

# Experimental Optimization of Catalytic Process In Situ for Heavy-Oil and Bitumen Upgrading

A. Shah, R.P. Fishwick, G.A. Leeke, and J. Wood, University of Birmingham; S.P. Rigby, University of Nottingham; and M. Greaves, University of Bath

## Summary

The worldwide conventional crude-oil demand is on the rise, and because of the rising prices, unconventional oils are becoming more economically attractive to extract and refine. However, technological innovation is needed if heavier oil supplies are to be exploited further. Toe-to-heel air injection (THAI) and its catalytic add-on processes (CAPRI) combine in-situ combustion with catalytic upgrading using an annular catalyst packed around the horizontal producer well. These techniques offer potentially higher recovery levels and lower environmental impact than alternative technologies (e.g., steam-based techniques). An experimental study is reported concerning the optimization of catalyst type and operating conditions for use in the THAI-CAPRI process. The feed oil was supplied from the Whitesands THAI-pilot trial. Experiments were carried out using microreactors containing 10 g of catalyst, with oil flow of 1 mL/min and gas flow of 0.5 L/min, under different temperatures, pressures, and gas environments. Catalysts tested included alumina-supported CoMo, NiMo, and ZnO/CuO. It was found that there was a trade-off in operation temperature between upgrading performance and catalyst lifetime. At a pressure of 20 bar, operation at 500°C led to an average of 6.1°API upgrading of THAI oil to 18.9°API, but catalyst lifetime was limited to 1.5 hours. Operation at 420°C was found to be a suitable compromise, with upgrading by an average of 1.6°API, and sometimes up to 3°API, with catalyst lifetime extended to 77.5 hours. Coke deposition occurred within the first few hours of the reaction, such that the catalyst pore space became blocked. However, upgrading continued, suggesting that thermal reactions or reactions catalysed by hydrogen transfer from the coke itself play a part in the upgrading reaction mechanism. The CAPRI process was relatively insensitive to changes in reaction-gas medium, gas-flow rate, and pressure, suggesting that the dissolution of hydrogen or methane from the gas phase does not play a key role in the upgrading reactions. By careful control of the temperature and oil-flow rate in the in-situ CAPRI process, additional upgrading compared with the THAI process alone may be effected, resulting in a more-valuable produced oil, which is easier to transport.

## Introduction

The worldwide production of conventional crude oil is expected to reach its peak in the second decade of this century and subsequently enter a phase of permanent decline (Stosur et al. 1998). The composition of the oil barrel is already becoming heavier, and diluent blending, assisted by limited coke upgrading capacity, will eventually be insufficient to cope with the increasing demand for light oil. However, large resources of heavy oil (estimated at 3,396 billion bbl) and bitumen (estimated at 5,505 billion bbl) exist throughout the world, most notably in Venezuela and Canada (Meyer et al. 2007). These reserves may account for more than three times the remaining combined world reserves of conventional oil and gas.

The Canadian and Venezuelan share in heavy oils and bitumen reserves together may account for approximately 55 to 65% (Curtis et al. 2002).

Heavy oils are asphaltic, dense, and viscous, having an API gravity between 10 and 20°API and a viscosity greater than 0.1 Pa·s. Bitumens or oil sands are yet more dense and viscous, with API gravity less than 10°API and viscosities usually greater than 10 Pa·s (Curtis et al. 2002). The elevated viscosity and density of these nonconventional crude oils demand more-energy-intensive operations not only for their production and upgrading but also for transportation, and consequently they are more costly to extract. Yet, with 6 trillion bbl of unexploited oil in place, they present a significantly underused resource, and with oil prices rising, production is becoming economically viable. To exploit heavy-oil and bitumen reservoirs, the petroleum industry has in the past relied on cold-production methods, predominantly surface mining. More recently, a variety of enhanced-oil-recovery technologies have been proposed and developed. Success has varied, with recovery levels ranging from as low as 10% (waterflooding), up to 70% with steam-assisted gravity drainage (SAGD), and potentially to greater than 80% with THAI (Shah et al. 2010). However, the use of large amounts of water and energy are potential disadvantages of SAGD (Donnelly and Pendergast 1999).

**THAI Process.** THAI is a novel in-situ-combustion technique whereby a small fraction of the oil in the reservoir is burnt in order to mobilize the heavy immobile oil, thus integrating in-situ-combustion and advanced horizontal-well concepts (Greaves and Xia 2000). The combustion front mobilizes the oil layer ahead of it. This mobilized oil ahead of the combustion front is drawn down into the exposed section of the horizontal producer well, immediately below. Thermally cracked heavy oil produced during the process not only aids oil recovery but also has the added benefit of upgrading the oil (Xia et al. 2002). This added side-effect of THAI is not only beneficial for the actual oil recovery but also aids transportation and downstream refining and subsequently increases the commercial value of the produced oil. Experimental and field pilot results indicate sulphur and heavy-metal content is reduced in the produced oil with THAI (Petrobank Energy and Resources Limited 2008). Petrobank has been able to extract partially upgraded oil with its first pilot studies of THAI in the range of 10.6 to 16.1°API, compared with the original bitumen value of 7.9°API. This means that only approximately 15% of diluent is needed to meet pipeline specifications, compared with 30 to 50% required for nonupgraded bitumen produced from SAGD and cyclic-steam-stimulation operations. The produced water is also of good quality; therefore, it can be treated fairly simply for industrial reuse [e.g., in SAGD (Greaves and Xia 2008)].

**Catalytic Upgrading Using CAPRI Process.** CAPRI is the catalytic extension to THAI developed in collaboration with the Petroleum Research Institute. The objective is to achieve further heavy-oil upgrading in situ by placing an annular layer of catalyst around the perforated horizontal producer well (Xia and Greaves 2001; Greaves et al. 2000) to create a downhole catalytic reactor.

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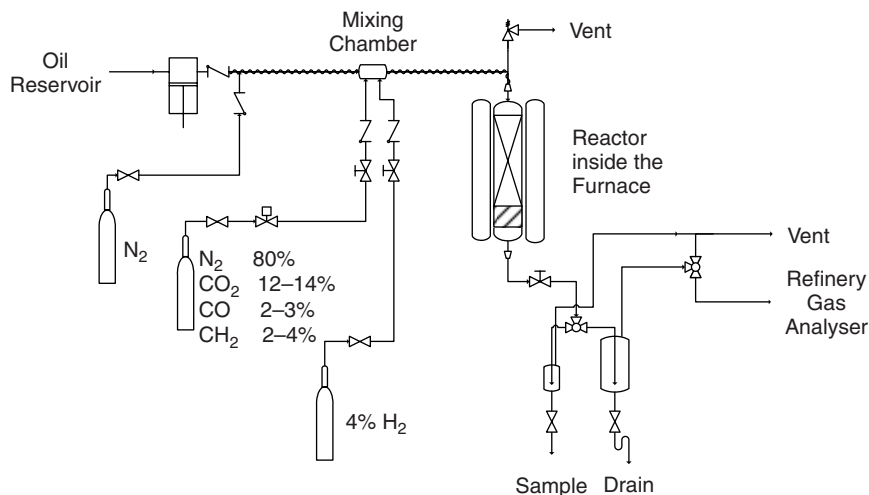


Fig. 1—CAPRI experimental rig.

TABLE 1—PHYSICAL PROPERTIES OF THAI OIL

Origin of Sample	Viscosity Pa·s at 20°C	°API
Athabasca Bitumen	10*	8
THAI Oil	0.577	13

\*Xia and Greaves (2000)

The thermal-cracking reaction of THAI, taking place in the coke and mobile-oil zone (MOZ), creates the precursor for CAPRI. The MOZ comprises water (steam), oil, combustion gases, some carbon monoxide, and a small amount of unconsumed oxygen at high temperatures of approximately 500 to 600°C and at reservoir pressure [typically 30 to 50 bar gauge]. Oil upgrading is thought to occur by a combination of carbon-rejection reactions (thermal cracking) and hydrogen addition at the surface of a hydroconversion or hydrotreating catalyst. The source of hydrogen is expected to be caused by gasification and/or water/gas-shift reactions (Hajdo et al. 1985). In summary, THAI-CAPRI creates ideal conditions for in-situ catalytic upgrading (Weissman 1997; Moore et al. 1999), and the reactor-upgrader is virtually cost free by virtue of the reservoir conditions, which already establish the necessary high temperature and pressure (approximately 400 to 600°C and 20 to 40 bar for Athabasca oil sands). Xia and Greaves (2001) demonstrated the capability of THAI-CAPRI to upgrade a Wolf Lake heavy oil using 3D-combustion-cell tests. Even without a catalyst, thermal-cracking conversion could upgrade Wolf Lake crude oil from 10.9°API to approximately 20°API. CAPRI tests using hydrodesulphurization (HDS) catalyst (not presulphided) showed that the THAI oil could be upgraded further by 4 to 8°API.

In previous 3D-combustion-cell tests (Xia and Greaves 2001), the catalyst in the active part of the horizontal reactor section was exposed to the reactant fluid for only approximately 1 to 2 hours, during the overall run time of 10 to 15 hours. However, in field-scale application, the catalyst activity needs to be maintained over significantly longer operating periods than in the 3D-combustion-cell reactor (of perhaps eventually a few days, or longer) whilst the MOZ moves through the active section of catalyst. THAI has been documented extensively in the literature; however, results with CAPRI are limited, especially at reservoir conditions (e.g., pressures of 20 to 50 bar). Therefore, it is necessary to understand how process conditions can be optimized to avoid catalyst deactivation, and to maximize conversion. The purpose of the present paper is to present a detailed investigation into the optimum catalyst and the effect of catalyst pretreatment, temperature, pressure, gas/oil ratio, and gas composition upon the upgrading performance of CAPRI. In order to study the CAPRI aspect of the process in particular, ex-

perimental trials were carried out using oil previously upgraded in the THAI Whitesands pilot trial, rather than a virgin feed. Therefore, oil representative of that processed using THAI is supplied to the catalyst bed, as occurs with the in-situ CAPRI reactor.

