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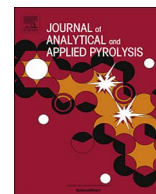
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Laboratory investigation of CAPRI catalytic THAI-add-on process for heavy oil production and *in situ* upgrading

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ABSTRACT

High viscosity and impurities make heavy oil and bitumen extraction, transportation and refining difficult and cost intensive. Subjecting them to catalytic pyrolysis *in situ* with the reservoir as free reactor would significantly enhance extraction, reduce environmental footprint and lower facility cost for surface upgrader. In this study, the catalytic “add-on” to Toe-to-Heel Air Injection (THAI) was simulated in the laboratory with fixed-bed reactor at established optimum conditions (425 °C, 20 barg, and WHSV 9.1 l⁻¹). The liberation of hydrocarbon gases (C₁–C₅) and hydrogen during catalytic upgrading require large carbon-rejection to achieve appreciable level of upgrade. These gases CH₄, C₂H₆ and H₂ have the highest H:C ratio, hence their significant presence in the gas phase could only result in better upgrading in terms of API gravity and viscosity in the early hours of operation provided it was accompanied by high carbon-rejection to conserve C and H between gas, oil and coke phases. As a consequence more coke formation was noticed with Ni/Zelite-Alumina catalyst 21.8 wt% compared to 11.4 wt% (Ni/Alumina) and 26.2 wt% (Alumina). As a function of time-on-stream, the API gravity increases from a value of 12.8° for the THAI feed oil by 1.4° for the first 20 min of reaction, increases by 6° after 120 min, rapidly decreases from 6° to 1.4° between 120 and 280 min, and settles at an average of 2.2°. The viscosity decreased respectively by 87% (Ni/Zelite-Alumina), 79% (Ni/Alumina) and 62% (Alumina) relative to 1.1 Pas (supplied THAI oil) after 920 min operation. The main challenge therefore is to sustain the activity of the catalyst long enough and mitigate the impact of liberated hydrogen and hydrogen-rich gases during the upgrading; possibly by adding external hydrogen-donor source to help suppress coke fouling on the catalyst and supply hydrogen for hydrogenation reactions.

1. Introduction

The world demand for energy continues to rise, but the conventional light crude oil resource is declining [1]. Thus, the refinery barrel is becoming heavier as companies increase their intake of heavier crudes. However, heavy crudes are more difficult and costly to produce, transport and refine. The energy necessary to produce and upgrade a barrel of heavy oil into a synthetic light oil (30° API) can be very high, hence balancing economics throughout the project is a challenge [2]. Therefore, effective and low cost reservoir technologies are required to exploit this huge resource. Heavy oil is a complex nanofluid (*i.e.*, the oil contains colloidal suspension of asphaltene nanoparticles) [3], in which nano-aggregates of asphaltenes dominate phase behaviour [4], during extraction, transportation and refining. It is dense and characterised with an API gravity less than 20°, high viscosity, high heteroatom (*e.g.*, S, N, *etc.*) and metals (*e.g.*, Ni, V, *etc.*), because of the high content of resins and asphaltenes.

These characteristics make production, pipeline transportation and refining a challenge [5]. Hence, diluents are used to aid pipeline transportation while a surface upgrader is employed prior to refining. To circumvent this capital expense, sub-surface upgrading *in situ* has been investigated in which the reservoir is seen as a “free reactor” [6]. One means of configuring the reservoir as a catalytic reactor is by combining the ‘short-distance’ displacement THAI *in situ* combustion recovery process with the ‘add-on’ CAPRI (*i.e.*, Catalytic upgrading PProcess *In situ*) for *in situ* catalytic upgrading process. The White Sand pilot, Conklin, Alberta, Canada THAI project was implemented in the Direct Line Drive (DLD) configuration and operated for 5 years (2006–2011). No premature oxygen breakthrough was observed and *in situ* upgrade of produced oil was 4–5° API [7]. Consequently, the Kerobert pilot field trial at Saskatchewan, Canada with the viscosity of the original oil in place 33 Pa s operated DLD configuration for 3.5 years (200–2012). It was also reported that no premature oxygen breakthrough, oil production up to 22m³/day/well and produced oil

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upgraded by 3–4° API [7]. The catalytic form of THAI is called CAPRI uses a pelletized catalyst-activated gravel packing surrounding the entire horizontal producer of THAI. The mobilised THAI oil, which is already partially upgraded, flows through the annular layer of CAPRI catalyst, so that it is further upgraded before flowing into the horizontal production well. The resulting, *in situ* upgraded oil is achieved for only a small incremental investment (gravel packed catalyst, or pre-installed liner). Partially upgraded oil produced via the THAI-CAPRI process can therefore significantly reduce the cost of operating surface upgraders [6,7]. Furthermore, since the viscosity of the partially upgraded oil is reduced by several orders of magnitude, it can be pipelined to the refinery without the need for a diluent. Hence, CAPRI is a catalytic augmentation of the THAI process with a very limited piloted field trial.

The subsurface process of THAI-CAPRI can potentially enhance production and partially upgrade heavy oil and bitumen with a reduced environmental footprint and cost [6,8–12]. Catalyst driven *in situ* pyrolysis of heavy oil and bitumen commonly improves naphtha and middle distillates product yields. Zeolite catalysts are commonly used in oil refining and petrochemicals production, because they possess stronger acid sites and activity superior to those of alumina and silica [13]. Hence, zeolite has greater cracking ability. Catalyst supports play a key role in influencing the functionalities of the active components [14]. Zeolites such as NaY, USY, ZSM-5, and β -zeolite have been used as supports. Kurmaran et al. [14] reported the test results of hydrodesulfurisation (HDS), hydrogenation (HYD), and hydrocracking (HCK) using prepared Mo and Co/Ni supported on H- β -Zeolite at 400 °C. This study will evaluate the effect of catalyst support and its contributions to the level of upgrading.

