A comparative study of fixed-bed and dispersed catalytic upgrading of heavy crude oil using-CAPRI

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HIGHLIGHTS

- Fixed-bed and dispersed catalytic upgrading of heavy oils was studied.
- The extent of upgrading is dispersed catalyst > fixed-bed > thermal cracking.
- Fixed-bed produces high middle distillate fractions than dispersed catalyst.
- Dispersed catalyst produces more light distillates compared to fixed-bed.
- High level of ultrafine particles dispersion improves catalytic activity.

ABSTRACT

CAtalytic upgrading PRocess In-situ (CAPRI) incorporated with Toe-to-Heel Air Injection (THAI) for heavy oil and bitumen recovery and upgrading was studied for fixed-bed and dispersed catalysts. The extent of upgrading was evaluated in terms of API gravity, viscosity reduction, impurity removal, and true boiling point (TBP) distribution. The test was carried out using Co-Mo/Al2O3 at temperature of 425 °C, pressure 20 bar, and residence time of 10 min. The dispersed catalyst was tested in a batch reactor. However, the residence time, catalyst-to-oil (CTO) ratios as well as the Reynolds numbers of both contacting patterns were kept the same to ensure dynamic similitude. It was found that the produced oil from dispersed ultrafine Co-Mo/Al2O3 catalyst (dp = 2.6 μm) exhibited superior light oil characteristics and quality than that produced with the fixed-bed of pelleted Co-Mo/Al2O3 (1.2 mm diameter × 2–5 mm length). The API gravity of the feed oil was 13.8° and the produced oil showed an increase of 5.6° with the fixed bed and 8.7° with the dispersed catalyst. Unlike the fixed-bed of pelleted Co-Mo/Al2O3 which may suffer from diffusion limitations, rapid deactivation, and channelling effect, the ultrafine particles presented high surface area to volume ratio, reducing the chances of pore plugging, have more accessible reaction sites per unit mass, and lead to enhanced cracking of macromolecules. Moreover, the reduction of sulphur of 38.6% and (Ni + V) content of 85.2% in the produced oil show greater heteroatom removal compared to 29% (sulphur) and 45.6% (Ni + V) observed in the product from the fixed-bed.

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1. Introduction

Heavy oil and bitumen are viewed as a large potential energy sources since their total reserve of about 9–13 trillion barrels outweighs conventional light crude oil reserves of about 1.02 trillion
barrels [1]. Heavy oil and bitumen contain resins and asphaltenes which give them the characteristics of high viscosity, high density/low API gravity, high metals and heteroatom content. Upgrading therefore improves refineability; reduces metals and heteroatom content as coke precursors such as resins and asphaltenes are converted into valuable liquid products. This can be achieved through carbon-rejection and/or hydrogen-addition. Heavy oil and bitumen are mainly extracted using thermal stimulation of the reservoir, and to a lesser extent cold production. The thermal methods include steam injection and on a smaller scale, In-Situ Combustion (ISC) technologies. The commonly used steam technologies are Cyclic Steam Stimulation (CSS) and Steam Assisted Gravity Drainage (SAGD). However, the steam-injection technologies are energy and cost intensive, consume large volumes of water and natural gas for steam generation, and subsequently their thermal efficiency drops with time owing to heat loss to adjacent reservoir formation [2]. In-situ combustion includes conventional ISC and Toe-to-Heel Air Injection (THAI). In the latter process a small portion of the oil in place is oxidised with its combustion front sustained by continuous injection of air through a vertical well. Over the past 12 years, the THAI process research and subsequent field studies have been carried out in conjunction with the CATalytic upgrading PrOcess In-situ (CAPRI) in which a pelletized refinery catalyst is incorporated with the horizontal production well to aid in-situ catalytic upgrading as the hot mobilised oil flows across the layer of pelleted catalyst [3–6]. This technology offers the advantage of using in-situ generated energy from the in situ combustion reactions to mobilise the oil and also catalytically upgrade it in the reservoir, thereby offering great potential cost advantages compared to SAGD and CSS which incur the cost of natural gas, steam generation and post water treatment. Moreover, Xia et al. [3] has demonstrated the potential use of regenerated industrial hydrodesulphurisation (HDS) catalyst in CAPRI which could reduce the cost of catalyst. Additionally, commercial catalysts are fairly cheap according to Shah et al. [7], it is estimated that 20 tonnes of new HDS catalyst for 500 m horizontal producer well cost about $60–100 k. The payback time is estimated to be only a few days, based on a production rate of about 800 bbl/d. If THAI/CAPRI can achieve 20 API gravity this could potentially add a $20–30/bbl margin of profit over conventional extraction.

