contains a low proportion of fuel constituents (with boiling point (BP) below 343 °C) compared to the upgraded oil. The TBP curves of feed and upgraded oil after thermal cracking and ultradispersed catalytic upgrading under nitrogen and hydrogen atmospheres at 425 °C, CTO 0.02 (g·g⁻¹), initial pressure 17.5 bar, agitation 500 rpm, reaction time from set point 10 min, and CH:oil ratio 0 to 0.08 (g·g⁻¹) are shown in Fig. 5.

Table 8

| Sample                        | Distillation fractions (vol%) |
|-------------------------------|-------------------------------|
|                               | IBP – 200 °C | 200–343 °C | >343 °C |
| Feed                          | 42            | 44.80      | 50.50   |
| Thermal cracking + N₂         | 4.5           | 50.83      | 44.17   |
| Ultradispersed + N₂ + H₂      | 6.2           | 50.13      | 43.17   |
| Ultradispersed + N₂ + CH:oil (0.01) | 5.2     | 50.13      | 43.17   |
| Ultradispersed + N₂ + CH:oil (0.02) | 6.8     | 53.86      | 38.84   |
| Ultradispersed + N₂ + CH:oil (0.04) | 7.8     | 54.86      | 36.84   |
| Ultradispersed + N₂ + CH:oil (0.08) | 15.3    | 52.40      | 31.80   |

Please cite this article as: A. Hart, et al., Effect of cyclohexane as hydrogen-donor in ultradispersed catalytic upgrading of heavy oil, Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.07.016.
upgraded oil samples. From Table 8, whilst the naphtha and middle distillates increase, the residue fraction (BP > 343 °C) decreases in the order thermal cracking, ultradispersed (N₂), and ultradispersed (H₂). With increasing CH:oil ratio the amount of the fraction with BP greater than 343 °C decreases (see Table 8).

The upgraded oils showed significant amounts of naphtha and middle fuel distillate boiling range (IBP > 343 °C) compared to the starting heavy feed oil. The residue fraction (BP > 343 °C) decreases from 50.5 vol.% to 44.17 vol.% (thermal cracking under N₂), 43.17 vol.% (ultradispersed under N₂), and 38.5 vol.% (ultradispersed under N₂). However, whilst the sum of the naphtha and middle distillate fractions (IBP < 343 °C) increases as the CH:oil ratio increases from 0 to 0.08 g·g⁻¹, the residue fraction (BP > 343 °C) decreases correspondingly. This implies that more of the residue fractions were converted into middle fractions in the presence of the cyclohexane hydrogen-donor solvent. It can be observed that the presence of hydrogen improved the naphtha fraction more compared to the cyclohexane donor solvent. A similar improvement in naphtha and middle distillate fractions was observed by Jarullah et al. [30], after hydrotreatment of a whole crude oil in a trickle-bed reactor. This observation is also consistent with the results reported on API gravity and viscosity of the feed and upgraded oils (see Table 7). The trend therefore suggests that the capping of cracked hydrocarbon radicals by active hydrogen during reaction helps to produce stable molecules with lower molecular weight and boiling point than starting hydrocarbon molecule.

The initial step towards the liberation of hydrogen from cyclohexane (CH) on the Ni–Mo/Al₂O₃ catalyst starts with the adsorption of the CH molecule followed by dehydrogenation to cyclohexene, cyclohexadiene and benzene at high temperature [16,27,31,32], as illustrated below. The overall reaction can be simplified by Eq. (3).

\[ C₆H₁₂ = C₆H₆ + 3H₂ \quad \Delta H^\circ = +205.9 \text{ kJ} \text{ mol}^{-1} \]  

The hydrogen produced dissociates at the active site of the Ni–Mo/Al₂O₃ particles and subsequently reacts with cracked hydrocarbon fragments and intermediates produced by thermal cracking to form stable and low molecular weight hydrocarbons. Consequently, the cyclohexane can undergo selective ring opening to methane, ethane, propane, and butane and their isomers at the reaction temperature (425 °C) range has been reported in the literature [22]. The two parallel reactions occurring are simplified by the reaction scheme shown below involving cracking of cyclohexane to light hydrocarbons and dehydrogenation to benzene [33]. Slagter et al. [33] observed that the produced alkane gases from C₄−C₆ are products of secondary reaction whilst the olefins C₃−C₅ are products of primary reaction of the CH ring opening.