Kim et al. [15] studied upgrading of bitumen-derived heavy oil using Ni-Mo/Al₂O₃ catalyst over the temperature range 352–412 °C and LHSV of 0.14–0.80 h⁻¹, at 13.7 MPa. The API gravity decreased from 16° to 13.5° as the time-on-stream increased from 0 to 500 h compared to 9.2° API (feed oil). This decrease in API gravity with time was attributed to catalyst deactivation as a result of inhibition of activity by coke from cracked hydrocarbons. At the experimental conditions of 425 °C, 20 bar, the oil weight hourly space velocity (WHSV) 9 h⁻¹ and Gas Hourly Space Velocity (GHSV) 5882.4 h⁻¹, Hart et al. [17] reported that the API gravity of the upgraded oil samples using Ni-Mo/Al₂O₃ catalysts increased from 19 to 21° starting at 13° API over 200 min of the experiment, but then decreased to about 16° after 200 min, remaining there for the rest of the experiment. Furthermore, Xia et al. [8] reported a 3-dimensional combustion cell experiment of the THAI-CAPRI, it was found that the oil API gravity and viscosity improved substantially in the THAI operation (respectively from 10.5 for the feed to 17.8° API for the upgraded oil and viscosity ~44 Pa s to 0.22 Pa s), which further increased in the CAPRI phase (23.1° API and minimum 0.025 Pa s) for Wolf Lake heavy oil with the catalyst not seriously affected by coke deposition. Thorough optimisation of the CAPRI process was conducted by Shah et al. [16] and Al-Marshed et al. [10], from which they found an optimum condition of 425 °C, 20 bar, the oil WHSV 9 h⁻¹ and GHSV 5882.4 h⁻¹ (nitrogen flow). More recently, the effect of hydrogen, methane, THAI gas (13% CO₂, 3% CO, 4% CH₄, and 80% N₂) and nitrogen as reaction media on the extent of upgrading and coke formation was investigated and reported by Hart et al. [17]. They found the level of upgrading to follow H₂ > CH₄ > THAI gas > N₂. The results obtained from the experiments, using a simulated section of the CAPRI reservoir reactor, indicate that additional upgrading of 2–5° API points is possible. Overall, this amounts to a total *in situ* upgrading of the produced oil of between 6 and 9° API points, potentially worth up to \$12/barrel, depending on crude oil price.

Most of these studies on *in situ* catalytic upgrading (upgrading within the reservoir) focus mainly on the extent of upgrading by assessing the upgraded oil samples and quantifying coke formation, with little or no attention has given to the liberated gas during cracking reactions. The liberated gas phase is rich in hydrogen (H₂, CH₄, C₂H₆,

Table 1
Properties of the THAI oil.

Properties	Results	Units
Density (20 °C)	0.9776	(g cm ⁻³)
API° gravity (20 °C)	12.8	(°)
Dynamic viscosity (20 °C)	1.1	(Pa s)
Asphaltene Content	13.6	(wt%)
Elemental analysis		
C	84.72	(wt%)
H	10.77	(wt%)
N	0.08	(wt%)
S	3.09	(wt%)
Ni	41	(ppm)
V	108	(ppm)
(Ni + V)	149	(ppm)
Simulated Distillation (SIMDIS) ASTM D2887		
Naphtha Fraction (Initial Boiling Point, IBP–177 °C)	10	(vol.%)
Distillate Fraction (177 °C–343 °C)	39.1	(vol.%)
Heavy Fractions (343 + °C)	50.4	(vol.%)

N.B. The calibration mix of the Simulated Distillation method on the Agilent 6850N GC contains hydrocarbons from C₅ to C₄₀. The maximum oven temperature is 280 °C; hence, macromolecules such as resins and asphaltenes outside this carbon range cannot be accounted for by this method (0.5% cannot be analysed by the GC due to low volatility).

C₃H₈, etc.) which depletes amount of hydrogen available in the reaction media; hence to achieve significant upgrading would require consequent carbon rejection to conserve H:C balance in the gas, liquid (upgraded oil) and solid (*i.e.*, coke) phases. This study relates the gas behaviour and the extent of upgrading achieved with the upgraded oil, by monitoring the concentration of the hydrogen rich gases such as hydrogen, methane and ethane and relates it with the observation in API gravity, viscosity and coke formation. Consequently, the role of the support and impregnated Ni metal was evaluated in terms of API gravity, viscosity, coke formation and produced oil distillates.

2. Experimental

2.1. Materials

The partially upgraded THAI oil used in this study was supplied by Petrobank Energy and Resources, Ltd. (now Touchstone Exploration Inc.), Canada. The heavy oil is a mixture of produced oils from eight separate well sections of the THAI process at Kerrobert, Saskatchewan, Canada; a conventional heavy oil field, previously operated on cold production. Table 1 displays the properties of the feedstock oil, as received. The THAI-produced oil is partially upgraded via *in situ* thermal cracking THAI and so its physical and chemical properties are significantly improved compared to the original reservoir crude.

2.2. Catalyst

A commercial cylindrical Ni/Alumina and prepared Ni/Zeolite-Alumina catalysts were used in this study. It has been reported that by modifying the catalyst support it is possible to improve its activity, stability, and selectivity as the surface properties are manipulated [18]. In this regard, a zeolite Ni-based catalyst was prepared by the incipient wetness impregnation method. 12 g of Ni(NO₃)₂·6H₂O was dissolved in 20 mL ethanol and 10 g HY-zeolite (*i.e.*, Zeolite) was added. The mixture was stirred vigorously for 2 h using a magnetic stirrer. After impregnation, the samples were filtered and dried at room temperature overnight, followed by calcination at 500 °C for 4 h in a muffle furnace. Furthermore, dry phase mixing of 50 wt.% of Ni/HY-zeolite and 50 wt.% of commercial alumina boehmite, was followed by peptization with 5% (v/v) acetic acid (CH₃COOH). Extrusion was performed and the extrudates were subsequently dried at 100 °C for 5 h and calcined at 500 °C for 5 h. The flowchart for the catalyst preparation is shown in