The down-hole upgrading method investigated and reported by Shah et al. [7] and Hart et al. [6,8,9] involved the fixed-bed contacting pattern with catalyst incorporated adjacent to the horizontal production well. Findings from the fixed-bed of catalyst studies showed that the catalyst rapidly deactivates as a result of deposition of asphaltenes, coke, metals and heteroatom during the process [6,7]. Typically, the duration of the catalytic process ranged from only 72–91 h, which is a major drawback of the fixed-bed pattern. Owing to the high level of metals, heteroatom and asphaltenes in heavy oil, dispersed ultrafine catalyst (i.e., submicron and nano-sized particles) upgrading has been found to be more suitable because it enables a once-through process [10]. Additionally, catalytic deactivation rate is a major yardstick for the selection of contacting pattern, and the complications of pre-packing the horizontal production well with pelleted refinery catalyst and associated bed plugging with coke are avoided. However, conveying the nano-sized catalyst particles to the mobile oil zone (MOZ) during the THAI process is not straightforward. Also, the recovery and re-use of the nano-catalyst after reaction need to be addressed. Reducing the particle size from pellets to powders with diameters in the range of microns or even nanometers could potentially shorten the diffusion path length, enhance active site exposure to macromolecules and improve mass and heat transfer [11]. The formulation of nanoparticulate catalysts is similar to that of conventional pelleted catalysts, derived from soluble precursors or water-in-oil emulsions containing Mo, W, Co, or Ni [12]. Galarraga and Pereira-Almán [13] tested trimetallic (Ni–W–Mo) submicronic catalyst in a batch reactor for dispersed-phase upgrading at 380 °C, a stirring speed of 500 rpm, and reaction time 3–70 h. After upgrading, they found that the produced oil sample (API gravity 16° and viscosity at 40 °C, 60 mPa s) was significantly upgraded compared to the Athabasca bitumen (API gravity 9.5° and viscosity 7680 mPa s).

The delivery of nano-sized catalyst into the oil-bearing formation for in situ catalytic upgrading can be accomplished by injecting it as a slurry, pneumatically conveying into the MOZ or alternatively precipitated in situ using a suitable metal precursors [12,14,15]. The separation challenges can be resolved by inducing magnetic characteristics to the ultrafine particles to enhance magnetic separation [16]. The nano-sized catalyst can be introduced into the reservoir in two forms namely: (1) as heterogeneous nano-sized catalyst, and (2) as dispersed precursor of water or oil soluble salts [17,18]. The latter is transformed into active catalyst phase in-situ during the upgrading reactions. In this study, the fixed-bed of pelleted catalyst and once-through dispersed catalyst contacting techniques of the THAI–CAPRI process were evaluated. However, the dispersed catalyst test was carried out in a batch reactor. The second phase of the study involves optimisation of the catalyst-to-oil ratio, reaction time and agitation for the dispersed catalyst. A further aim of the research was to identify new concepts, directions and strategies for future studies of THAI–CAPRI using dispersed nano-sized catalyst.

2. Materials and methods

The heavy oil sample used in this study was supplied by Touchstone Exploration Inc, from the THAI field operation, Kerrobert, Saskatchewan, Canada. The feedstock is a blend of oils recovered from eight wells, with properties summarised in Table 1. [Note: the original crude gravity was 10.9° API and increased to 13.8° API upon extraction with THAI process].

Physically, ultrafine or micron sized particles can be prepared mechanically via crushing [19]. Therefore, the pelleted Co–Mo/Al2O3 catalyst was crushed using a Tema laboratory disc mill model T 750 K (TEMA Machinery Ltd., UK). The size of the catalyst particles after pulverization was measured by laser diffraction particle size analyser (Helos-Rodos T4.1, Sympatec, Germany). The mean particle size is approximately 2.6 ± 1.08 μm. The temperature programmed desorption (TPD) of the fresh Co–Mo/Al2O3 catalyst was carried out with a Micromeritics AutoChem II 2920 analyser. This was performed to determine the number and strength of the acid sites based on the adsorption–desorption of tert-butylamine ([CH3]3CNH2). The catalyst has two acid sites; 2.86 mmol adsorbed ([CH3]3CNH2/g catalyst at 320 °C and 0.45 mmol adsorbed ([CH3]3CNH2/g catalyst at 500 °C, respectively. Detailed properties of the Co–Mo/Al2O3 have been reported.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity (°)</td>
<td>13.8</td>
</tr>
<tr>
<td>Viscosity at 20 °C (mPa s)</td>
<td>1091</td>
</tr>
<tr>
<td>Density at 15 °C (g cm⁻³)</td>
<td>0.9737</td>
</tr>
<tr>
<td>Sulphur (wt.%)</td>
<td>3.52</td>
</tr>
<tr>
<td>Nickel (ppm mass)</td>
<td>41</td>
</tr>
<tr>
<td>Vanadium (ppm mass)</td>
<td>108</td>
</tr>
<tr>
<td>Ni + V (ppm mass)</td>
<td>149</td>
</tr>
<tr>
<td>Asphaltenes (wt.%)</td>
<td>10.7</td>
</tr>
<tr>
<td>ASTM D2887 Distillation, (°C)</td>
<td>34.6 vol.%</td>
</tr>
<tr>
<td>IBP – 200 °C</td>
<td>200 – 343 °C</td>
</tr>
<tr>
<td>343 °C – FBP</td>
<td>24.0 vol.%</td>
</tr>
</tbody>
</table>
and subsequently the maxi-
catalyst samples with
increased by 7.6 m
is the weight of component
is the weight of component
in previous fixed-bed investigations [6,7].
For the dispersed ultrafine catalyst experiment, a small stainless
steel custom-designed stirred batch reactor (100 mL capacity) was
used to test the in situ catalytic upgrading. The reactions were car-
ried out at a temperature of 425 °C and 10 min reaction time, as
determined in previous fixed-bed investigations [6,7]. During the
heating stage to 425 °C, it has been reported that in situ activation
of the catalyst did occur as a result of the sulphur content of the
feed oil [10]. The gas atmosphere is nitrogen with initial pressure
of 20 bar, which increases with the ramp temperature rise and the
added gas due to cracking reactions to 74–80 bar, decreasing
to 21–23 bar upon cooling the reactor to room temperature. The
increased gas pressure is due to thermal expansion of initial gas
pressure of 20 bar and the additional gas produced from the reac-
tion. This is expected even in reality as a result of in situ combus-
tion which temperature ranges from 450 to 650 °C. Owing to the
pressures generated the technique is mainly suitable for wells of
at least 75 m depth. Some reaction could occur during heat up,
which takes about 2 h 15 min to reach the desired reaction temper-
ature of 425 °C. Once the desired temperature of 425 °C is reached,
10 min reaction time was allowed to match that of the fixed-bed
reactor residence time. The experimental conditions for the
fixed-bed and dispersed ultrafine particles are summarised in
Table 2. In order to evaluate the effect of the ultrafine catalyst,
other experiments were conducted without catalyst as a bench-
mark and also pelleted catalyst basket was used in batch reactor
to study the impact of system hydrodynamics.
The products of the upgrading reaction consist of liquid (i.e.,
light oil), gas and coke. The produced gas was analysed using Agi-
lent gas chromatography (GC). The liquid product (i.e., upgraded
oil) was collected; thereafter measurements of viscosity, API grav-
lence, and elemental composition were performed. The
pelleted catalyst from the fixed-bed after reaction was crushed before the TGA
analysis. The analysis was carried out with a ramp temperature
device to study the impact of system hydrodynamics.