The study is of industrial relevance because it uses feed from the Whitesands oil field in Alberta, where trials of the THAI process are being carried out by Petrobank Energy and Resources Limited. A new experimental test rig was constructed in Birmingham, UK, to carry out the experiments reported in this paper, such that the conditions of the underground reactor could be carefully replicated in the laboratory. A substantial set of experimental results was collected for presentation in this paper, illustrating the optimum catalyst and the effect of catalyst pretreatment, temperature, pressure, gas/oil ratio, and gas composition upon the upgrading performance of CAPRI. The results identify the optimum temperature, pressure, and gas environment for either the maximum upgrading or maximum catalyst lifetime, in which the most desirable operating point may be a trade-off between these variables. Results reported in this paper could potentially be used to scale up and optimize the industrial field-scale CAPRI reactor.

## Experimental

**CAPRI Reactor Rig and Materials.** A rig was developed consisting of two microreactors for the purpose of simulating in-situ oil-upgrading conditions in the horizontal producer well. Fig. 1 shows the flow diagram of one of these two identical reactors. The CAPRI microreactor contains a fixed bed of catalyst to represent a cylindrical core of 10.2-mm diameter taken in a radial direction through the annular layer of catalyst surrounding the producer well. The catalyst bed is located within a furnace, and the annular gap between the reactor tube and furnace wall is filled with marble chips to maintain thermal conduction from the furnace to the reactor. The furnace simulates the high underground-combustion temperature by heating the reactor to a maximum temperature of 500°C.

Pressurized vessels are used to supply oil to the reactor, which is forced from a reservoir tank into the microreactor through a calibrated metering valve. The metering valve is manually set in order to regulate the oil flow into the reactor. Oil then passes through trace-heated lines, in which it is heated to a temperature of 300°C before entering a chamber where it is mixed with the reaction gases. The oil/gas mixture then enters the microreactor bed from the top. System pressures up to 100 bar are achievable, although only experiments up to 40 bar are reported at this time.

The gas-supply system was designed for the use of several different reaction gases: pure nitrogen, nitrogen/hydrogen mixture, and "THAI gas." The nitrogen and hydrogen were supplied through separate mass flowmeters; therefore, they could be blended in the desired proportions. THAI gas consisted of a cylinder of preblended

TABLE 2—EXPERIMENTAL CONDITIONS AND RANGES INVESTIGATED

Temperature Range	380°C	400°C	420°C	425°C	450°C	500°C
Pressure Range Bar (gauge)		20		40		60
Reaction Media Used		Nitrogen	THAI gas*		Hydrogen**	
Catalyst		CoMo Extrusions		NiMo Extrusions		ZnO/CuO tablets
Wt% metal loading		11		16		70
Surface area m <sup>2</sup> ·g <sup>-1</sup>		125–175		–		60–100
THAI Oil Flow Rate				1 mL/min		
Gas-Flow Rate				0.5 L/min		
GOR†				500		

\* THAI gas a mixture of (N<sub>2</sub> 80%, CO<sub>2</sub> 12 to 14%, CO 2 to 3%, CH<sub>4</sub> 2 to 4%)  
 \*\* 4% of hydrogen was used and the rest of the reactant gas was either nitrogen or THAI gas  
 † The gas/oil ratio (GOR) fed into the reactor

gases in the proportions 80% N<sub>2</sub>, 13% CO<sub>2</sub>, 3% CO, and 4% CH<sub>4</sub> to represent the typical combustion gas mixture that would exhaust from the combustion zone into the catalyst bed in the in-situ process of the horizontal producer well. Hydrogen passes through a mass-flow controller, which facilitates blending with nitrogen in controlled proportions for either catalyst preactivation or upgrading experiments. Additionally, steam can be added to the reactor feed, but experiments using steam are not reported in the current paper.

The catalyst bed was packed to a length of 10 cm at the vertical centre of the reactor tube, with additional space above and below being filled with inert glass beads to provide a preheat zone in the region above the catalyst bed. The exhaust stream from the reactor is then cooled, and the liquid and gas fractions are separated. The gas stream can be diverted to a gas-sampling line connected to a refinery-gas analyzer (Agilent 7890A GC) or diverted to flue gas stream through the vent.

The crude oil used in this work was supplied from the Whitesands THAI-pilot trial at Christina Lake near Conklin, Alberta, with the properties shown in Table 1. Therefore, the feed to the experimental process was representative of oil produced from the actual THAI field trial and had been subjected to underground thermal upgrading by the in-situ combustion process.

**Reactor Operation Method.** The experimental conditions used and different parameters investigated in the present work along with the catalyst properties are shown in Table 2. In selected experiments, the catalyst was reduced with hydrogen before the experiments at 425°C for 30 minutes in the presence of 25% hydrogen to determine the effect of preactivation. The catalysts used for the experiments were industrial hydroprocessing catalysts with properties shown in Table 2. When starting up the reactor, the feed lines and furnace were preheated under a flow of nitrogen or hydrogen/nitrogen. The oil flow was started once the temperature and pressure reached the desired values in the reactor bed for a particular experiment and the trace heating surrounding the oil lines reached its set point of 300°C. Experiments continued either for a fixed duration, or until a sharp pressure rise indicated on the reactor pressure gauge occurred, which was indicative of bed blocking by coke. All experiments were terminated by first stopping the oil flow and then turning off the heating followed by stopping the gas flow. Liquid samples were withdrawn initially every 30 minutes for the first 3 hours, then once per hour except for the experiments in which added hydrogen was involved and samples were withdrawn every 20 minutes for the first 3 hours. Gas analysis was carried out periodically for particular runs.

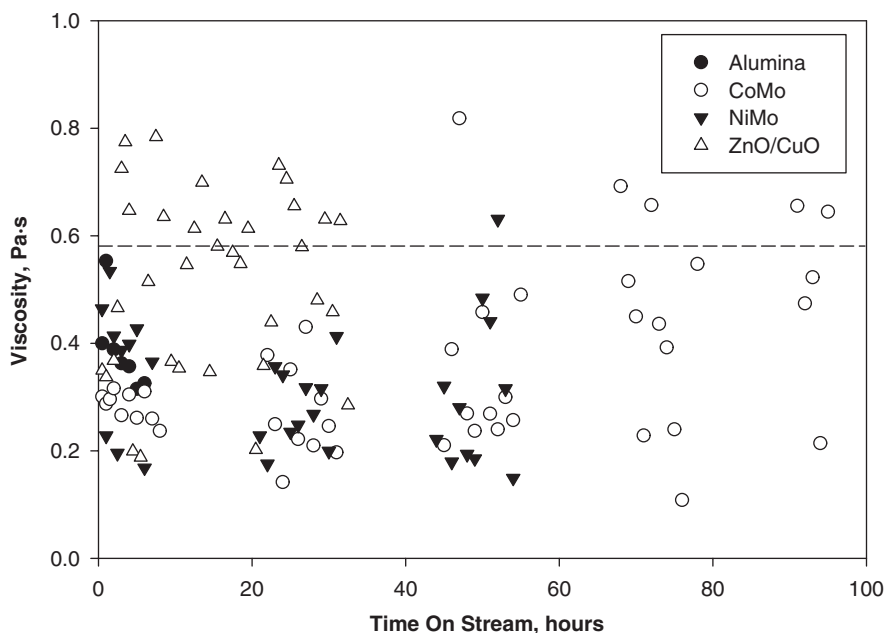


Fig. 2— Effect of catalyst upon viscosity. THAI-oil with viscosity of 0.58 Pa·s, at 400°C, 20 bar gauge, 1-mL/min oil-flow rate, and 0.5 L/min nitrogen, except for ZnO/CuO, which was 2 mL/min oil and 1 L/min nitrogen. The dotted lines in this and other figures represent the measured viscosity or API value of the field-THAI oil before upgrading in the experimental CAPRI reactor.

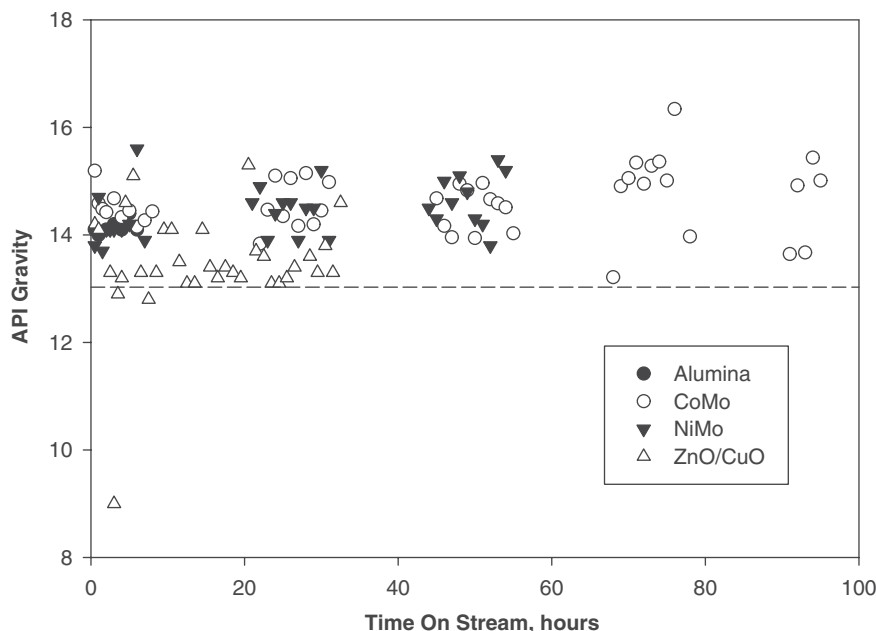


Fig. 3—Effect of catalyst upon API gravity. Conditions are the same as for Fig. 2.