These reactions are the reason for higher internal pressure observed and lower gas yields upon the use of cyclohexane relative to that without cyclohexane which is catalytic upgrading under nitrogen environment only (see Fig. 2 and Table 5). It is well known that hydrogen, methyl, and ethylene are the smallest species during heavy oil upgrading, hence in the presence of a catalyst they are readily incorporated with hydrocarbon intermediate and radicals to form stable molecules, which helps to increase the yields of low-boiling components and suppress coke formation.

3.5. Elemental, sulphur and metals analysis

Table 9 shows the sulphur and metal content and elemental analysis of the feed and upgraded oil samples. It can be seen that thermal cracking gave 2.96 wt.% carbon-rejection whilst ultradispersed catalytic upgrading under nitrogen rejected 2.85 wt.% carbon relative to the feed which contains 88.86 wt.% However, the addition of cyclohexane and hydrogen rejected lower amount of carbon 2.63 and 2.39 wt.%, respectively. It is well known that high portion of the elemental carbon in the feed oil is associated with poly-aromatics species such as resins and asphaltenes. Nonetheless, due to the supported hydrocracking and hydrogenation activities of the Ni–Mo/Al₂O₃ particles in the presence of hydrogen, components such as olefins and aromatics with high proportion of carbon are readily hydrogenated; hence the portion of hydrogen in the produced oil was improved. This notion is re-enforced in the increased elemental hydrogen in the produced oil upon the use of hydrogen atmosphere and cyclohexane addition (Table 9). Also, hydrodenitrogenation (HDN) increased nitrogen removal under these upgrading conditions compared to ultradispersed upgrading under nitrogen atmosphere only.

The high level of impurities in heavy oils such as metals (e.g., Ni, V, and Fe) and heteroatom (e.g., S and N) poses challenges to downstream processes. Hence, these impurities need to be removed through upgrading to be suitable as refinery feedstock. From Table 9, the metal (Ni + V) content of the upgraded oil by ultradispersed Ni–Mo/Al₂O₃ particles under nitrogen was 39 ppm whilst the extent of sulphur reduction is 19.1% compared to 44 ppm and 16.8% achieved with thermal cracking. This shows that the quality of the upgraded oil improved with ultradispersed catalyst upgrading. Moreover, the produced oil after ultradispersed upgrading under hydrogen atmosphere contains 26 ppm (Ni + V) and 37.5% sulphur content reduction relative to the feed oil. The further demetalisation and desulphurisation experienced under hydrogen atmosphere can be attributed to hydrodesulphurisation (HDS) and hydrodemetalisation (HDM) reactions in the presence of Ni–Mo/Al₂O₃ particles and hydrogen. The extent of sulphur reduction in the upgraded oil increased from 22.7 to 33.2% as the CH:oil increased from 0.01 to 0.08 (g·g⁻¹). This is because of the increased availability of hydrogen for HDS reaction as the amount of CH increased. However, the
Ni + V content decreased from 32 to 27 ppm for CH:oil ratio 0.01–0.04 and increased from 29 to 36 ppm for CH:oil ratio 0.06–0.08. Notably, the extent of demetallisation upon CH addition was high than ultradispersed upgrading under nitrogen atmosphere only (see Table 9). Generally, the iron (Fe) content of the upgraded oil is less than 1 ppm relative to 5 ppm for the feed oil. The Ni–Mo/Al₂O₃ catalyst particles showed a relatively high demetallisation activity compared to desulphurisation. The metals (e.g., Ni, V, and Fe) are present as oil soluble porphyrins, which upon adsorbing on the catalyst particles undergo hydrogenation and ring cleavage and subsequently deposited. Consequently, the concentration of sulphur in the feed oil is much higher than that of the metals (Ni + V) and is mostly present as sulphide, disulphide, and thiols (e.g., mercaptans). The sulphur in the heavy oil can be removed as hydrogen sulphide (Table 6) and also for sulfa
dation of the Ni–Mo during reaction, whilst the removed metals from the heavy oil ends up as metal sulphides (MₓSᵧ) on the surface of the catalyst particles [19,34]. It is believed that the deposited metal sulphides (MₓSᵧ) can provide some sort of auto-catalytic activity on the surface of the particles [34,35].