The results of experiments performed in the fixed-bed and the
dispersed ultrafine catalyst tested in a batch reactor at the same
residence time (10 min), CTO (0.1 g/g) and the same Reynolds
numbers (Re) of 0.2 (calculated using Eqs. (1) and (2)) to ensure
dynamic similitude are presented in this section.

\[
Re = \frac{nD^2}{\mu} \quad (1)
\]

\[
Re = \frac{nND^2}{\mu} \quad (2)
\]

where, \( N \) number of revolution per second (2.3), density of heavy
oil, \( \rho \) (974 kg m \(^{-3}\)), velocity of oil in fixed-bed, \( v \) (0.0032 m s \(^{-1}\)),
viscosity of heavy oil, \( \mu \) (1.091 Pa s), porosity of the fixed-bed, \( e \)
(0.48), diameter of impeller, \( D \) (0.01 m), and equivalent particle
diameter, \( d_p \) (0.035 m).

3.2. Comparison of upgrading with fixed-bed of pellets vs. dispersed
ultrafine catalysts

The quantitative and qualitative data showing the extent of
upgrading of the heavy oil after thermal cracking, fixed-bed and
dispersed ultrafine particles experiments are presented and dis-

cussed in the following sections.

3.1. Characterisation

The pelleted and ultrafine Co-Mo/Al\(_2\)O\(_3\) catalyst samples with
the same chemical composition were analysed by the nitrogen
sorption technique according to ASTM C1274 method, and the
results are presented in Fig. 1 and Table 3, respectively. A character-
istic type IV hysteresis loop from relative pressure of 0.35–0.9 can
be noticed for both samples, indicating the filling of mesopores.

Though the hysteresis loop is very similar in Fig. 1, the ultrafine
Co-Mo/Al\(_2\)O\(_3\) produced by crushing the pelleted Co-Mo/Al\(_2\)O\(_3\)
shows lower BET surface area and pore volume compared to the
pelleted counterpart (Table 3). However, the micropore area of the
ultrafine Co-Mo/Al\(_2\)O\(_3\) increased by 7.6 m\(^2\) g\(^{-1}\) above the pel-
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3.1. Characterisation

The pelleted and ultrafine Co-Mo/Al\(_2\)O\(_3\) catalyst samples with
the same chemical composition were analysed by the nitrogen

<p>| Table 2 |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fixed-bed cooled catalyst</th>
<th>Dispersed ultrafine catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst weight (g)</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Feedstock weight (g)</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>Catalyst-to-oil (CTO) ratio</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Residence time (minutes)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>425</td>
<td>425</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>0.195</td>
<td>0.195</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>20</td>
<td>20–75</td>
</tr>
<tr>
<td>Agitation (rpm)</td>
<td>133</td>
<td>133</td>
</tr>
<tr>
<td>Oil flow rate (mL min(^{-1}))</td>
<td>1 ± 0.2</td>
<td>1 ± 0.2</td>
</tr>
<tr>
<td>Effect of CTO</td>
<td>0 to 0.1</td>
<td>0 to 0.1</td>
</tr>
<tr>
<td>Effect of agitation (rpm)</td>
<td>250 to 1000</td>
<td>250 to 1000</td>
</tr>
<tr>
<td>Reaction atmosphere</td>
<td>N(_2)</td>
<td>N(_2)</td>
</tr>
</tbody>
</table>

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The main cause of catalyst deactivation is coke deposit due to cracking of hydrocarbons and macromolecules such as resins and asphaltenes [6,7]. The extent of deactivation as a function of spent catalyst coke content was determined by TGA of the recovered catalyst after upgrading. Fig. 2 provides the TGA weight loss curves as a function of ramp temperature increase for the fresh and spent pellets and micro Co-Mo/Al₂O₃ catalysts recovered after the upgrading experiments with fixed-bed and batch reactor. The weight loss (2.3 wt.%) by the fresh catalyst from 25 to 100 °C is due to loss of moisture. However, for the spent catalyst the weight loss from 25 to 208 °C represents loss due to de-volatilisation of residual oil on the catalyst. The weight loss from 208 to 780 °C therefore represents soft and hard coke burn-off [6,7]. Hence, the spent catalyst coke content after upgrading with fixed-bed is 32.7 wt.% and ultrafine particles after reaction in batch reactor is 53.6 wt.%. The higher coke produced with dispersed ultrafine Co-Mo/Al₂O₃ is due to increase reaction as a result of increase surface area with particle size reduction.