**Analysis.** A simulated-distillation (SIMDIS) unit [Agilent 6850 GC, based on the American Society for Testing and Materials (ASTM) Method D2887] for the compositioned analysis of the liquid streams was used to examine the degree of upgrading achieved. It is noted that this SIMDIS method is only applicable for the detection of petroleum products and fractions having a final boiling point of 538°C or less; and it therefore provides only a qualitative comparison of upgrading levels achieved. The gas stream was analyzed by the refinery-gas analyzer (Agilent 7890A GC). Viscosity and API measurements were carried out using an AR 1000 rheometer and Anton-Paar DMA 35N digital density meter, respectively. Because of the aforementioned limitations of the SIMDIS ASTM Method D2887, selected samples were analyzed further by Petrobank Canada using SIMDIS (ASTM Method D5307), from which residue content was determined. Additional analysis of selected samples was also performed by Intertek laboratories for saturates, aromatics, residue, and asphaltenes (SARA) by high performance liquid chromatography (Method IP143); sulphur analysis was conducted by Petrobank Canada using X-ray fluorescence spectroscopy (ASTM Method D4294); and metals analysis was conducted by Petrobank Canada by inductively coupled plasma emission spectroscopy (ASTM Method D5185). Thermogravimetric analysis (TGA) was performed for selected coke samples using NETZSH TG 209F1 equipment. The coke sample was placed in an alumina crucible, heated at a rate of 10°C/min

to 200°C in the presence of nitrogen, and this temperature was held for 30 minutes. The temperature was then raised to 1000°C at a rate of 10°C/min and maintained for 30 minutes. The last stage was burning the sample at 1000°C in the presence of air for a further 30 minutes.

## Results and Discussion

**Effect of Catalyst Type and Pretreatment.** Figs. 2 and 3 and Table 3 show the upgrading of oil in terms of viscosity and API gravity for the different catalysts initially tested. It was observed that NiMo displayed the highest level of average upgrading in terms of average viscosity reduction, followed by CoMo, then ZnO/CuO. CoMo catalyst displayed the best upgrading in terms of average API gravity, with performance similar to that of NiMo, whilst ZnO/CuO showed a poorer level of upgrading. The catalytic reactors were shut down when oil flow declined, which was thought to be caused by bed blockage created by coke deposition. From Figs. 2 and 3, it was observed that CoMo catalyst continued for the longest period of operation of up to 95 hours, although toward the end of the run, the data are more scattered than the earlier results. ZnO/CuO displayed the poorest upgrading and also was shut down after 32.5 hours. The data in Figs. 2 and 3 show some scatter, particularly for ZnO/CuO, in which a number of samples showed higher viscosity than the starting material, indicating undesirable degradation of the oil, rather than upgrading. From Table 3, it can

TABLE 3—AVERAGE AND STANDARD-DEVIATION VISCOSITY AND API GRAVITY AFTER UPGRADING OF HEAVY OIL WITH DIFFERENT CATALYSTS\*

	CoMo	ZnO/CuO	NiMo
Average flowrate (mL/min)	1.14	1.74	1.32
Standard deviation flowrate (mL/min)	0.68	0.83	1.10
Average viscosity Pa·s	0.357	0.514	0.315
Standard deviation viscosity Pa·s	0.185	0.169	0.120
Average API gravity	14.7	13.6	14.5
Standard deviation API gravity	0.640	0.619	0.503
Operation time (hours)	95	32.5	54

\* THAI oil starting material has a viscosity of 0.58 Pa·s and an API gravity of 13°. Experiments were carried out at 400 °C and 20 bar gauge pressure, with a flow of 1 mL/min oil and 0.5 L/min nitrogen except for ZnO/CuO which was 2 mL/min oil and 1 L/min nitrogen.

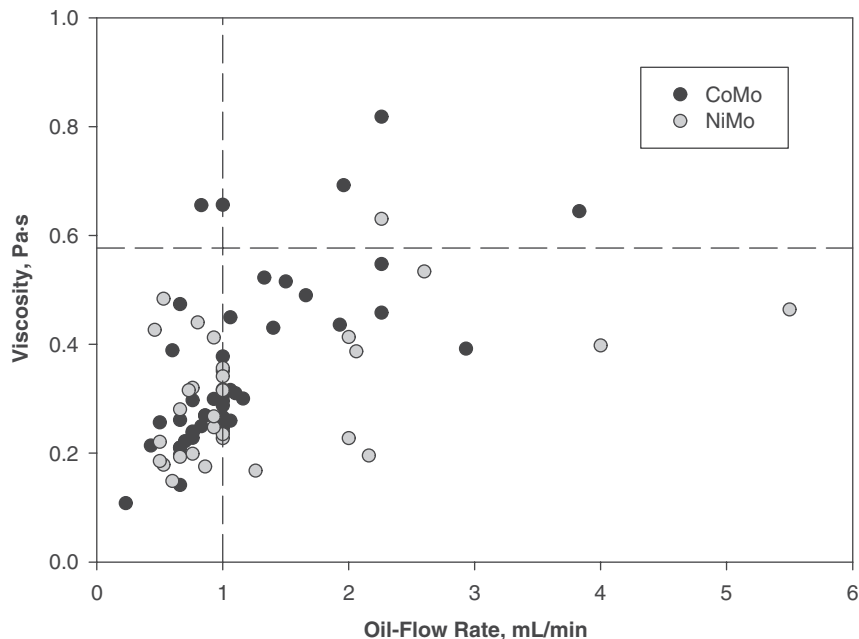


Fig. 4—Viscosity of the upgraded oil vs. oil-flow rate. Experimental conditions are the same as for Fig. 2.

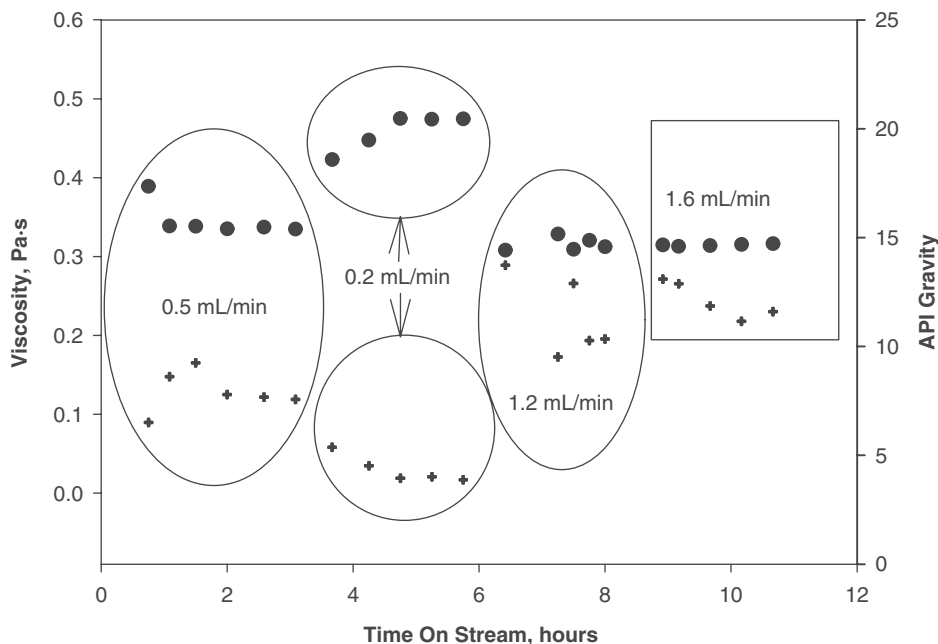


Fig. 5—Viscosity and API gravity of upgraded oil vs. variable oil-flow rate. THAI-oil viscosity of 0.58 Pa-s and an API gravity of 13°API at 425°C, 20 bar gauge, and a flow rate of 0.2 to 1.6 mL/min of oil and 0.5 L/min of THAI gas. API values (+), viscosity (●).

be deduced that the upgrading in terms of viscosity was a change of 0.066 to 0.265 Pa-s and the change in API gravity was 0.6 to 1.7°API. It should be noted that relatively moderate levels of upgrading occurred because the oil had already been cracked during processing in the Whitesands trial and a higher level of upgrading would have been expected if a virgin crude oil had been used in the experiments.