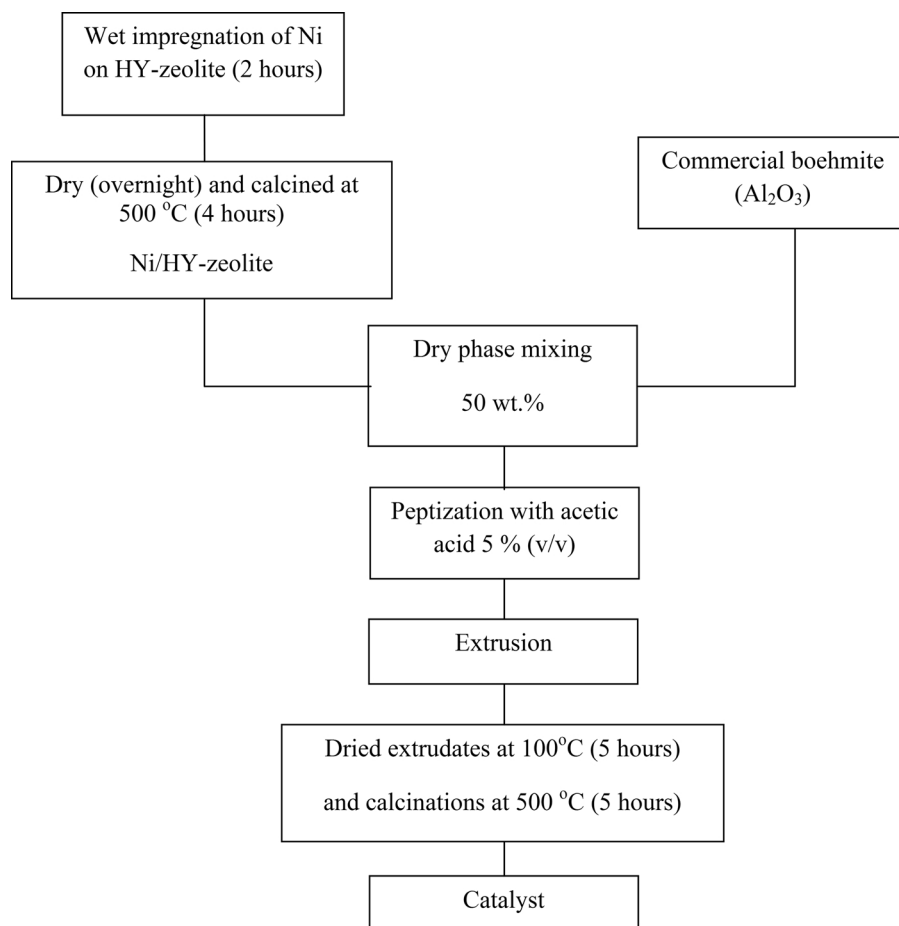


Fig. 1. Flowchart of the Ni/HY-Zeolite-Alumina catalyst synthesis.

Fig. 1. The composition and physical properties of the synthesised zeolite Ni-based catalyst was determined by X-ray fluorescence (XRF) analyser and nitrogen sorption, Brunauer–Emmett–Teller (BET) analysis, respectively. Zeolite was considered because of its use in oil refining processes such as catalytic cracking (e.g., FCC). The acidity of the catalyst was measured by Temperature Programmed Desorption (TPD) of t-butylamine in the temperature range of 50–500 °C using Micromeritics AutoChem II chemisorption analyser. The catalyst exhibited three different acid sites in the temperature range 15–250, 250–350 and 350–450 °C, but the acidity strength reported here is total sum.

2.3. Heavy oil upgrading apparatus

The experimental setup was built and commissioned at the School of Chemical Engineering, University of Birmingham, UK. The laboratory micro-reactors are used to replicate underground catalytic upgrading achievable with CAPRI add-on to THAI process and have been described in detail elsewhere [11,19]. Concisely, the micro-reactors are fixed catalytic bed representing cylindrical core of 1 cm diameter and 11.6 cm (catalyst bed) height taken in the radial direction of the annular packed gravel catalyst along the horizontal producer well. The length of the reactor tube is 41 cm. The reactors have three distinct zones: pre-heating, catalyst bed and post reaction zones. The first zone was packed with inert glass beads 3 mm in diameter to a length of 9.3 cm to ensure spread of oil and gas as they flow through the catalyst bed and subsequently enhance the radial contact and less axial mixing. Hence, the CAPRI reactor was replicated in the laboratory as a fixed catalytic bed reactor (bed porosity = 0.48) with spray flow pattern or regime based on the gas (10.55 m s^{-1}) and the oil (0.03 m s^{-1}) volumetric fluxes. The spray regime is characterised by low oil flow rate, high gas flow rate (i.e., large gas-to-oil ratio), gas phase is continuous

and oil phase discontinuous and the droplets entrained in the packed catalyst due to high gas velocity. The middle zone contains the catalyst bed comprised of 6 g of catalyst pellets. The post reaction zone of the reactor was also packed with an inert glass beads to facilitate the disengagement of the gas-oil mixture by the impingement of oil droplets upon the beads. The experimental conditions are presented in Table 2. These conditions have been reported as optimum [10,11,16].

A control experiment was carried out using Alumina, to validate the roles of impregnated Ni metal and the catalyst support.

2.4. Product analysis

The API gravity of the heavy and upgraded oils was measured using an Anton Paar DMA 35 portable density meter (Anton Paar GmbH, Austria) at 20 °C and reported in g cm^{-3} . Likewise the oil viscosity, was determined using Advanced rheometer AR 1000 (TA Instruments Ltd, United Kingdom) with an aluminium plate of diameter 40 mm and a parallel plate gap size of 150 μm , a shear rate of 100 s^{-1} and

Table 2
Experimental Condition.

Parameter	Value
Temperature (°C)	425
Pressure (bar)	20
Feed oil flow rate (mL min^{-1})	1
Gas-to-oil ratio (mL mL^{-1})	500
Residence time (minutes)	6
WHSV (h^{-1})	9.1
GHSV (h^{-1})	5882.4
LHSV (h^{-1})	11.8

temperature 20 ± 0.1 °C. The extent of viscosity reduction (EVR) is calculated using equation 1.

$$\text{EVR (\%)} = (\mu_0 - \mu) / \mu_0 \times 100 \quad (1)$$

where; μ_0 and μ viscosity of the THAI feed oil and produced oils (Pa.s), respectively.

SIMDIS with Agilent 6850N gas chromatography (GC) calibrated in accordance with the ASTM D2887 was used to characterize the feed and upgraded oils. The amount of coke deposited on the catalyst after experiment was determined using a thermogravimetric analyser (TGA) (NETZSCH-Geratebau GmbH, TG 209 F1 Iris[®] instrument). The analysis method was programmed as follows; a linear ramp temperature from 25 to 900 °C at a heating rate of 10 °C.min⁻¹ and an isothermal of 900 °C for 10 min under air atmosphere with flow rate of 50 mL.min⁻¹. The composition of the gas liberated from the catalytic upgrading was analysed using an Agilent 7890A GC to determine the percentage of the various component of gases such as H₂, CO, CO₂, and C₁–C₅ hydrocarbons present in the gas phase. A detailed description of the equipment and methods can be found in Hart [20].