Physical properties such as API gravity and viscosity of the crude oil are two measures used in the petroleum industry to assess its quality. The extent of upgrading achieved with fixed-bed and dispersed micro-particles of Co-Mo/γ-Al₂O₃ catalyst are presented in Table 4. For duplicate runs, the average API increment was 8.7 ± 0.7° API for dispersed ultrafine catalyst and 5.6 ± 1.8° API for the fixed-bed system. The API gravity achieved using ultrafine Co-Mo/γ-Al₂O₃ catalyst was 3° higher above that obtained with fixed-bed catalyst. Ovalles et al. [21] observed an API gravity increase of 7° and 55% conversion of heavy fractions using dispersed molybdenum catalyst at 410 °C reaction temperature. With regards to cost, the dispersed catalyst could therefore potentially lead to the production of oil with higher added value [22].

The API gravity of the produced oil was also compared for catalytic and thermal cracking runs. As can be seen in Table 4, the oil produced by non-catalytic route was upgraded by 6.6 ± 0.6° API, above the original feed oil of 13.8° API. Whilst the catalytic run with dispersed ultrafine Co-Mo/Al₂O₃ produced oil that was upgraded by 8.7 ± 0.7° API. This represents 2° API above thermal cracking alone. Abuhesa and Hughes [23] reported similar findings on catalytic and non-catalytic in situ combustion.

Viscosity is regarded as one of the key factors for crude oil pipeline transportation. The viscosity of 1091 mPa s (feed oil) was reduced to 28.4 mPa s (fixed-bed) and 7 mPa s (dispersed) after upgrading. This represents respectively 97.4% and 99.4% viscosity reduction, a 2% increase upon the use of dispersed ultrafine Co-Mo/γ-Al₂O₃ compared with the pelleted catalyst. Conversely, Wei et al. [24] reported 98.9% viscosity reduction of Liaohe extra-heavy oil using nano-nickel catalyst in batch reactor. Using a fixed-bed of inert glass beads [6], it was found that thermal cracking only produced an increase in API gravity of 1.7° and 52% viscosity reduction, at the same conditions as the present study. When using a catalyst, the reported viscosity reduction could increase the flow of the oil through the reservoir media, increasing the production rate as well as improving pipeline transport. However in the current work, the effect of dispersed ultrafine catalyst on viscosity of produced oil seems to be roughly the same as that obtained with only thermal upgrading. Chemical conversion to lighter components could achieve the same or more with the dispersed catalyst promoting hydroconversion as can be seen in the increased conversion of heavy fractions.

The difference in hydrodynamics and contacting pattern of fixed-bed and dispersed catalyst could have contributed significantly to the level of upgrading achieved with pelleted and micron particles of Co-Mo/Al₂O₃. To gain further insight, an alternative contacting technique using a spinning basket with pelleted Co-Mo/Al₂O₃ in batch reactor at the same experimental conditions was carried out. Although, the viscosity of the upgraded oil samples after thermal cracking, pelleted catalyst basket, and dispersed ultrafine catalyst upgrading was approximately the same, its API gravity showed an increase in the order: dispersed ultrafine catalyst > pelleted catalyst basket > thermal cracking (Table 4). This superiority of ultrafine catalyst over pellets (in basket) can be attributed to an increased contact, high surface area to volume ratio, and decreased diffusion path length with particle of smaller sizes.

Thermal cracking showed the lowest conversion of heavy fractions (BP > 343 °C) of 33.1%, whereas the conversion was improved upon using a catalyst to 46.4% (fixed-bed) and 59.7% (dispersed). Though the upgraded oil after thermal cracking in batch showed high naphtha fractions, however the conversion of 343 °C+ fractions into low-boiling fraction is low compared to catalytic counterpart in fixed-bed. This is because thermal cracking in batch reactor produced less middle distillates (200–343 °C) compared to fixed-bed of catalyst, due to re-cracking of middle fractions in the batch reactor pushes the products towards naphtha fractions (see Section 3.2.2). Additionally, the hydrodynamics difference between the fixed-bed and stirred batch reactor also contributed. The superiority of dispersed ultrafine catalyst over fixed-bed pellets could be because they offer better contact, whereas preferential channelling encountered in fixed-bed will drastically reduce oil-particle contact. Additionally, dispersed catalysts promote cracking reactions because of their reduced particle size and large surface-area-to-volume ratio, decreased diffusion path-length, and effective contact and wetting of the dispersed ultrafine catalyst compared to the fixed-bed catalyst [25,26]. According to Le Pechec et al. [26], dispersed nano-catalysts exhibit higher reaction rate than their fixed-bed counterpart, because hydrogen generated in situ promotes hydroconversion reactions which help to stabilise the free radicals produced during the cracking of heavy oil.