Analysis of the possible sources of error and scatter in the data showed that the viscosity measurement was repeatable to within  $\pm 4.6\%$ , as was the API-gravity measurement. However, control of the flow rate to the reactor proved to be difficult because of the highly viscous nature of the oil, presence of sand particles, and tendency to foul both pipework and the catalyst bed. Consequently, the actual flow rate in the bed fluctuated during the experiment, with the actual average values shown in Table 3, and determined

by collecting and measuring the volume of oil. These fluctuations led to associated changes in residence time and may have resulted in the observed scatter in the upgrading data. Whilst it is undesirable for such fluctuations in flow to occur experimentally, similar effects may also occur in the downhole CAPRI process because of the MOZ passing through regions of oil sands of different permeability and uneven depositions of coke within the catalyst bed. The intended operation of the reactor with a gas-flow rate of 0.5 L/min [the ZnO/CuO experiment was performed at 1-L/min gas-flow and 2-mL/min oil-flow rates, but in order to conserve both gases and oil the flow rate was reduced for all other experiments to 0.5 L/min of gas and 1 mL/min of oil, which does not change the gas/oil ratio (GOR) but only the quantity of the gas and oil used] and an oil-flow rate of 1 mL/min through the 11-cm length of the catalyst bed with a 10.2-mm tube diameter would lead to a mean resi-

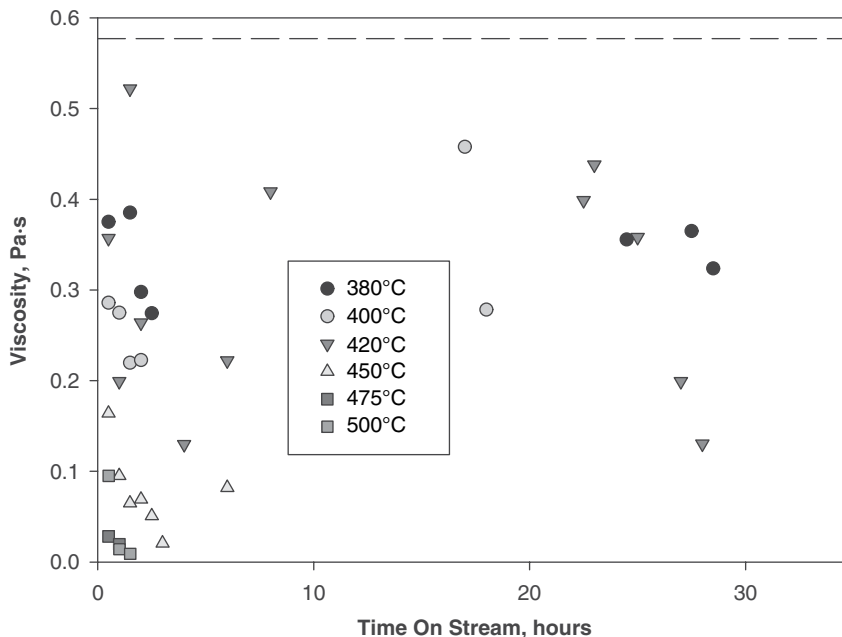


Fig. 6—Effect of temperature upon viscosity: 20 bar gauge, flow rate of 1 mL/min oil and 0.5 L/min nitrogen, CoMo catalyst.

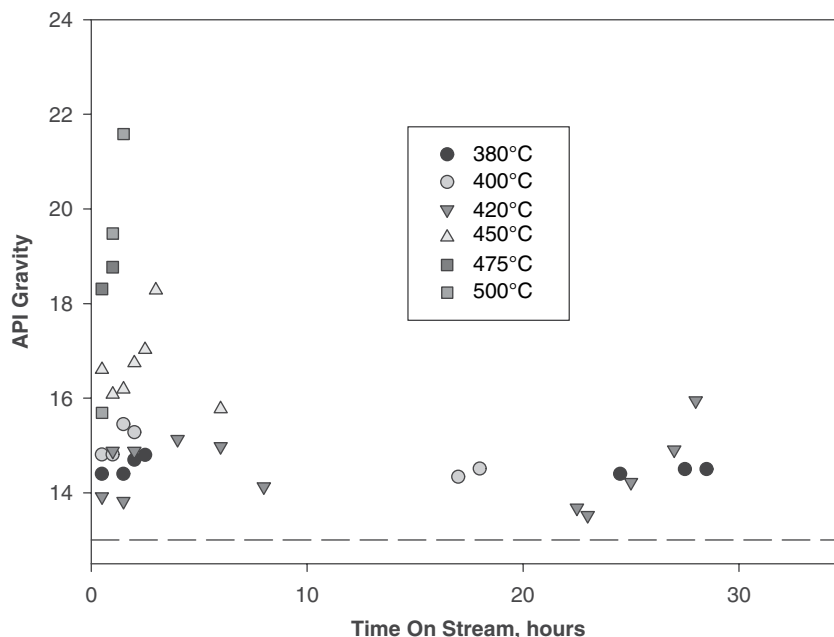


Fig. 7—Effect of temperature upon API gravity. Conditions are the same as for Fig. 6.

dence time of gas in the reactor of approximately 0.27 seconds. The liquid calculated hourly space velocity is 8.9 L/h, and mean residence time is 6.74 minutes. However, the actual residence time of the oil will depend upon whether the vapourized droplets are carried through the reactor with the gas flow or impact upon the catalyst particles and are retained there. Fig. 4 shows the viscosity of upgraded oil as a function of the actual oil-flow rate, indicating a “cone-shaped” correlation, whereby lower flow rates led to lower viscosity of upgraded oil because of increased residence time in the catalyst bed, whilst higher oil-flow rates gave higher viscosities because of insufficient residence time for further upgrading to occur. Fig. 5 further illustrates the effect of oil-flow rate upon upgrading when different oil-flow rates were used under the same conditions. The lowest flow rates led to higher upgrading in API gravity and greater reduction in viscosity in comparison to higher flow rates. This was particularly evident for the oil flow of 0.2 mL/min, which

led to API gravities in the range 18 to 20°API and viscosities below 0.1 Pa·s. Consequently, it was concluded that oil-flow rate is an important variable in control of the CAPRI process.

In order to check the catalytic effect further, the influence of the pretreatment method of the catalyst during startup was investigated. Experiments were carried out with and without prereducing the catalyst in hydrogen. The prereducing of the catalyst consisted of flowing 25% hydrogen in nitrogen over the catalyst at a temperature of 425°C for a period of 30 minutes. Thereafter, the oil flow and THAI gas, nitrogen, or 4% hydrogen in either THAI gas or nitrogen flows were started. Average values of the viscosity of the upgraded oil were 0.154 Pa·s with catalyst preactivation and 0.176 Pa·s without preactivation. API gravity values were 15.9°API with preactivation and 15.04°API without preactivation. The upgraded oil that was passed over the preactivated catalyst showed slightly lower viscosity and higher API gravity, compared with nonpretreat-

**TABLE 4—UPGRADING PERFORMANCE AT DIFFERENT TEMPERATURES USING A CoMo CATALYST WITH OIL-FLOW RATE OF 1 mL/min AND GAS-FLOW RATE OF 0.5 L/min AT PRESSURE OF 20 BAR**

Temperature (°C)	380	400	420	475	500
Average viscosity Pa·s	0.339	0.290	0.353	0.024	0.039
Standard deviation viscosity Pa·s	0.039	0.087	0.195	0.006	0.048
Average API gravity	14.5	14.9	14.43	18.54	18.92
Standard deviation API gravity	0.149	0.429	0.728	0.325	2.985
Operation time (hours)	28.5	18	77.5	1.0	1.5

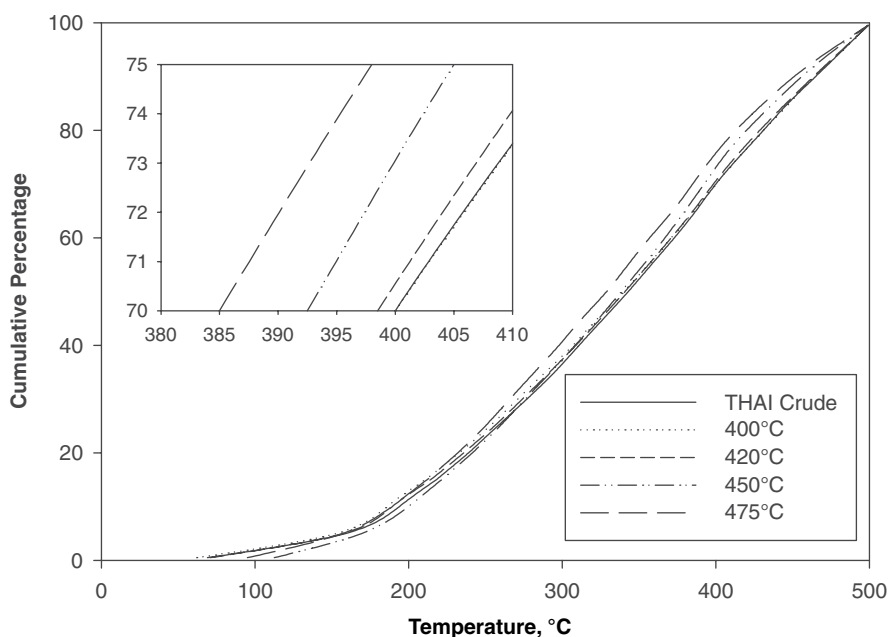
ment; however, this difference was within the experimental error of  $\pm 0.1$  Pa·s in viscosity and  $\pm 1^\circ$ API gravity and, therefore, the pre-treatment of the catalyst did not appear to significantly influence the upgrading performance.

**Effect of Short Run Times.** Short runs were repeated for different times on stream of 2, 4, 6, and 8 hours. The purpose of carrying out the short runs was twofold. First, repeating the early part of the experiment would provide several sets of results run under the same conditions to determine whether the experimental results are repeatable. Second, stopping the reactor at different lengths of time would enable the catalyst to be recovered for coke analysis. Catalytic runs at different operation times showed that viscosity results were repeatable to within  $\pm 0.1$  Pa·s, whilst the API-gravity results were repeatable to within  $\pm 1^\circ$ API. Visual inspection of the catalyst bed after each run showed considerable coke deposition, even at the shorter reaction times of 2 and 4 hours, illustrating that coke deposition occurred early in the reaction.