3. Results and discussion

3.1. Catalyst characterisation

Most studies on the catalytic upgrading of heavy oil have been carried out using Co-Mo, Ni-Mo, Ni-W, etc. hydrotreating catalysts supported on alumina or alumina-silica. The cracking activity of these catalysts is attributed to the acid sites of the support while the metals perform hydrogenation function. Table 3 shows the properties of the prepared Ni/Zelite-Alumina and commercial Ni/Alumina catalyst.

The BET N₂ adsorption-desorption isotherm for the commercial Ni/Alumina and prepared Ni/Zelite-Alumina catalyst both cylindrical are presented in Fig. 2.

The adsorption–desorption curves of both catalysts reveal a large hysteresis loop in their isotherm indicative of the type IV which is mesoporous. It also shows that Ni/Alumina possesses greater pore volume than Ni/Zelite-Alumina, which is revealed by the size of hysteresis loop and the volume of adsorbed (Fig. 2). From Table 3 however Ni/Zelite-Alumina has higher surface area when compared to the Ni/Alumina catalyst, because the majority of its pore sizes are microporous contributed by the zeolite portion of the support materials.

3.2. API gravity and viscosity

The API gravity and viscosity of the produced oil are basic benchmarks and have been used to ascertain the extent of upgrade in this study. The upgraded oil API gravity and viscosity as a function of time-on-stream for the prepared Ni/Zelite-Alumina, the commercial Ni/Alumina and the control experiment with Alumina are presented in Fig. 3. From Fig. 3a, the API gravity of the upgraded oil samples increased from 12.8° for the feed oil by 1.4–6° in 120 min, and from 120

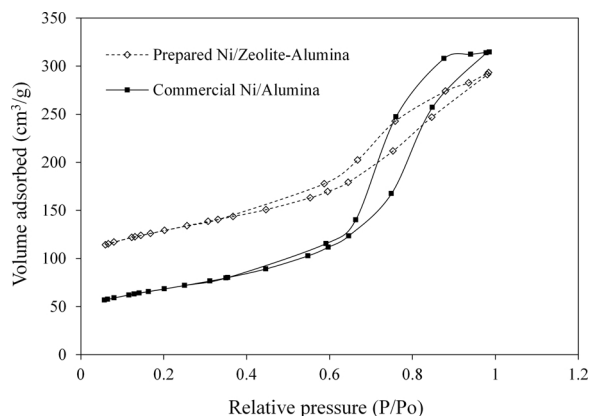


Fig. 2. Nitrogen adsorption-desorption isotherm of the Ni/Zelite-Alumina and Ni/Alumina catalysts.

to 280 min it rapidly decreases to 1.3° and thereafter settles at an average of 2.2° upon the use of Ni/Zelite-Alumina catalyst. Whilst for the use of Ni/Alumina catalyst, the API gravity increased from 0.6 to 4.4° in the time range 0–210 min, decreases rapidly to 1° at 410 min and finally settles at 1.2° for the rest of the experiment. It is clear therefore that except between 200 and 300 mins, the upgraded oil samples obtained using prepared Ni/Zelite-Alumina catalyst have higher API gravity compared to those of the commercial Ni/Alumina catalyst. A similar trend in API gravity and viscosity of upgraded oil samples has been observed and reported by Kim et al. [15] and Hart et al. [12] for Ni-Mo/Alumina catalyst.

On the other hand, the use of alumina without Ni metal impregnated produced oil whose API gravity increased to a maximum of 6° in 90 min and drastically fell to approximately 1° after 200 min. Beyond 400 min the API gravities of the produced oils approach that of the THAI oil, and between 700 and 900 min the produced oil API gravity measured 0.01–0.2° less than 12.8° API for the THAI oil. The acid sites of the Alumina could have contributed remarkably in cracking high molecular weight hydrocarbons which improved the API gravity of the produced oil at the early minutes of the experiment [20]. This shift in composition towards light end hydrocarbons could have caused the polymerisation and condensation macromolecular weight compounds, thus leading to the decrease in API gravity compared to that of the THAI oil observed after 600 min. The asphaltene content of the produced oil after 400 min was measured. It was found to be 0.2–0.6 wt.% higher than 13.6 wt.% (THAI oil), which reaffirmed polymerisation and condensation of active hydrocarbon intermediate species into macromolecular weight species such as asphaltene.

Referring to Fig. 3b, the viscosity of the upgraded oil samples with respect to time-on-stream represents an opposite trend to that of the API gravity. While the overall viscosity of the upgraded oil with Ni/Zelite-Alumina catalyst settles at 0.14 Pa s that of Ni/Alumina catalyst settles at 0.23 Pa s, which is 0.09 Pa s higher than that of Ni/Zelite-Alumina catalyst. This represents 86.5% (Ni/Zelite-Alumina catalyst) and 79% (Ni/Alumina) reduction compared to the viscosity of the THAI oil fed (1.1 Pa s). The viscosity of the produced oil using alumina without Ni metal relaxes at about 0.42 Pa s, that is 62% reduction compared to 79% achieved upon the incorporation of Ni. The Ni metals would have supported indirect hydrogenation of intermediate hydrocarbon fragments (i.e., free radicals) using liberated hydrogen from cracking of hydrocarbons, ring opening or conversion of aliphatic hydrocarbons to olefins [9,20]. Hence, the absence of Ni explains the polymerisation and condensation of these radicals to macromolecular weight species as noticed in the increased asphaltene content, decreased API gravity and increased viscosity of the produced oil using alumina with time-on-stream.

The catalytically active metal Ni impregnated on the Alumina and Zeolite-Alumina supports induced bifunctionality (i.e., acidic and

Table 3
Properties of used catalysts.

