DOWNHOLE UPGRADING OF WOLF LAKE OIL USING THAI/CAPRI PROCESSES - TRACER TESTS

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Introduction

With worldwide conventional oil production expected to peak during the present decade, the need to reevaluate heavy oil resources is becoming more imperative. The vast heavy oil and tar sands resources in Canada, Venezuela, the United States and other parts of the world will play an important role in sustaining our future energy supply [1].

THAI –'Toe-to-Heel Air Injection' is an integrated reservoir-horizontal wells process, which uses air injection to propagate a combustion front from the toe-position to the heel of the horizontal producer (HP). Fig 1 is a schematic representation of the basic features of the process [2].

THAI is a stable and robust in-situ combustion process, as defined by the absence of oxygen breakthrough at the production well, as well as no tendency for severe gas overriding [3]. The stability of the THAI process depends on two key factors: (1) a high temperature burning zone, which is more advanced in the top part of the oil layer, exhibiting controlled (stable) gas override behaviour, and (2) deposition of coke, or heavy residue, inside the HP. The coke which is deposited inside the HP acts as a gas seal.

THAI is a new, more advanced variant of the conventional in-situ combustion (ISC) process, which operates as a short-distance, as opposed to long-distance displacement process [4]. Due to the well arrangement used in THAI, the mobilised oil ahead of the combustion front only travels a short distance (down) to the exposed section of the HP. Since THAI operates at much higher temperatures than SAGD, it can achieve significant in-situ upgrading, andn thereby maximize oil recovery. THAI is currently the subject of a pilot development at Christina Lake, Canada (2005).

CAPRI is the catalytic extension of the THAI process, incorporating an annular layer of catalyst, emplaced on the outside of the perforated horizontal producer well, along its whole length [5, 6]. The reaction conditions created ahead of the combustion front, prior to reactants passing down through the mobile oil zone to contact the catalyst, are established by the THAI process. Further upgrading of the produced oil is achieved by catalytic conversion, as the mobilised oil passes through the catalyst layer.

Although, extensive tests on the performance of THAI and CAPRI have been made, only basic upgrading data have been reported so far. The present study aims to quantify the extent and nature of the oil upgrading during an experiment dry and wet phases of THAI and CAPRI. Gas, oil, water and solid residue analyses are used to infer mechanisms of upgrading and to begin to gauge the economic (sweep and recovery) and environmental (gas emissions and produced water quality) impact associated with the eventual field operation of the process.

Experiments

Two three-dimensional in situ combustion tests were carried out in a rectangular, low pressure stainless steel cell, measuring 0.6 m x 0.4 m x 0.1 m, equipped with ports for air injection and production. Heavy Wolf Lake crude oil (10.5 °API) was mixed with wet sand prior to packing into the cell, representing a homogeneous oil reservoir. A NiMo hydrodesulfurization (HDS) catalyst was packed around the downstream half of the horizontal producer, as shown in Fig. 2. The tests were designed in such a way as to incorporateboth THAI and CAPRI modes in a single test..

Details of the construction of the 3-D combustion cell and operation have been reported previously [2, 6]. The test conditions are listed in Table 1. Synthetic brine was used in the first THAI/CAPRI test (Run 2000-07), in order to simulate the connate water in the reservoir formation. In the second test (Run 2001-01), a tracer was added to the oil, consisting of a mixture of hydrocarbons (see Table 2). The purpose of the organic tracer was to investigate the mechanisms for oil upgrading achieved during the THAI and CAPRI processes.

It should be noted that the sandpack used in these tests did not contain kaolinite. While 3% kaolinite was added into the sandpacks used in all previous 3-D cell tests, more closely simulating an oil reservoir. The Canadian heavy oil reservoirs typically contain 5% ~ 10% of clays, such as kaolinite, illinite, montmorillionite, and chlorite[7]. It is well-known that kaolinite is a thermal cracking catalyst. Therefore, the present series of experiments represents the a worst case scenario for thermal upgrading of heavy oil by THAI-CAPRI.

Results and Discussion

The main results from the two THAI/CAPRI tests are summarised in Table 3.