**Effect of Temperature.** Figs. 6 and 7 and Table 4 show the effect of temperature upon upgrading performance. In Figs. 6 and 7, the data are displayed up to 35 hours of operation to facilitate comparison with upgrading in shorter runs, although the experiment carried out at 420°C continued up to 77.5 hours. Average data in Table 4 are calculated from the full duration of each experiment. At lower temperatures of 380 to 420°C, moderate levels of oil upgrading were observed, with viscosity reduction of approximately 0.3 Pa·s and an API gravity increase of 1.5 to 2°API. However, the data at 400 and 420°C show some scatter, with occasionally poorer-upgrading results being achieved. Upgrading levels improved with increasing temperature, with viscosity of the upgraded oil processed at

475°C being decreased by 5.8 Pa·s (96%) from the THAI-oil value, the API being increased by 5.7°API, and similar upgrading performance occurring at 500°C. However, catalyst operation time was severely limited with operation at 475 to 500°C because the oil-flow rate declines and pressure drop increases sharply because of bed blockage by coke. Greaves and Xia (2001) obtained upgrading of 4 to 6°API with CAPRI above that achieved using only THAI (nuncatalytic process), with final viscosities decreasing to less than 0.1 Pa·s, or as low as 0.02 Pa·s in selected runs, which is comparable with the upgrading performance observed in the experiments reported in this paper at temperatures of 475 to 500°C. SIMDIS analysis of the produced liquid oil samples further confirms that the higher temperature favoured lighter-end products in liquid fractions in comparison with the partially upgraded THAI oil, in which approximately a 10 to 15°C shift was observed toward the lighter-end products (Fig. 8) at the higher upgrading temperatures.

Fig. 9 shows a graph of viscosity vs. On-stream time of the cross section of the catalyst bed after coke deposition when operating at the higher temperature of 475°C with the CoMo catalyst, illustrating that the pore space is almost completely filled with coke. Millan et al. (2008) studied catalytic activity in heavily coated hydrocracking catalysts and found that, although a large coke deposit was observed to form early in the runs, catalyst samples recovered from the initial coking experiment displayed continued activity despite a large drop in surface area and a complete apparent pore blockage. Similarly, attempts to characterize the pore structure of spent catalysts using gas-sorption methods in the experiments reported here showed that almost complete pore blockage occurred. However, even toward the end of the run, some upgrading of the oil still occurred. This suggests that either the catalyst retains its activity despite a heavy-coke deposition, which could occur because



**Fig. 8—SIMDIS graph showing effect of upgrading temperature on the boiling range of the liquid fraction.**



**Fig. 9—** Photograph of cross section of catalyst bed showing coke deposition on and around CoMo pellets at 475°C.

of exchange of carbonaceous deposits with the oil, such that catalyst activity continues. A second possible effect would occur if the coke itself were acting as a catalyst, through exchanging hydrogen with the oil molecules in the liquid phase. Alternatively, it could be because of thermal reactions, which are not dependent on catalytic activity. It is noted that if classical catalyst deactivation effects occurred, the extent of upgrading would be likely to follow exponential decay behaviour, with the exact deactivation function depending on the way in which the network of pores becomes plugged by coke (Beeckman and Froment 1979). However, in most of the runs, the viscosity and API gravity were scattered around a band of values, but did not show a clear decline with time on stream. This suggests that some thermal reactions occur, leading to carbon rejection and deposits upon the catalyst surface, but that catalytic hydroconversion reactions do not predominate in the upgrading.

The previously described results suggest that there is a trade-off between catalyst operation time and upgrading performance. The higher temperatures lead to high rates of reaction, but large deposits of carbon upon the catalyst limit the useful lifetime. In the CAPRI process, the catalyst within a particular section of the horizontal well must be active for sufficient time for the MOZ to pass through it. The width of the MOZ may depend upon numerous factors (e.g., the rate of combustion, oil quality, and others). Yet it is estimated that several days may be required for the MOZ to pass through a section of the horizontal well, and hence, through the gravel-packed catalyst. Thus, any catalyst to be applied in the CAPRI process in the field would have to be active for tens of hours, up to several days. For this reason, a trade-off between the catalyst life and activity was found to be 420°C, with acceptable upgrading and a catalyst lifetime sufficiently long to be comparable to the time required for the MOZ to pass through the catalyst.

**Effect of Pressure.** Average experimental viscosities and API gravities recorded at different upgrading pressures are shown in

**Table 5.** Although the highest API gravity occurred at 20 bar and the lowest viscosity at 40 bar, the measurements at all three pressures tested lay within a similar range. However, differences in the SIMDIS measurements (**Fig. 10**) are discernable, where the 20-bar line shows a small improvement toward the lighter-end products. The 40 and 60-bar lines indicate a shift toward the heavier fractions, suggesting a decrease in the quality of the produced oil. In the case of catalytic hydroconversion, the effect of pressure would be thought to have the result of increasing the rate of reaction through increased concentration of reactants presented at the catalyst surface, improving the penetration of oil into the catalyst pores and increasing the solubility of gases (e.g., hydrogen and methane) within the liquid oil. However, the relative insensitivity of the upgrading results to pressure suggests that the dissolution of gas-phase components (e.g., hydrogen or methane) in the oil does not play a significant role in the reaction. This observation is consistent with thermal reactions, or the possible transfer of hydrogen from the coke layer to the upgrading oil molecules to leave behind a carbon-rich deposit.

**Effect of GOR.** **Table 6** shows the average viscosity and API gravities at different GORs, in which the oil-flow rate was kept constant at 1 mL/min and the gas flow varied according to the desired ratio. The viscosities of the upgraded oil lie within a narrow band of values of  $0.24 \pm 0.4$  Pa·s. Although the viscosity is slightly lower at the smallest and highest GOR, all of the values are within the margin of error of the experiment. Similarly, the average API gravities lie within the band of  $14.7 \pm 0.3$ . The lack of effect of GOR upon the upgrading performance suggests that it is only the residence time of the oil upon the catalyst that influences the upgrading performance, rather than interactions between the gas and liquid phases.

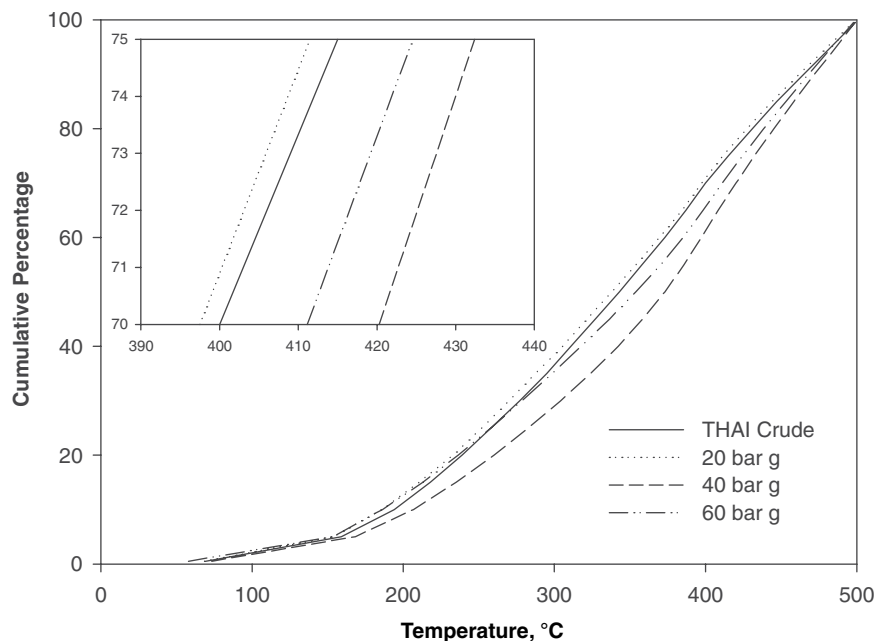
**Effect of Gas Composition and Hydrogen Content.** During the THAI process, the burning of oil produces a number of gases inside the reservoir. The reaction of these gases with the free radicals produced during the cracking of large molecules could be important. In particular, gases (e.g., hydrogen or methane) could potentially participate in the upgrading reactions—for example, in the case of hydrogen, through hydroconversion processes. To understand how the CAPRI process performs under different reaction media, three different types of gases were used in the optimization of the CAPRI process: nitrogen, THAI gas, and a nitrogen/hydrogen mixture. **Figs. 11 and 12** show the viscosity and API gravity of the upgraded oil in the presence of nitrogen, THAI gas, 4% hydrogen in nitrogen, and 4% hydrogen in THAI gas, respectively. The reduction in viscosity with the 4%-hydrogen/nitrogen mixture was the highest, leading to the lowest viscosity reading of 0.034 Pa·s compared with a value of 0.58 with THAI oil. Upgrading with nitrogen and THAI gases led to minimum viscosity readings of 0.21 Pa·s and 0.12 Pa·s, respectively (**Fig. 11**). The API-gravity results show similar upgrading trends, with the highest levels of upgrading being achieved by the nitrogen/hydrogen mixture (**Fig. 12**). Averaged upgrading parameters are shown in **Table 7**, also showing 4% hydrogen/nitrogen to lead to the greatest upgrading. However, SIMDIS curves for the produced oil show sparse difference in the composition of the

**TABLE 5—EFFECT OF PRESSURE UPON VISCOSITY AND API GRAVITY OF UPGRADED OIL\***

Pressure (bar)	20	40	60
Average viscosity Pa·s	0.154	0.146	0.213
Standard deviation viscosity Pa·s	0.085	0.07	0.090
Average API gravity	15.9	15.6	15.1
Standard deviation API gravity	1.20	1.38	1.08
Operation time (hours)	29.5	13	4.5

\* Experimental conditions were CoMo catalyst, 425°C upgrading temperature, 1 mL/min oil-flow rate, 0.5 L/min gas-flow rate (4% hydrogen in nitrogen).





**Fig. 10—SIMDIS graph showing effect of upgrading pressure on boiling range of liquid fraction: 425°C, flow rate of 1 mL/min oil and 0.5 L/min 4% hydrogen in nitrogen.**

liquid fractions (Fig. 13), which means that the addition of hydrogen did not improve the quality of the produced oil significantly. Although in theory it may be expected that the higher concentration of hydrogen could stabilize the free radicals and lead to less coke and increased quantities of lighter-end products, in practice the addition of hydrogen was found to have minimal effect upon the quality of the produced oil. This result confirms earlier findings that the gas-phase variables (e.g., pressure and GOR) do not significantly influence the quality of the produced oil.