Composition	Amount	
	Ni/Zelite-Alumina	Commercial Ni/Alumina
HY-zeolite (wt%)	46.8	
Al ₂ O ₃ in support (wt%)	36.2	42.5
SiO ₂ in support (wt%)		39.4
NiO (wt%)	17	18.1
Diameter × length (mm)	3 × 4.3 ± 1.2	1.8 × 5.2 ± 1.9
Specific surface area (m ² g ⁻¹)	444.1 ± 5.85	239.7 ± 1.52
Average pore diameter (Å)	62.3	85.2
Total acidity (mmol/g catalyst)	0.52	0.38

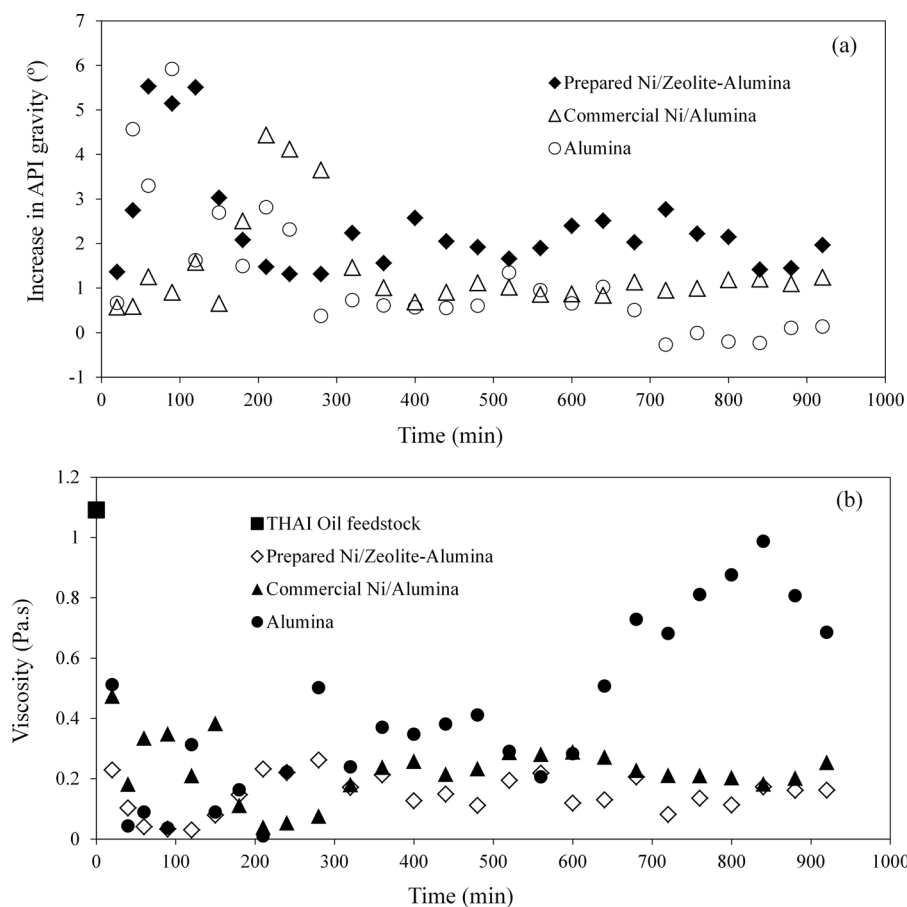


Fig. 3. Upgraded oil (a) API gravity increase and (b) viscosity as a function time-on-stream at temperature 425 °C, pressure 20 barg, WHSV 9.1 h⁻¹ and GHSV 5882.4 h⁻¹.

metal). While the acid sites promote cracking of large molecular weight compounds, the Ni metal performs hydrogen-transfer functions. However, the inherent sulphur in the heavy oil can readily form Ni-S [21]. This results in the gradual conversion of the Ni metals present in oxide form on the supports to the active sulphide form due to sulphidation process by the sulphur containing compounds present in the feed oil [22]. This explains the early observation in API gravity and viscosity from 0 to 120 min (Ni/Zelite-Alumina catalyst) and 0–210 min (Ni/Alumina catalyst). However, the rapid decrease after achieving maximum API gravities can be attributed to the loss of catalytic activity due to early coke deposits upon the catalyst as result of cracking heavy hydrocarbons in the feed oil. Consequently, the additional increase in API gravity observed for the upgraded oil using Ni/Zelite-Alumina catalyst can be attributed to the molecular sieve structure of the zeolite and their crystalline aluminosilicates nature enhance the cracking functions, because the Si-O-Al framework within the zeolite pore channels optimise the acid strength (see Table 3) and distribution within the catalyst [23]. It is well known that these acid sites promote cracking and isomerisation reactions while the metal (*i.e.*, Ni) supports hydrogen transfer reactions [20]. Conclusively, the type of support had a remarkable effect on the performance and activity of the catalyst used in upgrading heavy oil.

3.3. True boiling point (TBP) distribution

Fig. 4 shows the change in boiling range distribution of the THAI partially upgraded heavy oil before and after further upgrading with commercial Ni/Alumina, the control experiment with Alumina and prepared Ni/Zelite-based alumina catalysts at the same conditions. Due to the occurrence of upgrading, 50% cumulative amount distilled from the TBP curves occurred at 333 °C (THAI oil), 317 °C (upgraded oil

with Alumina), 310 °C (upgraded oil with Ni/Alumina) and 301 °C (upgraded oil with Ni/Zelite-Alumina). This represents 16, 23 and 32 °C shift to the left of the temperature axis, for upgraded oil with Alumina, Ni/Alumina and Ni/Zelite-Alumina, respectively. This implied the presence of lighter boiling hydrocarbon components in the upgraded oils than the THAI oil.

To establish changes in composition of the heavy and upgraded oils, the TBP data were deduced by grouping them into several boiling range fractions, the naphtha fraction IBP–177 °C is about 15 vol.% (upgraded oil with Ni/Zelite-Alumina), 11 vol.% (upgraded oil with Ni/Alumina) and 10 vol.% (heavy oil) while the middle distillate fractions between 177 and 343 °C is 48 vol.% (upgraded oil with Ni/Zelite-Alumina), 51.5 vol.% (Ni/Alumina) and 39.1 vol.% (THAI oil). While the naphtha fraction of the upgraded oil with Ni/Zelite-Alumina catalyst was 4% higher than that of Ni/Alumina, the latter middle distillate fraction was 3.5% higher. This is because the yield of naphtha fractions is promoted by the acid sites of aluminosilicates of the Ni/Zelite-Alumina catalyst. This result is consistent with those reported for the API gravity and viscosity of the upgraded oil, which showed that the lighter hydrocarbons of the naphtha fraction in the upgraded oil with prepared Ni/Zelite-Alumina catalyst could have contributed.

The TBP curves of the upgraded oils by alumina and Ni/Alumina was approximately identical from IBP – 280 °C, and beyond this temperature, the upgraded oil by Ni/Alumina contains more middle distillates than that obtained upon the use of Alumina. The high yield of naphtha fractions compared to middle distillates when Alumina was used confirmed cracking characteristics of its acid sites. Notably, the TBP curve of upgraded oil by Alumina and that of the THAI oil feedstock were identical from temperature of 400 °C, which reaffirmed the polymerisation of intermediate radicals upon the use of Alumina without Ni impregnated.