The material balance presented in Table 4 shows that the amount of coke produced at 425 °C was 12.95 wt.% (thermal cracking only) compared to 12.07 wt.% (pelleted catalyst basket) and
Comparison of upgrading level with fixed-bed Co-Mo/Al₂O₃ pellets, pelleted catalyst basket and dispersed ultrafine Co-Mo/Al₂O₃ at temperature 425 °C, pressure 20 bar, CTO 0.1, Stirring speed 133 rpm, and thermal cracking only (in batch). Feed oil (13.8 °API and 1091 mPa s).

<table>
<thead>
<tr>
<th>Experimental run</th>
<th>API increment (°)</th>
<th>Viscosity (mPa s)</th>
<th>Conversion (343 °C) (%)</th>
<th>Coke (wt.% of feed oil)</th>
<th>Gas (wt.% of feed oil)</th>
<th>Liquid (wt.% of feed oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal (no catalyst in batch)</td>
<td>6.6</td>
<td>8</td>
<td>33.1</td>
<td>12.95</td>
<td>8.15</td>
<td>78.9</td>
</tr>
<tr>
<td>Dispersed ultrafine catalyst (batch)</td>
<td>8.7</td>
<td>7</td>
<td>59.7</td>
<td>7.1</td>
<td>8.05</td>
<td>84.85</td>
</tr>
<tr>
<td>Fixed-bed catalyst</td>
<td>5.63</td>
<td>28.4</td>
<td>46.4</td>
<td>1.86</td>
<td>3.34</td>
<td>93.8</td>
</tr>
<tr>
<td>Pelleted catalyst basket (batch)</td>
<td>7.41</td>
<td>7.6</td>
<td>48.3</td>
<td>12.07</td>
<td>7.88</td>
<td>80.05</td>
</tr>
</tbody>
</table>

It is clear that while the residue fraction decreased from 24 vol.% in the feedstock to 13.3 vol.% and 10 vol.% respectively for the produced oils from fixed-bed and dispersed Co-Mo/Al₂O₃ catalysts, the gasoline fractions respectively increased from 34.6 vol.% (feedstock) to 45.5 vol.% and 56.6 vol.%. However, for the fixed-bed, more middle distillates (200–343 °C) were produced compared to dispersed ultrafine Co-Mo/Al₂O₃. The enhanced gasoline fraction with dispersed catalyst could have occurred since the heavy molecules are transported to the more readily accessible active sites of the microns particles faster, unlike in the fixed-bed of pelleted catalyst with long diffusion path length leading to pore plugging and deactivation [31,32]. As can be seen in Fig. 3, thermal cracking produced the highest residue fraction of 16.6 vol.% (343 °C – FBP) compared to dispersed micron particles, pelleted catalyst basket and fixed-bed of pelleted Co-Mo/Al₂O₃. The increased low-boiling fractions caused the improvement of API gravity and viscosity reported in Table 4, compared to the original feed oil. A comparison of the yields of the different range of distillates after upgrading with fixed-bed and dispersed catalysts showed that the light distillate increases from 47.5 vol.% (fixed-bed) to 56.6 vol.% (dispersed). However, the middle distillate decreased from 39.2 vol.% (fixed) to 33.4 vol.% (dispersed), while the residue fractions are 13.3 and 10 vol.%, respectively. It can be concluded that dispersed catalyst upgrading in a batch reactor favours the production of lighter boiling fractions, whereas a fixed-bed of pelleted catalyst favours the middle distillates fractions. The increased yield of low-boiling distillates (IBP-200 °C) by 5.5 vol.% after upgrading with pelleted catalyst basket above 47.5 vol.% (fixed-bed), re-affirms the effect of hydrodynamics and contacting pattern despite keeping the Reynolds number, residence time, temperature, and CTO in both dispersed and fixed-bed the same.

3.2.3. Elemental analysis

The results of the elemental analysis of the samples obtained from thermal, fixed-bed and dispersed ultrafine Co-Mo/Al₂O₃ upgrading and also of the feedstock are shown in Table 5. It can be seen that the H/C atomic ratio increased after thermal and catalytic upgrading which supported the earlier notion of increased hydrogenation with the dispersed ultrafine catalyst. However, the thermally upgraded oil sample showed the highest carbon-rejection of 5.16 wt.% and the lowest atomic hydrogen of
10.06 wt.%. Notably, the amount of carbon-rejected by thermal upgrading is approximately 3 times that of catalytic upgrading. This confirms the mass balance presented in Table 4 and that upgrading by thermal cracking is due to carbon-rejection. As a consequence, the incorporation of a catalyst improved the H/C ratio and suppressed carbon formation (see Tables 4 and 5).

It has been reported by Klerk et al. [33] that an increase in H/C ratio indicates a decrease in naphthenic and aromatic content relative to the feed oil. The poly-form of these could have an adverse impact on the H/C, API gravity and viscosity because of their high density and carbon content.

### 3.2.4. Asphaltenes, sulphur and metals removals

The asphaltene content of a crude oil confers high viscosity and low API gravity. The presence of heteroatoms (e.g., N, S, etc.) and metalloporphyrins of nickel, vanadium, iron, etc. are known to impact on downstream refining processes and catalysts. In Table 6, the asphaltene, metals and sulphur contents before and after upgrading, via thermal cracking, fixed-bed of pelleted Co-Mo/Al₂O₃ and dispersed ultrafine Co-Mo/Al₂O₃ catalysts are presented.