Analysis of the gas-product stream reveals small amounts (0.02 to 0.38%) of light hydrocarbons, as shown in Table 8, for an experiment conducted with hydrogen in the THAI-gas feed. Comparison with the vapour generated by low-temperature heating of the starting material suggests that these are not present as dissolved components, but are produced during the reaction. The predominant products are unbranched alkanes with smaller amounts of branched alkanes and unsaturated compounds, and in total approximately 1.7 to 1.8% of the outlet-gas stream consists of produced hydrocarbons. This suggests that cracking of larger molecules to produce gas-phase alkanes and alkenes together with higher-molecular-weight compounds that remain in the liquid phase is occurring. Interestingly, the net change in hydrogen content is negligible while a small but significant fraction of carbon monoxide is also generated. Possibly the reverse water/gas-shift reaction could lead to the consumption of hydrogen and carbon dioxide to produce carbon monoxide. Alternatively, gasification reactions could include the Boudouard reaction, which leads to the production of carbon monoxide from the reaction of carbon dioxide with coke.

**Analysis of Residue, Metals, and Sulphur.** In addition to the general indications of upgrading obtained from viscosity, API-gravity, and SIMDIS measurements, analyses of selected samples were also performed to determine their chemical properties, to gain an insight into the extent of catalytic activity vs. thermal reactions. Table 9 displays the SIMDIS temperature at which 70%-cumulative-product percentage occurred for the THAI-pilot oil and several samples from the CAPRI experiment over a range of process temperatures, pressures, and gas environments. SIMDIS results reported in Table 9 were derived from the samples tested using ASTM Method D5307 by Petrobank laboratories; thus, providing more information about the residue than SIMDIS results determined using ASTM Method D2887. Samples were collected at various on-stream times because of the different operating durations of experimental runs, and are thus representative of a snapshot of typical upgrading behaviour. The temperature at which 70%-cumulative-product percentage occurred showed a decrease from the THAI-field-oil value for all of the CAPRI-processed samples, indicating upgrading toward the lighter-end products. This is particularly evident for Samples P30 and P37, where at a 70%-cumulative-product percentage there were reductions in SIMDIS temperatures to 395.2 and 403.9°C, respectively, compared with the temperature of 542.3°C for THAI-field oil.

The residue conversion was also largest for experimental Runs P30 and P37 (Table 9). The residue of 29.7% for the THAI-field oil decreased to 4.9% in Experiment P30, which was thought to occur because of the high CAPRI operating temperature of 500°C, leading to improved upgrading and thus the shift toward lighter products. For the lowest CAPRI process temperature of 400°C for

**TABLE 6—EFFECT OF GOR RATIO UPON VISCOSITY AND API GRAVITY OF UPGRADED OIL\***

GOR	235.5	375	500	641.4	744
Average viscosity Pa·s	0.202	0.276	0.249	0.247	0.200
Standard deviation viscosity Pa·s	0.054	0.034	0.036	0.055	0.046
Average API gravity	15	14.56	14.52	14.43	14.46
Standard deviation API gravity	0.524	0.169	0.129	0.288	0.228
* CoMo catalyst, 1mL/min oil-flow rate, 0.25 – 0.75 L/min ga-flow rate (4% hydrogen in THAI gas), 425°C, 20 bar gauge.					

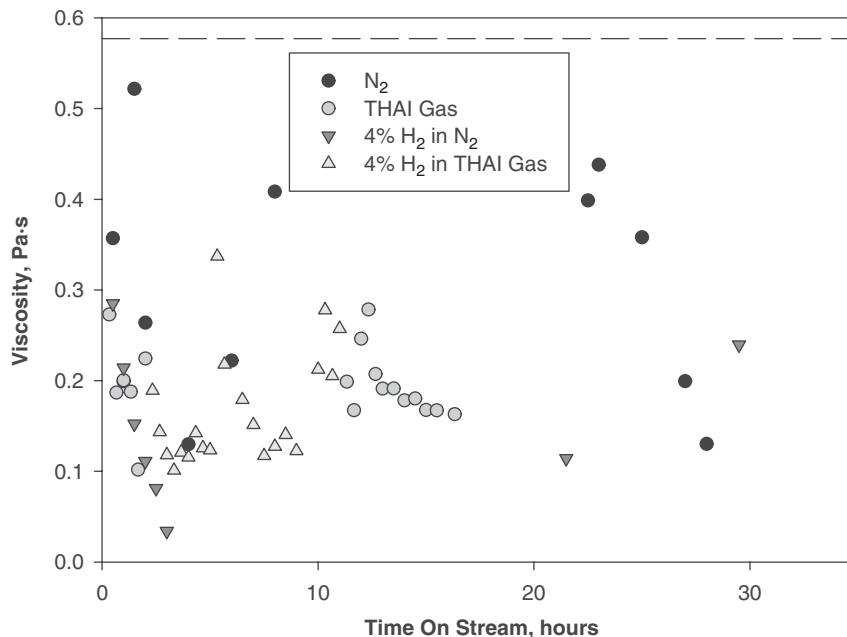


Fig. 11—Effect of reaction media upon viscosity: 425°C; 20-bar gauge pressure; flow rate of 1 mL/min oil and 0.5 L/min nitrogen, THAI gas, 4% hydrogen in nitrogen, and 4% hydrogen in THAI gas; CoMo Catalyst.

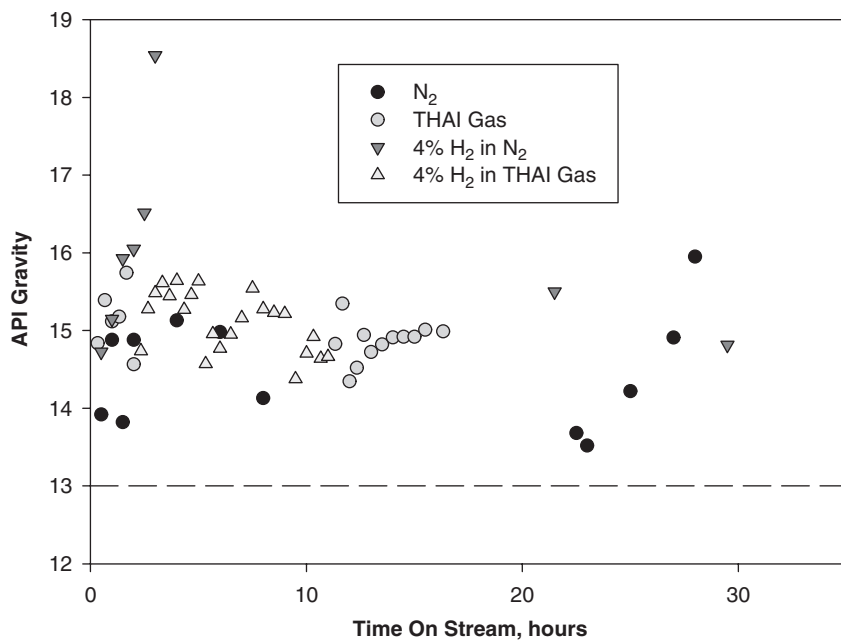


Fig. 12—Effect of reaction media upon API gravity. Conditions are the same as for Fig. 11.

TABLE 7—EFFECT OF REACTION MEDIA UPON VISCOSITY AND API GRAVITY OF UPGRADED OIL*				
	N <sub>2</sub>	THAI Gas	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in THAI gas
Average viscosity Pa·s	0.353	0.195	0.154	0.163
Standard deviation viscosity Pa·s	0.196	0.042	0.086	0.061
Average API gravity	14.4	15.0	15.9	15.1
Standard deviation API gravity	0.728	0.331	1.233	0.383
Operation time (hours)	77.5	16.3	29.5	10.7

\* Temperature of 425°C and 20 bar gauge pressure with a flow rate of 1 mL/min oil and 0.5 L/min gas.

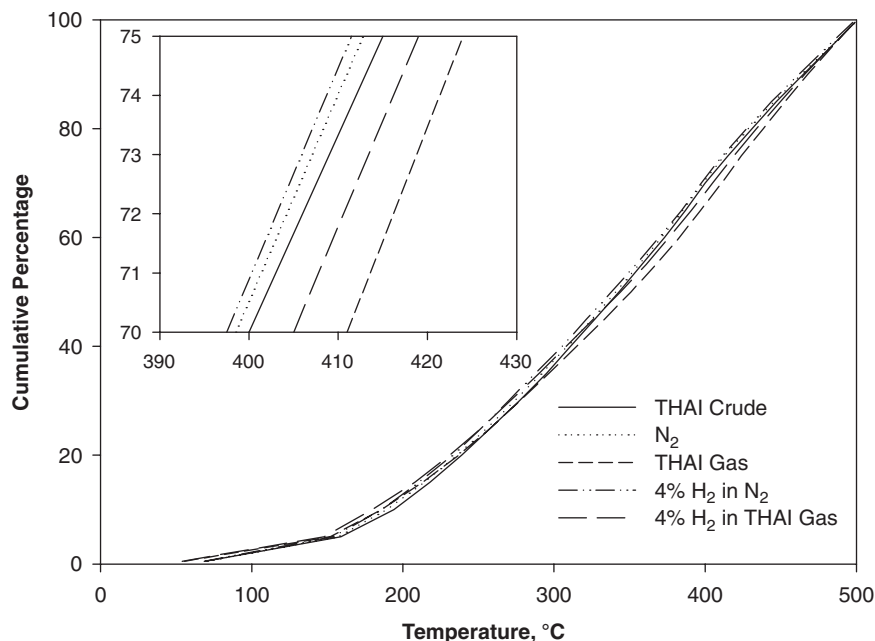


Fig. 13—SIMDIS effect of reaction media upon the boiling range of the liquid fraction.

which analysis was carried out, the residue was only slightly decreased to 28.9%, indicating that sparse upgrading occurred. For the experiments carried out at process temperature of 425°C and 20-bar pressure, there is some variability in the extent of upgrading that occurred, with residue values in the range of 3.9 to 19.7%, possibly resulting from fluctuations in flow rate that occurred during the experiments. Increased pressure in the CAPRI process did not lead to reductions in residue or an increase in lighter products.