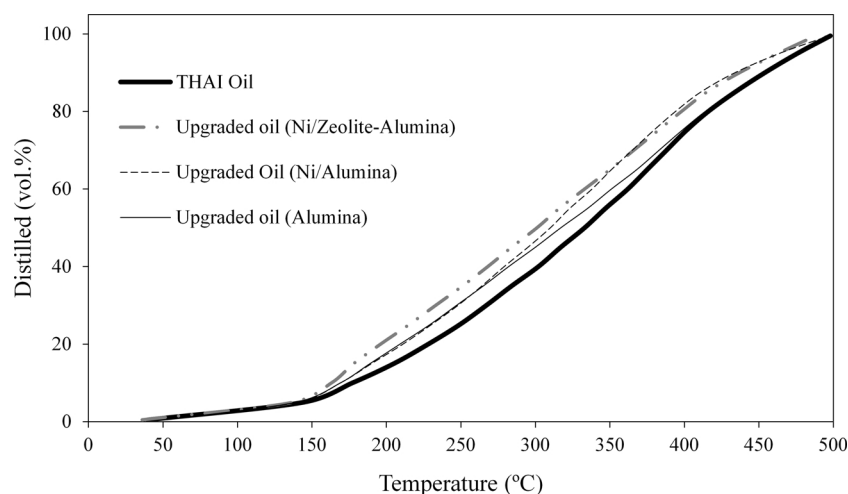


Fig. 4. TBP distribution curves for the THAI oil and upgraded oils with Ni/Zelite-Alumina, Ni/Alumina and Alumina catalysts at temperature 425 °C, pressure 20 barg, WHSV 9.1 h⁻¹ and GHSV 5882.4 h⁻¹.

3.4. Coke

The activity and performance of heterogeneous catalyst used for heavy oil upgrading is impeded by coke formation from the cracking of large molecular weight hydrocarbons and metals deposits. In this study, the deposited coke on the catalyst after upgrading experiment is determined by TGA. Fig. 5 shows the thermograms of weight loss curves (TGA) and derivative of the weight loss curve (DTG) as a function of ramp temperature for the recovered catalyst after experiments. It has been reported that the burn-off observed beyond 600 °C during the TGA of the coked catalyst can be defined as coke [11,24–29].

It can be observed that the weight loss curve (TG) of the Ni/Alumina lies above that of the Ni/Zelite-Alumina and Alumina catalyst after the same time-on-stream experiments of 15 h 33 min. This means the amount of coke formed upon the use of Ni/Alumina catalyst is lower than that of Ni/Zelite-Alumina and Alumina catalyst. Quantitatively, the coke content of the recovered catalyst at the end of experiment is 11.4 wt% (Ni/Alumina), 26.2 wt% (Alumina) and 21.8 wt% (Ni/Zelite-Alumina). The higher coke content observed for Ni/Zelite-Alumina catalyst can be ascribed to the strong acid sites of the incorporated zeolite, which have been documented to promote cracking of large molecular weight hydrocarbons. Moreover, zeolite-based catalysts are known to possess small pores which are prone to plugging from coke deposit when hydrocarbons are cracked. Coke formation

contributed to loss of activity in the early 2 h of reaction as revealed in the API gravity and viscosity (Fig. 3).

At the end of the experiment with Alumina, 26.2 wt.% coke content was observed compared to 11.4 wt.% for Ni/Alumina catalyst. This increased coke formation can be attributed to the increased hydrocarbon cracking promoted by the acid sites of the Alumina without the hydrogenation functionality of Ni metal [20]. The high coke formation in the first 90 min of the reaction could have contributed to the increased API gravity and the lower viscosity observed in the upgraded oil by Alumina in 90 min (Fig. 3a). Beyond 90 mins, the deposited coke would have rapidly deactivated the Alumina acid sites as revealed in the significant drop in API gravity while the polymerisation and condensation of radicals resulted to more coke formation as observed in its coke content. Hence, the hydrogen-transfer function of the Ni impregnated in Ni/Alumina contributed to the decreased coke content observed for the same experimental conditions.

3.5. Produced gas

The produced gas compositions for the use of Ni/Zelite-Alumina and Ni/Alumina catalysts are presented in Table 4. Typical gas composition for thermal and catalytic upgrading has been reported in Hart [20] and Hart et al. [12]. The presence of isomers (iC₄-C₅) in the produced gas composition is an indication that catalytic cracking reaction

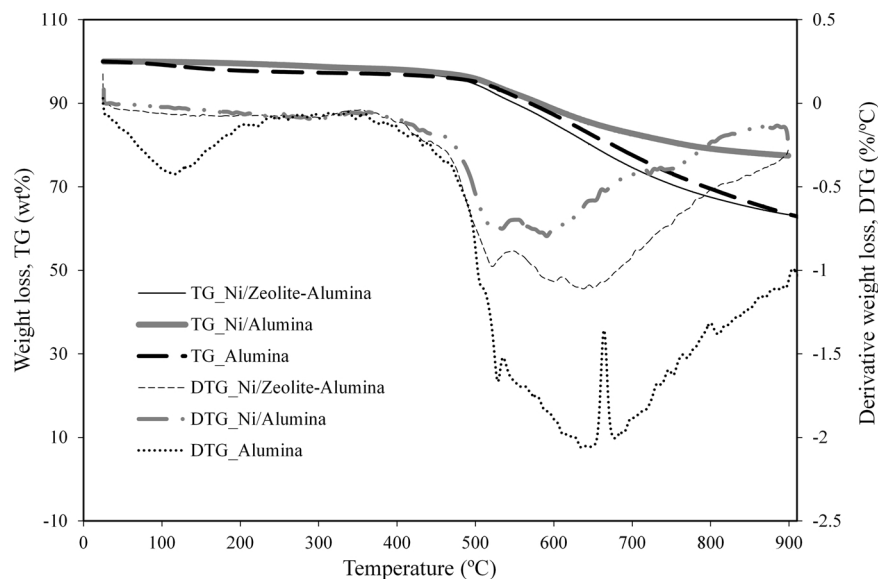


Fig. 5. Thermogram of recovered Ni/Zelite-Alumina, Ni/Alumina and Alumina catalysts after experiment at reaction temperatures of 425 °C, pressure 20barg, WHSV 9.1 h⁻¹ and GHSV 5882.4 h⁻¹.