Run 2000-07. This was a combined dry and wet THAI/CAPRI test, in which deuterated water was injected together with the injected air (CAPRI), as tracer during the second wet combustion period. The performance of the combustion process obtained in this test was similar that observed from standard 3-D combustion cell test on Wolf Lake heavy oil (sandpack containing 3% kaolinite) [2]. A stable, high temperature combustion front (500~600°C) was propagated along the HP, during the dry and wet combustion periods. The excellent sweep of the combustion front, in a 'Toe-to-Heel' manner, achieved a high oil recovery, at 87% OOIP.

Figure 3 shows the variation of the API gravity and viscosity for samples of the produced oil collected during the experiment. Before the combustion front reached the catalyst layer, the degree of thermal upgrading of the produced oil was only about 2 API points. This is very low, compared to a normal THAI test on Wolf Lake heavy oil. This is because no clay was added into the sandpack for Run 2000-07.

The effect of catalyst on the produced oil is clearly evident in Figure 3. The API gravity of the produced oil jumped from an API value of 14 , up to 24, during the period of 240 to 400 minutes. As the combustion front approached the catalyst section along the HP, mobilized oil, already partially upgraded in the THAI process , underwent further catalytic conversion reactions. During the second wet combustion mode, with deuturated water injection, the upgrading trend was reduced slightly from 22 °API to 20 °API. The viscosity of the produced oil achieved by CAPRI was 10 ~ 40 mPas, down from the original 24,400 mPas for Wolf Lake Crude Oil.

Run2001-01. The Wolf Lake oil was 'spiked' with the hydrocarbon mixture, before it was mixed with the previously wetted sand for the THAI/CAPRI test. The performance of this test was similar to Run 2000-07. The cumulative oil recovery achieved was also very high, at 82% OOIP, again because of the high effective 'toe-to-heel' sweep of the combustion front (500~600°C) through the sandpack. The produced oil was also upgraded to 23 API point, mainly during the CAPRI test.

In addition to post-mortem insoection of the collected liquid and solid samples, a number of further analyses on the bulk materials were conducted. Metals analysis and molecular analysis were performed on the selected samples of gas, oil, water and solid residues from Run 2001-01 (see Table 4). The results are discussed below.

SARA/PIN. Improvement in the produced oil quality during THAI/CAPRI is quantified using SARA(Saturates, Aromatics, Resins, Asphaltenes) and PIN (Paraffins, iso-Paraffins, Naphthenes). This HPLC procedure shows some variability, but no substantial change through the THAI stage. However, there is a substantial increase in the more desirable oil component (saturates) during the CAPRI stage. It is noticeable that Resins + Asphaltenes fractions decrease substantially (Figure 5), indicating the conversion of these groups to saturates, is one possible mechanism for oil upgrading.

Elemental analysis. This can be used a measure of carbon rejection, or hydrogen addition, associated with oil upgrading (see Table 4). Elemental sulfur decreases once the THAI wet stage commences, but is maintained at lower levels through the CAPRI stage. The maximum sulfur reduction of 39% was achieved in the CAPRI stage. The onset of lower sulfur numbers with start of water injection suggests a mechanism of hydrogen donation from the water , or water-gas-shift reactions in the presence of exposed sulfur (after cleavage of S-C bonds) and evolution as H_2S (hydrodesulfurization). This appears to be effective prior to the combustion front encountering with the HDS catalyst. A similar mechanism might be relevant for nitrogen, which is reduced to nearly one fifth of its original level.

Distribution of organic tracer compounds. The distribution of tracer compounds in the produced oil from Run 2001-01 was measured by GCMS. The ratio of tracer concentration, to that in the original 'spiked' oil, is shown in Figure 6. The increase in n-paraffins just before the start of water injection in THAI is considered a significant indicator of hydrous pyrolysis as an upgrading mechanism. Because normal alkanes have been reduced in-reservoir from the Wolf Lake oil (via biodegradation), these compounds must have been generated de novo. Hydrous pyrolysis of asphaltenes is the proposed mechanism as normal alkenes are virtually absent and the abundance of normal alkanes increases during the wet stages. Changes in the relative abundance of the introduced compounds are variously attributed to continuous (nC_{11}, alkylphenyls) or episodic (and nC_{20}) distillation, cracking and converting to derivative products (squalane, perhydrofluorene), cracking with polymerization downstream with subsequent cracking later in the run (decylthiophene, dimethyldibenzothiophene).