**Table 10** shows the metals and sulphur analysis of the THAI-pilot oil and selected samples collected from the CAPRI process. It can be observed that the THAI-field oil contains a number of metals in trace quantities, but nickel, vanadium, and iron are present in the largest quantities and, thus, are of greatest significance in this work. Because the feed had already been processed in the THAI-pilot trial, it was expected that metals (e.g., nickel and vanadium) present in the metallic state would already have been reduced significantly and the remaining metals might be more difficult to remove (e.g., as chelates in metal porphyrins). The only experiment in which substantial removal of nickel and vanadium occurred was in Run P30 at 500°C. It is thought that the higher processing temperature was sufficiently severe to lead to some destruction of organically bound metals. However, the other experimental conditions did not show a significant removal of nickel and vanadium. Iron showed some removal under all experimental conditions and showed complete

removal at a processing temperature of 500°C. Iron may be easier to remove from the feed if it is in a metallic rather than an organically bound form (Baker and Louda 1986). However, with the exception of some iron removal, it could be concluded that there was relatively sparse hydrodemetallation occurring, suggesting that the catalyst is not active for this type of reaction.

Sulphur content of the oil is shown in Table 10, from which it is observed that most of the experimental conditions led to only a marginal reduction in sulphur from 3.8 to approximately 3.6 wt%, although the experiment carried out at 500°C led to a slightly higher removal to 3.2 wt%. Some removal of loosely bound sulphur in the virgin crude would already have occurred during the THAI-field upgrading; thus, the remaining sulphur would be expected to be organically bound and more difficult to remove. It appears that the hydrodesulphurization activity of the catalyst was weak, possibly because only up to 4% hydrogen was present in some of the feed gases, whereas in refinery hydrodesulphurization operations the feed gas is mostly hydrogen at a pressure of 40 to 80 bar; thus, the CAPRI process may not have sufficiently high hydrogen partial pressure to achieve substantial sulphur removal.

**Analysis of SARA.** Table 11 displays the SARA analysis of the THAI-field crude and two selected CAPRI-process samples. It can be observed that after CAPRI processing, the quantity of saturates

**TABLE 8—TYPICAL OUTLET-GAS COMPOSITION AS MEASURED BY REFINERY-GAS ANALYZER FOR CoMo CATALYST AT 425°C, 20 bar gauge, AND FEED GAS COMPOSITION OF 4% HYDROGEN IN THAI (4% H<sub>2</sub>, 76.8% N<sub>2</sub>, 12.48% CO<sub>2</sub>, 3.84% CH<sub>4</sub>, 2.88% CO)**

Compound	Volume Fraction (%)	Compound	Volume Fraction (%)
Methane	4.24–4.27	<i>cis</i> -2-Butene	0.02
Produced Methane	0.35–0.38	<i>i</i> -Pentane	0.10
Ethane	0.20	<i>n</i> -Pentane	0.17–0.19
Ethene	0.04	Total Hydrocarbon Produced	1.69–1.79
Propane	0.23–0.24	Carbon Dioxide	12.51–12.59
Propene	0.19–0.21	Carbon Monoxide	3.09–3.10
<i>i</i> -Butane	0.04	Produced Carbon Monoxide	0.17–0.18
<i>n</i> -Butane	0.20	Hydrogen	3.89
1-Butene	0.07–0.08	Consumed Hydrogen	0.01
<i>trans</i> -2-Butene	0.07–0.08	Nitrogen	74.73

**TABLE 9—CUMULATIVE PRODUCT PERCENTAGE AT 70% AND RESIDUE REDUCTION COMPARISON OF SELECTED SAMPLES (SIMDIS METHOD ASTM D5307)**

Experiment Number	THAI Field Oil	P13	P30	P37	P65	P66	P66	P67
Time of sample (h)		53	1	21.5	3	6.5	14.5	2.5
Processing temperature (°C)		400	500	425	425	425	425	425
Process pressure (bar g)		20	20	20	60	20	20	40
Reaction gas		N <sub>2</sub>	N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>
SIMDIS temperature at which a cumulative product percentage of 70% occurs (°C)	542.3	534.2	395.2	403.9	485.2	430.0	467.3	448.9
Residue %	29.7	28.9	4.9	3.9	22.8	12.0	19.7	16.6

and aromatics increased, whilst the amount of polars (naphthenes) and asphaltenes decreased, particularly at the higher processing temperature of 500°C. These changes are thought to be representative of catalyst deactivation reactions over oxide and sulphide catalysts, in which smaller naphthenic or aromatic ring structures condense into larger multiring aromatic structures (Farruto and Bartholomew 1997). Such reactions include the polymerization and cyclization of olefins and chain-reaction formation of polynuclear aromatics, which condense as coke on the catalyst surface. Therefore, it appears that the catalyst retains or filters the coke or pre-coke, thus leading to the observed decrease in naphthenes and asphaltenes in the produced oil. This would also explain why the use of catalyst (e.g., ZnO/CuO) with a lower surface area in comparison with CoMo and NiMo led to lower levels of apparent upgrading in terms of viscosity and API gravity, as shown in Table 3.

**Analysis of Coke Deposits.** A number of selected samples for different temperatures were analyzed using TGA to determine the amount of coke being deposited on the surface of the catalyst during different experiments. **Table 12** shows the amount of soft, hard, and total coke deposited upon the catalyst. Soft coke refers to coke removed at temperatures below 1000°C, which would be extractable by chloroform, whilst hard coke refers to coke removed from the sample by burning in air at 1000°C. From Table 12 it can be

observed that, at 400°C, there is 7.91% soft coke and 21.43% hard coke. Upon increasing the temperature to 425°C, sparse change in coke is observed; but upon further increase to 450°C, the amount of soft coke decreases whilst the amount of hard coke increases. Sangrama et al. (2004) reported that soft coke mostly consists of alkylated mono- and di-aromatics and lesser amounts of polyaromatics. Soft coke is thought to form by condensation of components of the feed onto the catalyst surface, whilst hard coke forms by reaction of the coke upon the catalyst. The formation of hard coke indicates the polymerization and breakage of side chains from aromatic compounds because hard coke has been associated with the presence of large polynuclear aromatics (Zeuthen et al. 1994). The increased deposit of hard coke at 450°C indicates that the catalyst was more reactive toward coke at this temperature and that the more-severe conditions, led to the possible formation of polynuclear aromatics upon the catalyst surface, rather than the larger quantity of soft coke formed at the lower reaction temperatures. It is also noted that the larger deposit of coke at higher temperatures is consistent with visual observations of coke deposit after opening the reactor and bed blockages during operation, leading to early shutdown of the process that occurred at the higher reaction temperatures. **Table 13** displays material-balance data for the same selected experimental runs as the TGA data presented in Table 12. The average feed and liquid volumes were measured over the course of the experiment

**TABLE 10—METALS AND SULPHUR ANALYSIS OF SELECTED SAMPLES\***

Experiment Number	THAI Field Oil	P13	P30	P37	P65	P66	P66	P67
Time of Sample (hr)		53	1	21.5	3	6.5	14.5	2.5
Temperature (°C)		400	500	425	425	425	425	425
Pressure (bar g)		20	20	20	60	20	20	40
Reaction Gas		N <sub>2</sub>	N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>
Metals content (ppm)								
Aluminum	6	7	1	6	7	7	6	6
Silicon	0.4	2	0	0.4	1	0.4	0.1	0.2
Iron	10	3	0	4	4	4	3	4
Chromium	0	0.2	0	0.3	0.1	0.1	0.1	0.1
Zinc	2	0.6	0	0.3	0.5	0.5	0.5	0.5
Nickel	54	56	21	50	55	55	54	54
Sodium	0	2	0	0	0	0	0	0
Calcium	0	0.7	0	0	0	0	0	0
Vanadium	144	149	58	136	148	150	146	146
Phosphorous	0.3	0.6	0.2	0.1	0.3	0.2	0.4	0.3
Molybdenum	6	5	0	3	4	5	4	4
Boron	0.6	1.1	0.6	0.8	1	0.8	0.7	0.7
Total Sulphur (wt%)	3.8	3.7	3.2	3.6	3.6	3.6	3.6	3.6

\* In all the experiments Akzo CoMo catalyst was used. Tin, lead, copper, silver, magnesium, barium, and manganese were also analyzed but were not detected in any of the samples.

TABLE 11—SARA ANALYSIS OF SELECTED SAMPLES

Experiment Number	THAI Field Crude Oil	P30	P37
Temperature (°C)	—	500	425
Pressure (bar g)	—	20	20
Reaction Gas	—	N <sub>2</sub>	4% H <sub>2</sub> in N <sub>2</sub>
Saturates (%)	15.38	20.59	16.37
Aromatics (%)	57.04	72.38	67.62
Polars (Naphthenes) (%)	20.18	4.53	9.11
Asphaltenes content by IP143 (%)	7.4	2.5	6.9

and converted to mass; the mass of coke was determined by TGA of the catalyst after reaction, and the mass of gas was determined by subtraction of the weights of the produced liquid and coke from the feed weight. It was observed that the mass of recovered liquid product varied from 92.32 to 97.5%, with higher recovery of liquid product at the lowest reaction temperature. The amount of coke and produced gases increased with reaction temperature, which is consistent with earlier observations of coking and increased catalyst activity at the highest temperature.