Table 4
Produced gas composition for Ni/Zeolite-Alumina and Ni/Alumina catalyst.

Gas components	Ni/Zeolite-Alumina (vol.%)	Ni/Alumina (vol.%)
CH ₄	0.511	0.419
H ₂	1.270	1.970
C ₂ H ₆	0.360	0.280
CO ₂	0.022	0.030
C ₂ H ₄	0.080	0.040
C ₃ H ₈	0.234	0.131
C ₃ H ₆	0.096	0.078
i-C ₄ H ₁₀	0.103	0.032
n-C ₄ H ₁₀	0.135	0.071
1-C ₄ H ₈	0.035	0.048
cis-2-C ₄ H ₈	0.010	0.010
trans-2-C ₄ H ₈	0.010	0.030
n-C ₅ H ₁₂	0.100	0.050
i-C ₅ H ₁₂	0.123	0.027
CO	0.020	0.020
Total Olefins	0.231	0.206
Total Paraffin	1.566	1.010

N.B. The reported values are average of 10 periodic gas analyses with the following standard deviations in the range of ± 0.003 – 0.15 (C₁–C₅), ± 1.01 (H₂) and ± 0.01 – 0.03 (CO and CO₂).

occurred, because they are promoted by the acid sites of the catalysts. The liberation of light end hydrocarbons (*i.e.*, nC₁–C₅, iC₄–C₅, Olefin (C₂–C₄) and H₂), implies high carbon rejection is needed to converse the elemental hydrogen and carbon distribution between the gas, upgraded oil and coke in order to achieve significant upgrading. It can be seen in Table 4 that more paraffinic and olefinic gases were produced in the presence of Ni/Zeolite-Alumina catalyst compared to Ni/Alumina. Hence, for the level of upgrading observed in the API gravity and viscosity presented in Fig. 3 and the TBP curve (Fig. 4), sufficient carbon rejection is required which is supported by the high coke content of Ni/Zeolite-Alumina observed in Fig. 5.

The hydrogen in the gas is a product from cracking of hydrocarbons, ring opening and dehydrogenation of aliphatic hydrocarbons to olefins. It originates from two reaction routes: first through hydrogen subtraction from the excited saturated hydrocarbon to form an unsaturated hydrocarbon molecule (olefin or aromatic). Second, C–H bond cleavage can produce hydrocarbon radicals and active hydrogen. The active hydrogen on collision with the next hydrocarbon molecule could abstract hydrogen to form a hydrogen molecule, as illustrated by reaction equations 2–4 [19]. As a consequence, the hydrocarbon radical would continue to grow further resulting polymerisation and condensation to

coke precursor, which is deposited on the catalyst surface leading to coke formation due to continuous hydrogen removal.



where, R is a hydrocarbon molecule.

Since these hydrogen and H-rich gases are liberated from the catalytic upgrading of heavy oil, it would require adequate carbon rejection to achieve appreciable level of upgrade. Hence, in order to suppress carbon deposition on the catalyst it would be necessary to supply hydrogen in some form. However, this would be prohibitively expensive to supply directly into the reservoir. It is possible to operate a form of wet combustion that could generate enough hydrogen via water – gas shift to mitigate the severity of carbon deposition and deficiency of hydrogen, depending on the pressure.

3.5.1. Hydrogen, methane, ethane and carbon dioxide

The smallest and stable free radicals in the reaction media during the catalytic upgrading process are active hydrogen, methyl, and ethyl radicals. These radicals capture hydrogen or hydrocarbons radicals to form stable hydrocarbon and/or a new radical. Their incorporation is aided by the Ni metal and the support acidic sites. The produced hydrogen, methane, ethane, and carbon dioxide gases as a function of time-on-stream are presented in Fig. 6(a–d). The concentration of hydrogen, methane, and ethane gases in the produced gas phase decreased with time-on-stream. The presence of these gases could help to halt free radicals aggregation which would reduce the chances of forming larger molecular weight species in the reservoir, which is not the case in this study. Table 4 shows the detailed gas composition limited to the calibration gas.

Higher concentration of methane and ethane as well as hydrogen in the gaseous stream have two main demerits for the catalytic pyrolysis: 1) these gases abstract more hydrogen from the heavy oil (*e.g.*, methane consumes four hydrogen per carbon and ethane six hydrogen per two carbon atoms), and 2) it would be difficult to remove hydrogen from methane and ethane once liberated into the gas phase and incorporate such hydrogen onto a free radicals in the reaction medium. It is noteworthy in Fig. 6a that hydrogen liberated at the early stage of the experiment with Ni/Alumina was higher than that of Ni/Zeolite-Alumina, with lower coke content (*i.e.*, less carbon-rejection) observed in Fig. 5, which explain the level of upgrading reported in Figs. 3 and 4. However, under the reservoir enclosure, these gases can actively participate in the catalytic upgrading reaction by helping to suppress coke

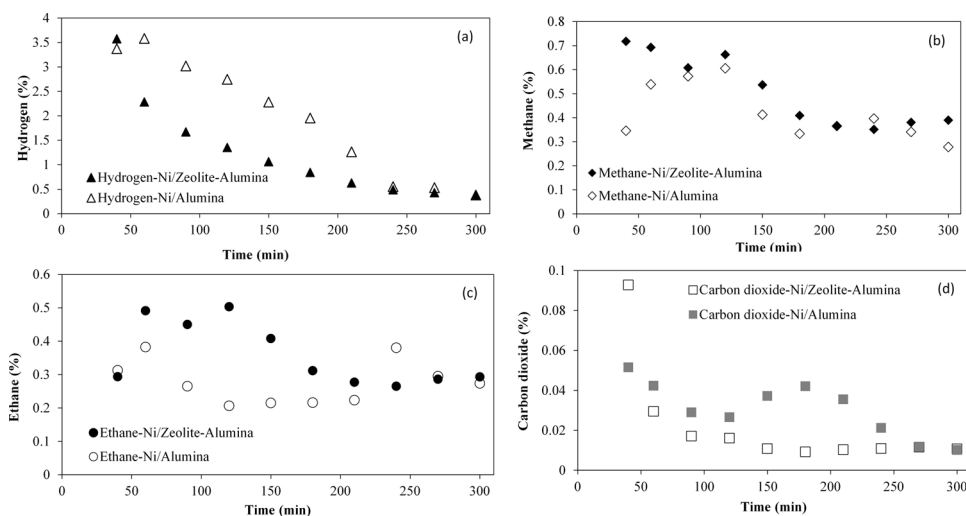


Fig. 6. The concentration of (a) hydrogen, (b) methane, (c) ethane and (d) carbon dioxide in the produced gas as a function of time-on-stream during upgrading with Ni/Zeolite-Alumina and Ni/Alumina catalysts at temperature 425 °C, pressure 20 barg, WHSV 9.1 h^{−1} and GHSV 5882.4 h^{−1}.