The coincidence of increased normal alkane generation during the THAI and CAPRI wet phases supports a hydrous pyrolysis (kerogen or oil + $H_2O \rightarrow CO_2 + H_2$) or the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). Coke gasification coupled with the water-gas-shift reaction could accompany this mechanism or become dominant in the near vicinity of the combustion front, particularly in the CAPRI stage.

Conclusion

In situ upgrading of heavy oil using THAI (thermal) and CA*PRI* (thermal–catalytic) processes achieves substantial upgrading of produced oil and as well as high oil recovery, up to 87%OOIP. The results of two tracer THAI/CAPRI tests indicate that hydrous pyrolysis of asphaltenes and the water-gas shift reaction are the main mechanisms, or routes of hydrogenation of the thermally or catalytically cracked oil, producing alkenes in the upgraded oil. The distillation effect of the light fraction also contributes to some (small amount) of upgrading of the produced oil.

The catalytically upgraded oil contains substantially higher levels of saturates and reduced heavy ends. There are also significant environmental benefits because of the large reduction in heavy metals and sulphur, with potential reductions in refinery loadings. Thus, THAI and CAPRI processes are likely to make an important contribution towards sustainable energy supply in the near future.

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Table 1 Experimental Conditions of 3-D cell THAI/CAPRI Tests

Run	**2000-07**	**2001-01**
3-D Cell	0.6m × 0.4m × 0.1m	
Internal insulation	6 mm ceramic fiber layer	
Silicon Sand, W50, (kg)	34.1	29.09
Porosity (%)	39.05	
Gas permeability (mD)	1503	
Wolf Lake oil (kg)	6.90	
'Spiked' oil (kg)		5.63
Water (kg)		1.48
Synthetic Brine (kg)	1.74	
Na (ppm)	7,474	
Ca (ppm)	140	
Mg (ppm)	73.5	
Cl (ppm)	11,506	
SO_4 (ppm)	560	
HCO_3 (ppm)	254	
Total Salt (ppm)	20,007	
Catalyst (CoMo HDS)	Regenerated, 1/16" extrudate	
Catalyst loading (g)	191.1	172.5
Catalyst length (m)	0.3	
Well configuration	2VIHP	
Ignition	Hot Nitrogen	
Air flux (Sm3/m2h)	15	
Initial sandpack temp. (^oC)	20	
Back pressure (psig)	20 - 25	

Table 2 Tracers used in Run 2001-01

		ρ	Amount		
Standards		g/ml	g	moles	ppm
undecane	n-C_{11}	0.74	2.1	0.013	282
1-phenylhexane	$C_{12}H_{18}$	0.86	4.2	0.026	570
perhydrofluorene	*tricyc*-C_{13}	0.92	2.1	0.012	282
9,10-dimethyl anthracene	$C_{16}H_{14}$	1.10	1.9	0.009	265
4,6-dimethyld ibenzothiophene	$C_{14}H_{12}S$	1.20	2.1	0.010	282
1-phenyldecane	$C_{16}H_{26}$	0.86	2.3	0.011	315
3-decylthiophene	$C_{14}H_{24}S$	0.91	2.0	0.009	277
eicosane	n-C_{20}	0.78	2.1	0.007	282
cholestane	*tetracyc*-C_{48}	1.49	2.1	0.006	282
squalane	*i*-C_{30}	0.86	4.2	0.010	565
Synthetic Crude Standard		0.88	25		3401
DILUANTS			29	ml	
hexadecane	n-C_{12}		5	ml	
dodecane	n-C_{16}		65	ml	
1-phenyltridecane	$C_{19}H_{32}$		40	ml	
Total Mixture (liq at 50^oC)			139	ml	

ρ -Density

Table 3 Results of THAI/CAPRI Tests
(Wolf Lake Heavy Oil, 10.5 ^{o}API)