### Results and Discussion

The optimization studies showed that the variables that most influenced upgrading in the CAPRI process were temperature and oil-flow rate. Gas-flow rate, gas composition, and pressure all showed relatively sparse effect upon the upgrading performance. Several types of reactions may be occurring during the CAPRI process. Early in the reaction, catalytic cracking and a hydroconversion process may start to occur as a result of the catalytic activity. This may, for example, be the case in the early stages of the tests with nitrogen/hydrogen mixtures, in which the lowest product viscosities were observed at short reaction times. Sanford (1994) studied the reactions occurring during residuum conversion, and concluded that during the early stages of coking and hydrocracking reactions, the main reactions occurring involve the breaking of carbon-carbon bonds. However, these reactions are accompanied by carbon-rejection reactions at the surface of the catalyst pellets similar to the reactions occurring in the THAI process, which would be responsible for the heavy coke deposit upon the catalyst. Thereafter, the pores of the catalyst become completely blocked and there is also a heavy deposit upon the outside surface of the pellet.

In the next stage of the reaction, because the catalytic metals become completely covered with coke, further catalytic reactions involving the metal are limited; thereafter, the catalyst acts to retain or filter coke, thus removing some larger molecules from the oil and causing some apparent upgrading of the product. At this point further reactions could occur through thermal cracking, carbon deposition, or catalytic effects of the coke itself. The latter reactions could occur if the coke contains hydrocarbons that could release hydrogen to react with the oil, thus increasing the carbon fractional content. Reyniers et al. (2000) studied coke formation on the conversion of alkanes over ultrastable Y-type (USY)-zeolite and found that an increase in the molar H/C ratio of the products as a function of coke yield was observed because of hydride-transfer reactions with coke. Coke molecules could not be considered as being inert, with respect to the cracking reactions, and their formation led to the occurrence of reactions that strongly influence the catalyst performance. These reactions occur through the ability of the coke to act as a hydride donor toward carbenium ions at the surface and facilitate reaction pathways toward paraffinic reaction products. Sanford (1994) postulated that initial homolysis of aromatic rings in the oil produces two radicals of different reactivity, an aliphatic carbon radical and an aromatic carbon radical. The aliphatic carbon radical undergoes fragmentation to produce distillate and gas, which would explain the aliphatic components detected by refinery-gas analysis in this study. The aromatic component can condense with other similar species to produce coke, or the aromatic carbon radical can react with hydrogen to form a carbon-to-hydrogen bond and a hydrogen atom. The hydrogen atom adds to the aromatic ring, leading to the production of gases and distillate. The most logical source of the hydrocarbon gases was the breaking of side chains from naphthenic rings. Such reaction mechanisms would be consistent with the experimental observations reported in this work. Dupain et al (2003) made observations similar to the results reported in this study for the aromatic gas/oil cracking in fluid catalytic cracking (FCC) conditions (575°C and with a catalyst/oil ratio of 4.8 g catalyst/g oil) within a microriser reactor. Coke was formed early in the reaction, and cracking reactions involved the paraffinic fraction of the feed and alkyl groups associated with the benzene ring, and were accompanied by complex dealkylation and hydrogen-transfer reactions. Gas-phase alkenes and alkanes were produced by thermal-cracking reactions.

The variables that showed greater influence upon the process upgrading in this study were temperature and oil-flow rate. Operation at temperatures in the range of 475 to 500°C led to the highest levels of upgrading, but heavy coke deposition occurred, leading to premature reactor shutdown. This effect is thought to be because the higher temperatures provide sufficient activation energy to accelerate carbon-rejection reactions, rather than hydroconversion, leading to complete plugging of the catalyst interparticle pore space. The effect of oil-flow rate is to simply increase or decrease the residence time of oil in the bed, with longer residence times leading to improved upgrading, as evidenced by lower product viscosity.

The results presented in this paper demonstrate that the CAPRI add-on to the THAI process can achieve moderate levels of upgrading over up to 95 hours of operation, but that coke deposition presents a limitation to the lifetime of the catalyst. Control of the in-situ process in the oil well could possibly be affected by adjusting the air-injection rate in order to achieve a controlled rate of combustion, thus controlled operating temperature in the MOZ. Further developments of the CAPRI process will seek to extend further the catalyst lifetime, improve its activation, and reduce coke deposition. Activation of the catalyst by presulphiding, use of a guard bed to remove heavy molecules from the feed, or use of large-pore catalysts that are more resistant to coke deposition are possible ways in which the process may be improved further in future studies.

### Conclusions

CAPRI technology is an emerging heavy-oil extraction and upgrading technology, and the current work has demonstrated some of its key strengths, which are listed as follows:

- In the CAPRI process, some further upgrading is observed to the partially upgraded THAI oil, with upgrading levels of viscosity and API gravity, dependent upon temperature and oil-flow rate. However, this may be partly because of further thermal reactions and rejection of carbon from the oil on the catalyst surface, leading to apparently lighter produced oil. The catalyst activity for desulphurization and demetallation was low, suggesting that there is further scope to improve catalyst formulation and increase activity in these types of reactions.

- There is a trade-off in operation temperature between upgrading performance and catalyst-bed lifetime. For example, at

**TABLE 12—TGA ANALYSIS OF USED CoMo CATALYSTS:  
20-bar gauge PRESSURE OF THAI GAS**

Type of Coke	400°C	425°C	450°C
Soft Coke	7.91%	6.62%	4.46%
Hard Coke	21.43%	21.09	30.02%
Total Coke	29.34%	27.71%	34.66%

500°C, upgrading of up to 6°API occurs, but catalyst-bed lifetime is reduced to 1.5 hours. Catalytic activity can be maintained for up to 95 hours at a relatively low operation temperature of 400°C and 20-bar pressure.

- The optimum temperature was determined to be 420°C at a pressure of 20 bar, for which additional upgrading by up to 3°API of partially upgraded THAI oil was observed with operation time of 77.5 hours. This temperature represents a compromise between extending catalyst lifetime and achieving satisfactory upgrading.

- Upgrading of heavy oil is relatively unaffected by the pressure of the experimental system and the gas-flow rate.

- Boiling fractions of the produced oil show a reduction of up to 15°C, as determined by SIMDIS analysis; therefore, the product would be expected to have greater commercial value than the THAI-oil starting material.

- The gases evolved from the CAPRI process contain trace amounts of lighter hydrocarbons, which suggests that the cracking of hydrocarbons, including side chains of naphthenic rings, may be taking place in the process.

- Catalyst coking occurs relatively early in the process and rapidly leads to complete pore plugging. The effect is particularly severe at temperatures in the range of 475 to 500°C. Upgrading continues after the catalyst has a heavy coke deposit, suggesting that thermal-cracking reactions occur or that the coke itself exhibits a catalytic effect.

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**TABLE 13—MATERIAL BALANCE\***

Material Balance of Each Phase (wt%)	400°C	425°C	450°C
Gases	1.40	1.72	4.98
Liquid	97.5	96.21	92.32
Coke	1.07	2.08	2.70

\* CoMo catalyst, 20 bar gauge pressure, THAI gas as feed

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## Authors



**Amjad Shah** is a PhD degree candidate at the University of Birmingham in the UK. His interests lie in catalysts and reaction engineering applied to the recovery and upgrading of heavy oils and bitumen. Shah holds MSc and MPhil degrees in fuel chemistry from the University of Peshawar in Pakistan.



**Robert Fishwick** is a Research Fellow at the University of Birmingham in the UK, whose research interests lie within the area of catalysis and reactor optimisation. He joined the Catalysis and Reaction Engineering Group in 1999, where Fishwick obtained his PhD degree in chemical engineering studying mass transfer in three-phase stirred reactor systems. He also holds an MEng degree in chemical engineering and applied

chemistry from Aston University.



**Gary Leeke** is a lecturer at the University of Birmingham in the UK, whose research interests include high-pressure processing at sub- and supercritical conditions, high-pressure reaction engineering, and heavy-oil recovery. After working in the oil and gas industry, he returned to the University of Birmingham to undertake post-doctoral research and in March of 2006 he took up his lectureship. He holds a PhD degree in chemical engineering from the University of Birmingham.



**Joseph Wood** is a reader in catalytic reaction engineering at the University of Birmingham in the UK. He also leads the research group in Catalysis and Reaction Engineering, which encompasses studies of multiphase reactors, hydrogenation catalysis, CO<sub>2</sub> capture, and heavy-oil upgrading. After 3 years of industrial experience with BP and Albright and Wilson, Wood joined the Department of Chemical Engineering at the

University of Birmingham. He holds a BEng degree from Loughborough University and a PhD degree from Cambridge University in the UK.



**Sean Rigby** is an associate professor at the University of Nottingham in the UK, whose research interests include characterisation of porous media, phase transitions in confined geometries, catalysis, applications of nuclear magnetic resonance, enhanced-oil recovery, and controlled drug delivery. Following university, he worked for the catalyst business Katalco of the British chemical company Imperial Chemical Industries (ICI)

for 4 years. After leaving ICI, Rigby joined the University of Bath and in 2010 moved to the University of Nottingham. He holds MEng and PhD degrees in chemical engineering from Cambridge University in the UK.



**Malcolm Greaves** heads the Improved Oil Recovery Group in the Department of Chemical Engineering at the University of Bath in the UK, where he is Professor Emeritus of chemical engineering and a consultant. Greaves has worked for ICI and Shell UK, and he was previously assistant professor at the University of Saskatchewan before moving to Bath. His main research interests are in thermal techniques and advanced processes for in-situ recovery and upgrading of heavy oil and bitumen, light oil-air injection, downhole gasification, and reservoir simulation. Greaves is the principal inventor of the THAI process for heavy-oil recovery and coinventor of the CAPRI process for downhole catalytic upgrading. He holds BTech and PhD degrees in chemical engineering from Loughborough University.

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