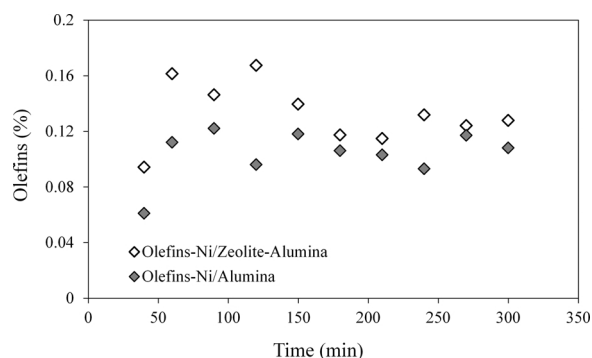


Fig. 7. The concentration of olefins in the produced gas as a function of time-on-stream during upgrading with Ni/Zeolite-Alumina and Ni/Alumina catalysts at temperature 425 °C, pressure 20 barg, WHSV 9.1 h⁻¹ and GHSV 5882.4 h⁻¹.

formation while improving viscosity and API gravity as reported in Hart et al. [17]. The presence of hydrogen in the produced gas could potentially support an indirect hydrogenation reaction provided the pressure is within the range 30–150 bar, activated by the metal and acid sites of the catalyst. Furthermore, Ovalles et al. [30] reported the mechanism of methane activation using MoS₂ catalyst at a reaction temperature of 420 °C and pressure of 0.3 MPa. It was observed that methane decomposes to form CH_x (where x = 1, 2, or 3) and H_{4-x} species on the surface of the catalyst, with the richness of methyl (CH₃) species which can be incorporated onto free radicals to form methylated products. While the H_{4-x} species are available to hydrogenate other free radicals within the reaction medium; coke formation could be suppressed and sulphur removed in the form of H₂S.

It is well known that the elemental balance (i.e., C and H) between the upgraded oil, gas and coke phases should equate that of the THAI feed oil; hence, the continuous liberation of these hydrogen rich gases from the catalytic upgrading process is detrimental to the process without an external hydrogen-donor source. The concentration of hydrogen atom available for transfer in the oil-phase is higher than that of the gas-phase; hence it is easier to remove hydrogen from the oil-phase [31]. The amount of hydrogen present in the gas-phase at any time is not enough (Table 4) to hydrogenate olefins and suppress coke formation as they are readily removed from the reaction medium based on the configuration used in this study, whereas in reality they would have been contained within the reservoir to support hydrogenation and hydrocracking reactions. The decreasing production of hydrogen and methane with time from the reaction is due to the fouling of the catalyst active sites by coke.

3.5.2. Olefins

The olefins considered here are unsaturated aliphatic hydrocarbons; they include ethene, propene, i-butene, *trans*-2-butene and *cis*-2-butene. Fig. 7 shows the concentration of olefins (i.e., ethene, propene, i-butene, *trans*-2-butene and *cis*-2-butene) in the liberated gas as a function of time-on-stream. The olefin increases in the first hour before decreasing and finally settles at 0.13% (Ni/Zeolite-Alumina) and 0.1% (Ni/Alumina). Compared to saturated hydrocarbon gas (Fig. 6), the amount of olefins is small, which is an indication of the dominance of catalytic cracking over thermal cracking.

Due to their high reactivity, these olefin groups readily undergo polymerisation reactions in the oil phase into large molecular weight hydrocarbons upon formation during cracking of hydrocarbons, if the conditions are favourable. The higher amount of olefins with Ni/Zeolite-Alumina could have promoted more coke formation as observed in Fig. 5. The impact of these olefin groups could be controlled with the presence of hydrogen-donor source, to hydrogenate and inhibit their polymerisation and consequently condensation to coke [31].

4. Conclusions

Reported in this study are laboratory results of fixed bed catalytic reactor mimicking *in situ* catalytic upgrading of heavy oil by the CAPRI add-on to the THAI process at established optimum conditions of 425 °C, 20 barg, WHSV 9.1 h⁻¹ and GHSV 5882.4 h⁻¹ (nitrogen flow). Prepared Ni supported on Zeolite-Alumina and its commercial counterpart supported on alumina was studied, validated with a control experiment of Alumina without impregnated Ni. Using the prepared Ni/zeolite-alumina catalyst, the maximum upgrade was approximately 6° API. Since the feed oil was produced using THAI, the THAI oil was already partially upgraded to 12.8° API, this therefore represents additional *in situ* upgrading of nearly 4–5° API augmented by catalytic cracking. The Ni/Alumina catalyst achieved lower maximum upgrading of 4.4° API. The viscosity of the upgraded oils was reduced by approximately 87% (Ni/Zeolite-Alumina), 79% (Ni/Alumina) and 62% (Alumina) compared to the THAI oil (1.1 Pa s), which represent improved fluidity for extraction and pipeline transportation.

The main problem affecting the long term operation of the CAPRI reactor is the susceptibility of the catalyst to carbon fouling. However, it was possible to operate the CAPRI reactor for nearly 15 h, during which *in situ* catalytic upgrading was reduced to approximately 2° API. It was also found that the produced oil with Ni/Zeolite-Alumina catalyst possess more naphtha and middle distillate fractions than that of Ni/Alumina and the control experiment with Alumina. Thus, any improvement in the quality of produced heavy oil, gained through *in situ* upgrading, is of great value to the producers and also refiners. It has been demonstrated that, the ‘add-on’ catalytic CAPRI process, essentially annular emplacement of a catalyst layer around the horizontal well in the THAI process, can add further value.

The liberated gases revealed the presence of much hydrogen-rich gases (e.g., H₂, CH₄ and C₂H₆) from the reaction, which could have contributed to high carbon rejection in order to achieve appreciable upgraded oil. Coupled with the production of olefins, it is clear that the need to supply hydrogen through the introduction of hydrogen-donor will help suppress olefins polymerisation, mitigate the adverse impact of the liberated H-rich gases and inhibit coke formation on the catalyst.

Conflict of interest

The authors declare no competing financial interest.

Data access

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

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