4. Conclusions

The role of cyclohexane as a hydrogen-donor solvent in increasing the yield of upgraded oil whilst decreasing the coke yield, using ultradispersed Ni–Mo/Al₂O₃ catalyst, during THAI process for recovery and upgrading of heavy oil was investigated at 425 °C, under hydrogen and nitrogen atmospheres. The yields of upgraded oil and coke were respectively found to be 78.71 wt.% and 7.95 wt.% (thermal cracking under N₂), 83.79 wt.% and 4.67 wt.% (ultradispersed catalyst under N₂), and 86.81 wt.% and 2.74 wt.% (ultradispersed catalyst under H₂). It was found that increasing the cyclohexane-to-oil ratio from 0.01 to 0.08 g·g⁻¹ did not only suppressed coke yield from 4.38 to 2.55 wt.% respectively, but also increased the yield of upgraded oil from 86.97 to 88.76 wt.% relative to ultradispersed catalyst under nitrogen without cyclohexane added. However, it was observed that the API gravity of the upgraded oils slightly increased from 21.51 to 22.31° relative to 21.2° achieved under nitrogen without cyclohexane added. The viscosity of the upgraded oils reduced by approximately 98.85% relative to the feed oil viscosity (840 mPa·s). There was a significant reduction in coke yield during catalytic upgrading under a hydrogen atmosphere. By comparison, the addition of cyclohexane increased the amount of upgraded oil.

Acknowledgement

The authors acknowledge the financial support of EPSRC (Grant numbers EP/E057977/1 and EP/J008303/1), United Kingdom, and Touchstone Exploration Inc, Canada, for supplying the heavy crude oil used in this study. The sulphur and metals content analysis was performed by Intertek Laboratories Sunbury Technology Centre, UK, using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry), whilst the elemental microanalysis was used for CHN.

Note: The sulphur and metals content analysis was performed by Intertek Laboratories Sunbury Technology Centre, UK, using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry), whilst the elemental microanalysis was used for CHN.

Data from this publication can be accessed online free of charge via http://erepositories.bham.ac.uk/.