Clearly, the asphaltene content after upgrading decreased for all samples. However, a more significant decrease was recorded after upgrading with dispersed ultrafine Co-Mo/Al₂O₃ compared to thermal cracking and fixed-bed of pelleted Co-Mo/Al₂O₃ catalysts. Based on the correlation between asphaltene content with the viscosity and API gravity of the produced oil, it is clear that the result presented in Table 6 is consistent with viscosity and API gravity presented in Table 4.

The produced oil after upgrading with ultrafine particles of Co-Mo/Al₂O₃ dispersed for in situ catalytic upgrading showed measurable reduction in sulphur and metals compared with the produced oil after thermal cracking alone. As can be seen in Table 6, the ultrafine particles of Co-Mo/Al₂O₃ led to greater reductions of each component than the fixed-bed pelleted catalyst counterpart. The produced oil after upgrading with ultrafine particles of Co-Mo/Al₂O₃ has sulphur and metals (Ni + V) contents of 2.16 wt.% of feed oil and 22 ppm, respectively. This signifies respectively 38.6% and 85.2% reduction of sulphur and (Ni + V) content of the produced oil relative to the feedstock after upgrading. While the produced oil from fixed-bed of pelleted Co-Mo/Al₂O₃ has sulphur and metals (Ni + V) content of 2.50 wt.% offeed oil and 81 ppm, respectively relative to 3.52 wt.% and 149 ppm (feed oil). This represents 29% and 45.6% reduction of sulphur and (Ni + V) content after upgrading with fixed-bed of pelleted Co-Mo/Al₂O₃. This shows therefore that the use of ultrafine particles of Co-Mo/Al₂O₃ further decreased the sulphur and (Ni + V) content by 9.6% and 39.6% compared to that obtained from their pelleted fixed-bed counterpart.

Pelleted catalysts are relatively large with limited surface area compared to ultrafine catalyst, so the accessibility to active sites and interaction with many C–S bonds will be more limited. However, ultrafine catalyst have a large surface-to-volume ratio, easy access to active sites, more particles per unit volume, and therefore the interaction with molecules and C–S bonds will be increased also [34]. Also, some of the sulphur in the heavy oil was removed as a result of catalyst sulfidation during upgrading and coke deposition. Clearly, the cleavage of large carbon chains, removal of sulphur, metals and yield of distillable is greater than their pelleted counterpart. It is important to note that the rejected sulphur and metals during upgrading reactions are associated with deposited coke. This in reality will be left behind in the oil reservoir during

![Fig. 3. Feed and produced oils distillate fractions after upgrading with thermal cracking (batch), pelleted fixed-bed, pelleted catalyst in basket (batch), and dispersed ultrafine catalyst (batch) of Co-Mo/Al₂O₃ catalyst at temperature 425 °C, pressure 20 bar, nitrogen gas media, CTO ratio 0.1, stirring speed 133 rpm (batch), 1 mL min⁻¹ (fixed-bed), and residence time 10 min.](image-url)
3.2.5. Produced gas composition

The produced gas is a major by-product of the upgrading process. This was determined using RGA and the results are presented in Table 7 on the basis of volume of gas analysed (Table 8 on the basis of amount heavy oil fed into the reactor). The THAI-CAPRI process achieves heavy oil upgrading mainly by carbon-rejection, dehydrogenation, and hydrogen-transfer reactions. From Table 7, while 2.4 vol.% (0.137 wt.% of feed oil) hydrogen was produced from fixed-bed catalytic CAPRI, 1.7 vol.% (0.111 wt.% of feed oil) was produced from the dispersed ultrafine catalyst counterpart and 1.5 vol.% (0.0858 wt.% of feed oil) from thermal cracking in batch reactor.

This difference in hydrogen can be attributed to the immediate release of the produced gas from the gas-liquid separator in the fixed-bed, which was not the case with the dispersed ultrafine catalyst. The presence of hydrogen in the gas moreover promotes hydroconversion of the heavy oil fragments into smaller and stable molecules, if the partial pressure of hydrogen is high enough. This hydrogen-transfer reaction could moderate generated free radicals and decrease coke formation, which explains the low yield of coke with ultrafine catalyst compared with the thermal cracking experiment in batch reactor.

The amount of light hydrocarbons gases n(C1-C5) produced from thermal upgrading was higher than that from catalytic upgrading (Tables 7 and 8). This observation is in agreement with the results of normal asphaltene gases detected in the off-gas during thermal upgrading of blend of vacuum residues in a batch reactor by Sawarkar and co-workers [27]. This is because thermal cracking proceeds through a free radical mechanism with methyl and ethyl being the smallest hydrocarbon radicals generated by arbitrary splits of the hydrocarbon chains while catalytic cracking of the hydrocarbon chains in the oil proceeds in a systematic fashion of carbonium ion intermediates and beta-scission. Also, the presence of catalyst promotes the incorporation of materials such as active hydrogen, methyl and ethyl radicals from the gas phase to cracked hydrocarbon fragments in the liquid phase forming a stable molecule. The latter releases a large amount of gas from the promoted carbon-rejection to balance the elemental hydrogen and carbon between the upgraded oil, produced gas, and coke deposit (see Tables 4 and 5 for thermal upgrading alone).