Run	**2000-07**	**2001-01**
Recovery method	Primary	
Combustion mode	Dry and Wet	
Overall period (hr)	12.25	12
Pre-ignition period (hr)	2.25	2.25
Air injection period (hr)	10.0	9.75
Dry phase (hr)	7.0	6.75
Wet phase (hr)	3.0	3.0
Normal water injection (hr) WOR ($m^3/1000Sm^3$)	1.5 0.3	3.0 0.3
Air injection rate (l/min)	10	
Peak temperature (^oC)	500~600	
Produced gas composition (% average) CO_2 CO O_2	 14.56 4.88 3.25	 15.38 5.49 3.88
$CO/(CO+CO_2)$	0.251	0.263
H/C ratio	0.05	0.0
O_2 utilisation (%)	84.5	81.5
Furn consumption (%OOIP)	7.7	9.6
Oil Recovery (%OOIP)	87.1	82.0
Residual oil (%OOIP)	2.9	5.39
AOR (Sm^3/m^3)	1130	1070
Combustion front velocity (m/hr)	0.05	0.05

Table 4 Elemental Analysis of Produced Oil (Run 2001-01)

Sampling time (min)		**%C**	**%H**	**%O**	**%N**	**%S**
0		83.89	10.74	1.07	0.41	4.86
20		76.28	11.38	7.84	0.37	4.50
65		76.38	10.47	7.54	0.36	4.39
123	Wet	71.41	10.95	12.75	0.30	3.73
180	THAI	60.04	11.06	21.37	0.22	2.99
209	CAPRI	75.56	12.45	6.73	0.22	3.18
356		85.27	11.23	0.83	0.08	2.97
389		84.73	12.60	1.08	0.07	3.05
453	Wet	84.56	10.59	0.76	0.13	3.41
512		84.57	10.59	0.74	0.13	3.46
>512		84.17	11.56	0.68	0.15	3.47

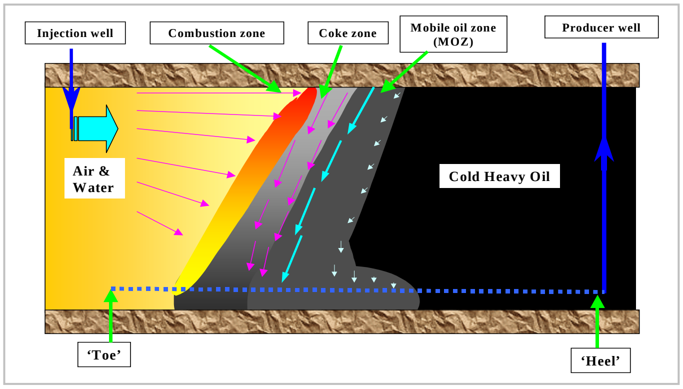

Figure 1. THAI – 'Toe-to-Heel Air Injection' Process

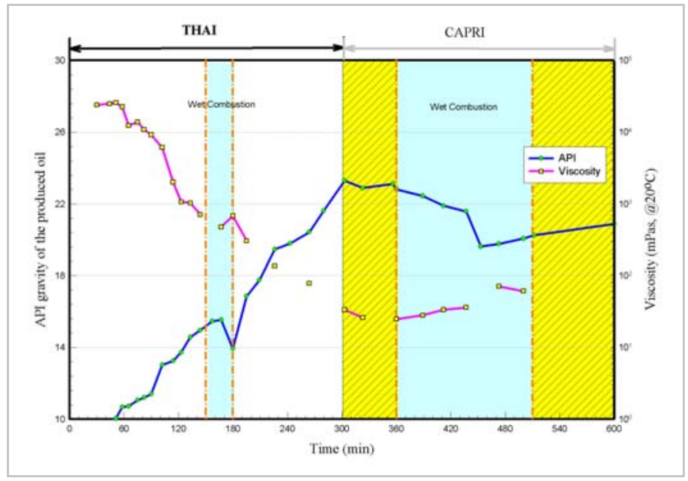

Figure 4. In situ upgrading of produced oil (Run 2001-01)