References

[1] A. Shah, R.P. Fishwick, J. Wood, G.A. Leeke, S.P. Rigby, M. Geavres, A review of novel techniques for heavy oil and bitumen extraction and upgrading, Energy Environ. Sci. 3 (2010) 700–714.
[2] M. Geavres, L.L. Dong, S.P. Rigby, Simulation study of the Toe-to-Heel Air Injection three-dimensional combustion cell experiment and effect in the mobile oil zone, Energy Fuel 26 (2012) 1656–1669.
[3] A. Hart, A. Shah, C. Leeke, M. Geaves, J. Wood, Optimization of the CAPRI process for heavy oil upgrading: effect of hydrogen and guard bed, Ind. Eng. Chem. Res. 52 (2013) 15394–15406.
[4] T.X. Xia, M. Geavres, W.S. Werrifili, R.R. Kithbone, Downhole conversion of Lloydonester heavy oil using THAI-CAPRI process, SPE Petroleum Society of CIM/CHOA 78998, Presented at International Horizontal Well Technology Conference, Calgary, Alberta, Canada, 2002 (November 4–7).
[5] A. Shah, R.P. Fishwick, J. Wood, G.A. Leeke, S.P. Rigby, M. Geaves, Experimental optimisation of catalytic process in situ for heavy-oil and bitumen upgrading, J. Can. Pet. Technol. 50 (11–12) (2011) 33–47.
[6] A. Hart, G. Leeke, M. Geaves, J. Wood, Down-hole heavy crude oil upgrading by CAPRI: effect of hydrogen and methane gases upon upgrading and coke formation, Fuel 119 (2014) 226–233.
[7] A. Hart, G. Leeke, M. Geaves, J. Wood, Downhole heavy crude oil upgrading using CAPRI: effect of steam upon upgrading and coke formation, Energy Fuel 52 (44) (2014) 15394–15406.
[8] A. Hart, Advanced Studies of Catalytic Upgrading of Heavy Oils (PhD thesis) University of Birmingham, UK, 2014.
[9] E.C. Galarre, P. Pereira-Almaga, Hydrocracking of Athabasca bitumen using submicron multimetallic catalysis at near in-reservoir conditions, Energy Fuel 24 (2010) 2383–2389.
[10] C. Nguyen-Huy, H. Kweon, H. Kim, D.K. Kim, D-W. Kim, S.H. Oh, E.W. Shin, Slurry-phase hydrocracking of vacuum residue with a disposable red mud catalyst, Appl. Catal. A Gen. 447–448 (2014) 186–192.
[11] E.C. Galarre, C. Scott, H. Loria, P. Pereira-Almaga, Kinetic models for upgrading Athabasca bitumen using unsupported NiMo catalyst at low severity conditions, Ind. Eng. Chem. Res. 51 (2012) 140–146.
[12] G. Wenlong, C. Xi, Y. Chen, X.M. Zhang, L. Jinzhong, H. Jihong, W. Jian, Fire-flooding technologies in post-steam-injected heavy oil reservoirs, Pet. Explor. Dev. 38 (4) (2011) 452–462.
[13] L. Jinzhong, G. Wenlong, J. Youwei, X. Changfeng, W. Bojun, L. Xiaoling, Propagation and control of fire front in the combustion assisted gravity drainage using horizontal wells, Pet. Explor. Dev. 39 (6) (2012) 764–772.
[14] C.H.F. Peden, D.W. Goodman, Kinetics of cyclohexane dehydrogenation and hydrodenitrogenation over Ru(001) and Cu/Ru(001), J. Catal. 104 (1987) 347–358.
[15] Y. Liu, H. Fan, The effect of hydrogen donor additive on the viscosity of heavy oil during steam stimulation, Energy Fuel 16 (2002) 842–846.
[16] R.B. Binwale, N. Kariya, M. Ichikawa, Dehydrogenation of cyclohexane over Ni, V and W catalysts supported on activated carbon using spray-pulsed reactor and enhancement in activity by addition of a small amount of Pt, Catal. Lett. 105 (2005) 83–87.
[17] L.O. Almén-Vázquez, J.L. Cano-Domínguez, J.L. García-Gutiérrez, Effect of terephthal, decalin and naphthalene as hydrogen donors in the upgrading of heavy oils, Fuel Process. Technol. 42 (2012) 532–539.
[18] P. Dim, A. Hart, J. Wood, B. Macnaghten, P.S. Rigby, Characterization of pore coking in catalyst for thermal downhole upgrading of heavy oil, Chem. Eng. Sci. (2015), http://dx.doi.org/10.1016/j.ces.2015.03.052.
[19] A. Hart, M. Geaves, J. Wood, A comparative study of fixed-bed and dispersed catalytic upgrading of heavy crude oil using CAPRI, Chem. Eng. J. (2015), http://dx.doi.org/10.1016/j.cej.2015.01.101.
[20] L. Ali, A.A.-G. Ali, S.M. Aboul-Fotouh, K.A. Aboul-Gheit, Dehydrogenation of cyclohexane on catalysts containing noble metals and their combinations with platinum on alumina support, Appl. Catal. A Gen. 177 (1999) 99–110.
[21] A.N. Sawarkar, A.B. Pandit, J.B. Joshi, Studies in coking of Arabian mix vacuum residue, Trans. IChemE Part A Chem. Eng. Res. Des. 85 (A4) (2007) 481–491.