The light hydrocarbon gases C1-C3 produced with dispersed catalyst in the autoclave were higher than that of the fixed-bed. This affirmed the increased rate of reaction with ultrafine catalyst. Hashemi et al. [35] found that in addition to low-boiling fractions being produced, the produced gases generated by in situ upgrading could contribute towards viscosity reduction via miscible displacement and subsequently enhance oil recovery. It is worth mentioning that the produced H2S using dispersed ultrafine Co-Mo/Al2O3 was 4.8 and 8 times more than that produced by fixed-bed process and thermal upgrading respectively (see Table 7). This corresponds to the trend in produced oil sulphur content reduction after upgrading reaction presented in Table 6.

3.3. Effect of catalyst-to-oil (CTO)

In Fig. 4, the effect of CTO on the mass balance of gas, light oil and coke yields after reaction at a temperature of 425 °C, agitation of 500 rpm and 10 min reaction time is presented. Clearly, while the yield of coke and gas decreases, the yield of light oil increases with increasing CTO. During the experiment, the change in composition, temperature and pressure cause the precipitation of asphaltenes as their aliphatic side chains are cracked. However, in thermal cracking (non-catalytic) the asphaltenes readily aggregate thereby leading to high coke formation and less light oil for the experiment without catalyst, at 0 CTO (see Fig. 4). Whilst in the catalytic slurry environment the asphaltenes readily diffuse to the active sites of the catalyst particles and are cracked into light components with hydrogen-transfer helping to stabilise coke precursors, thereby causing less coke formation. This is believed to improve the yield of light oil with increasing CTO.
The yield of liquid product in Fig. 4 increases with CTO, which is consistent with findings of Ortiz-Moreno et al. [10], who reported a similar observation with vacuum residue being transformed to valuable light oil product as catalyst loading increases. Thus, as the catalyst loading falls below 0.02 (g/g), thermal cracking upgrading effect could have been dominant. However, increasing the catalyst loading decreases the thermal cracking effect as the catalytic reaction becomes dominant, resulting in the decreased yield of coke.

The reaction temperature of 425 °C applied here has already been shown to lead to high production of coke and gas with low yield of liquid product [6]. Despite this limitation, the metal contaminants in the feed are deposited on the fine particles as metal sulphides during the reaction, the aggregate could act as supplementary catalyst material such as micrometallic-coke [18]. Therefore, increasing catalyst loading suppresses asphaltene precipitation and moderates the polymerisation and condensation of coke precursors.

3.3.1. Effect of catalyst-to-oil on API gravity and viscosity

The high macromolecular weight components of the heavy oil confer low API gravity and high viscosity to the feedstock. The change in API gravity and the viscosity of the produced oils after upgrading at 425 °C, agitation at 500 rpm, and 10 min reaction time with CTO in the range 0–0.1 (g/g) are presented in Fig. 5.

As CTO increases, the API gravity of the produced oil increases and an opposing trend of viscosity decrease were also observed after reaction. The increase in CTO from 0 to 0.02 (g/g) has a much bigger effect on change in API gravity and viscosity of the produced oil than increase of catalyst from 0.02 to 0.1 (g/g). Considering a trade-off between amount of catalyst used in the reaction and API gravity of produced oil, it was observed that at CTO (0.1 g/g) the produced oil has 27° API compared to 24° API at CTO (0.02 g/g), however given the relatively small difference in API the effect at 0.02 g/g is more economical with only one fifth of the amount of catalyst from the higher loading of 0.1 g/g. However, thermally upgraded oil showed the lowest change in API gravity and highest viscosity at the same conditions.

The viscosity of the produced oil decreased significantly as the CTO increased from 0 to 0.01, but only marginally decreased with further increase of CTO from 0.01 to 0.1 g/g. This reduction of viscosity of the heavy feedstock will enhance fluidity for production as well as pipeline transport to refineries. A similar trend with catalyst loading was observed and reported by Ortiz-Moreno et al. [10]. The observed narrow trend can be attributed to the increase in catalyst active sites per unit mass and more contact with increasing CTO.

3.3.2. Effect of catalyst-to-oil on TBP distribution

In Fig. 6, the amount of the different distillate fractions before and after upgrading using dispersed ultrafine Co-Mo/Al2O3 as a function of CTO is shown. The three major reactions occurring in the slurry upgrading media at 425 °C are: (a) free-radical formation from C–C bonds cleavage, (b) hydrogen-transfer reactions (i.e., hydrogen-abstraction by C–H bond scissions and hydrogen-addition capping free-radicals), and (c) condensation and polymerisation reactions between free-radicals.

It is noteworthy that compared to the feed oil, the produced oils are lighter as CTO increases. Generally, the light fractions are formed at the expense of the heavy fractions, resulting in gas and coke formation. Thus, increasing CTO leads to decreased coke formation (mainly caused by thermal cracking effect). It can also be seen that using low CTO does not alter the level of upgrading significantly compared to thermal cracking, whereas high CTO (0.1 g/g) increases the conversion of heavy fractions (BP > 343 °C). Though liquid yield and API gravity show similar trends, the decrease in liquid and residue fraction (BP > 343 °C) relative to the feed oil indicates that gas and coke are produced at their expense. From Fig. 6, the fraction of the feedstock displaying highest conversion was the residue fraction (BP > 343 °C), with residue fractions after upgrading in the range ~18 to 7.4 vol.% with increasing CTO from 0 to 0.1 respectively. A comparison of the API gravity, viscosity, and yield of distillates with gas, liquid and coke products obtained after upgrading with CTO in the range of 0–0.1, showed that an optimum CTO of 0.02 is more economical.