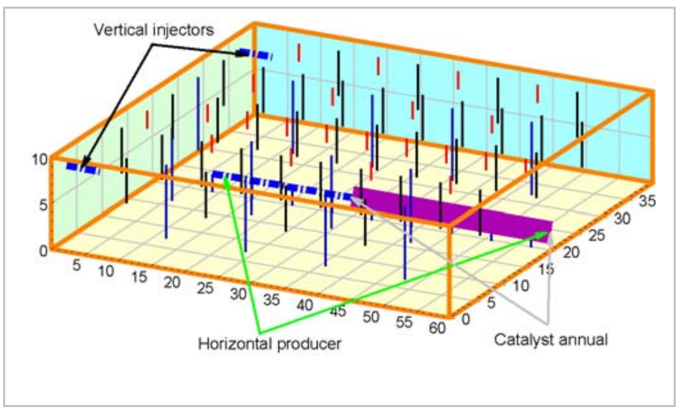

Figure 2. 3-D Combustion cell for the THAI/CAPRI tests

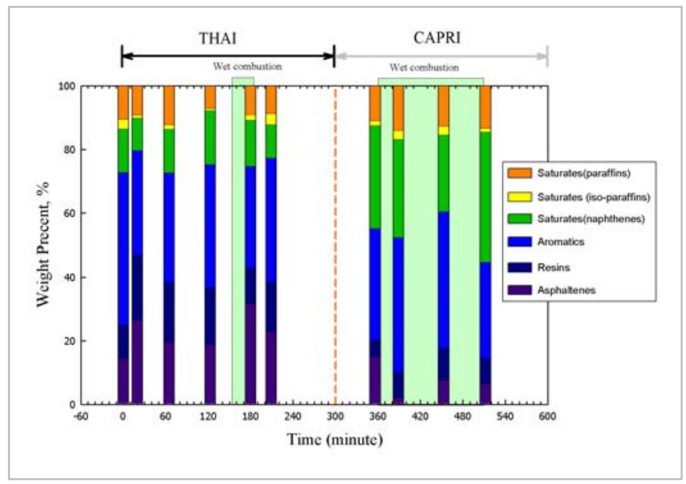

Figure 5. SARA/PIN analysis of produced oil (Run 2001-01)

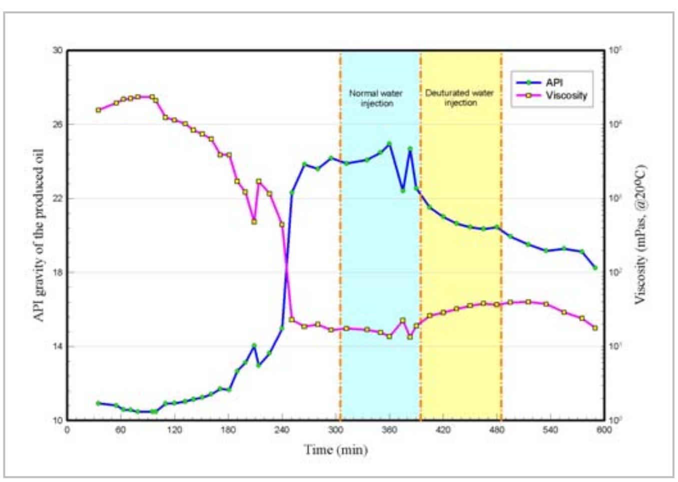

Figure 3. In situ upgrading of produced oil (Run 2000-07)

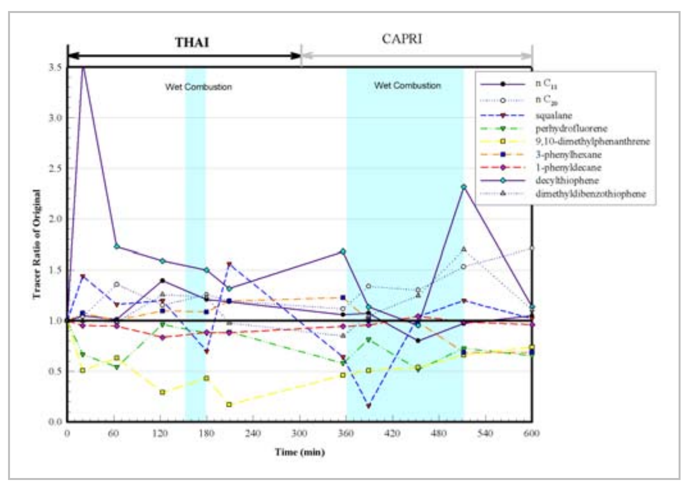

Figure 6. Tracer compounds in produced oil (Run 2001-01)