Please cite this article as: A. Hart, et al., Effect of cyclohexane as hydrogen-donor in ultradispersed catalytic upgrading of heavy oil, Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.07.016
[22] H. Shi, X. Li, L.G. Haller, Y.D. Gutierrez, A.J. Lercher, Active sites and reactive intermediates in the hydrogenolytic cleavage of C–C bonds in cyclohexane over supported iridium, J. Catal. 295 (2012) 133–145.

[23] H. Du, D. Liu, H. Liu, P. Gao, R. Lv, M. Li, B. Lou, Y. Yang, Role of hydrogen pressure in slurry-phase hydrocracking of Venezuela heavy oil, Energy Fuel (2015), http://dx.doi.org/10.1021/ef502457p.

[24] H. Du, D. Liu, M. Li, P. Wu, Y. Yang, Effects of the temperature and initial hydrogen pressure on the isomerisation reaction in heavy oil slurry-phase hydrocracking, Energy Fuel (2014), http://dx.doi.org/10.1021/ef5024143.

[25] R.M. Gray, W. McCaffrey, Role of chain reactions and olefin formation in cracking, hydroconversion, and coking of petroleum and bitumen fractions, Energy Fuel 16 (2002) 756–766.

[26] R.F. Meyer, E.D. Attanasi, Heavy oil and natural bitumen-strategic petroleum resources, USGS Fact Sheet 70-03, August, 2003 (Available at http://pubs.usgs.gov/fs/fs070-03/fs070-03.html, Accessed March 4, 2015).

[27] Z. Kou, S. Shen, K. Liu, G. Xu, Y. An, C. He, Kinetic analysis of dehydrogenation reaction of cyclohexane catalyzed by Raney-Ni under multiphase reaction conditions, Int. J. Hydrog. Energy 38 (2013) 1193–11936.

[28] J. Liu, Y. Zhao, S. Ren, Molecular dynamics simulation of self-aggregation of asphaltenes at an oil/water interface: formation and destruction of the asphaltene protective film, Energy Fuel (2015), http://dx.doi.org/10.1021/ef5019737.

[29] L. Carbognani, J.C. Arambarri, H. Molero, P. Pereira-Almao, High temperature simulated distillation of bitumen fractions with open tubular capillary columns depleted in silicone/siloxane stationary phases, Energy Fuel 27 (2013) 2033–2041.

[30] T.A. Jarullah, M.J. Mujtaha, S.A. Wood, Improvement of the middle distillate yields during crude oil hydrotreatment in a trickle-bed reactor, Energy Fuel 25 (2011) 773–781.

[31] J. Li, Y. Chai, B. Liu, Y. Wu, X. Li, Z. Tang, Y. Liu, C. Liu, The catalytic performance of Ni₃P/Al₂O₃ catalyst in comparison with Ni/Al₂O₃ catalyst in dehydrogenation of cyclohexane, Appl. Catal. A Gen. 469 (2014) 434–441.

[32] A.A. Balandin, L.D. Rzhdestvenskaya, Mechanism of dehydrogenation of cyclohexane on the crystalline α-oxide of chromium, Bull. Acad. Sci. USSR Div. Chem. Sci. 10 (1961) 1824–1829.

[33] A. Slagten, L.M. Dahl, K.J. Jens, T. Myrstad, Cracking of cyclohexane by high Si HZSM-5, Appl. Catal. A Gen. 375 (2010) 213–221.

[34] M.S. Rana, J. Ancheyta, S.K. Maity, P. Rayo, Characterisation of Maya crude hydrodemetallization and hydrodesulfurisation catalysts, Prepr. Pap. — Am. Chem. Soc., Div. Fuel Chem. 49 (2004) 573–574.

[35] A. Del-Bianco, N. Panariti, S. Di Carlo, J. Elmouchinino, B. Fixari, P. Le Perchec, Thermocatalytic hydroconversion of heavy petroleum cuts with dispersed catalyst, Appl. Catal. A Gen. 94 (1993) 1–16.