It can be seen that secondary cracking of middle-distillates (200–343 °C) into low-boiling fractions (IBP-200 °C) increases as the CTO increases in addition to the conversion of heavy fractions (> 343 °C). The decline in the residue and middle distillate fractions with increasing CTO indicates that their conversion contributed to the increase of low-boiling fractions (IBP-200 °C). The improved physical properties (i.e., viscosity and API gravity) of the produced oil after upgrading are a reflection of this observation. Compared with the mass balance presented in Fig. 4, it was shown that
increasing CTO improved the conversion of heavy fractions into valuable liquid product. Therefore, the produced oil containing significant amounts of IBP-200 °C fractions also corresponded to the maximum decrease in viscosity.

3.4. Effect of agitation

In Fig. 7, the effect of agitation on the API gravity and viscosity of the produced oils after reaction using ultrafine Co-Mo/Al₂O₃ at 425 °C, nitrogen reaction medium, 0.02 CTO, and 10 min reaction time is presented. The API gravity of the produced upgraded oils increased from 7.4 to 9.8 points as the agitation increased from 250 to 1000 rpm. It was noted that the level of upgrading achieved at agitation speed 250 rpm is only 1° API higher than that obtained after the thermal cracking experiment. Conversely, the viscosity of the produced oil decreased from 8.1 to 4.8 mPa s, as the agitation increased from 250 to 1000 rpm, relative to the 1091 mPa s (feedstock). It is well known that high viscosity of the heavy feedstock can be attributed to their high content of macromolecular weight species such as resins and asphaltenes. The reduced viscosity is therefore thought to be the result of cleavage reactions of the macromolecules into smaller fragments of lower molecular weight, which increased with agitation.

Evidence of cleavage of heavy molecules can also be seen in the simulated distillation of the samples before and after upgrading (Fig. 8). On average, the extent of viscosity reduction is 99.4% of the original heavy oil. Li et al. [34] found 96% viscosity reduction after upgrading of Xinjiang oilfield heavy oil using carbon nanocatalyst. Clearly, the results showed that fine particulate catalyst activity and performance are controlled by the degree of dispersion in addition to simply the catalyst-to-oil ratio and catalyst composition. An increase in agitation causes improved particle dispersion within the reaction medium, which would reduce the mass transfer barrier between the solid–liquid–gas. At low agitation, the cracking rate could be limited by the extent of contact and the transfer of large molecules to the dispersed catalyst. However, the produced oil reached an optimum API gravity and viscosity at 500 rpm.

The amount of the distillate fractions of the feed and produced oils after reactions at varying agitations from 250 to 1000 rpm are presented in Fig. 8. Compared to the feedstock, the low-boiling
fractions (IBP-200 °C) in the produced oil after reaction increased by 25–32 vol.% as the agitation increased from 250 to 1000 rpm, with 500 rpm giving a maximum of 32.7 vol.% increase. However, a mirror trend can be observed for the middle distillate (200–343 °C) which decreased by 10–15 vol.% as the agitation increases from 250 to 1000 rpm relative to 41.4 vol.% (feedstock). A similar trend can be noticed with the residue fractions (BP > 343 °C). This showed that significant portion of the middle distillates and residue fractions in the feedstock has been converted to low-boiling fraction after reaction. However, low yield of IBP-200 °C fractions and conversion of residue fractions was observed at 250 rpm (see Fig. 8). Also, from 500 rpm and above the level of agitation has an insignificant effect upon the conversion of heavy molecules even though the extent of dispersion and the transfer of molecules have increased.

3.5. Effect of reaction time

Fig. 9 shows the effect of reaction time on the level of upgrading using dispersed ultrafine Co-Mo/Al₂O₃ catalyst at 425 °C, initial
pressure 20 bar (N$_2$), CTO 0.02 (g/g), and 500 rpm agitation. It is clear that while the API gravity of the produced oil increases with reaction time, its viscosity decreases correspondingly. It is important to note that the results at time zero corresponds to the upgrading obtained once the reactor reaches its set operating condition of temperature 425 °C. Therefore some partial upgrading may have occurred during the heating up phase. Furthermore, the extent of upgrading from 0 to 30 min was 1.2° API (increase) and 6 mPa s viscosity (reduction) and from 30 to 60 min was 0.7° API (increase) and 2 mPa s viscosity (reduction), respectively.

Based on these results, the level of improvement obtained after 60 min of reaction time was within a margin of error of ± 0.53 °API and ± 1.1 mPa s relative to that achieved after 30 min of reaction time. Therefore, at 425 °C, 0.02 CTO, and 500 rpm the optimum reaction is 30 min from the set point.

4. Conclusions

The challenges confronting the THAI–CAPRI process involving the use of a fixed-bed of pelleted catalyst surrounding the horizontal production well has led to the investigation of an alternative contacting pattern using dispersed ultrafine catalyst. The comparative studies reported here showed the superiority of ultrafine catalyst. The dispersed ultrafine Co-Mo/Al$_2$O$_3$ catalyst promoted the cracking of larger molecular weight components to light components and produced oil thereafter was less viscous and higher in quality compared to that produced from a fixed-bed of pelleted catalyst. Therefore, injecting nano-sized catalyst into the mobile oil zone (MOZ) during the THAI process could potentially assist the extent of upgrading from 0 to 30 min was 1.2° API (increase) and 2 mPa s viscosity (reduction), and from 30 to 60 min was 0.7° API (increase) and 2 mPa s viscosity (reduction), respectively.

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