

Oil & Natural Gas Technology

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Quarterly Report April 2012 – June 2012 Post Retort, Pre Hydro-treat Upgrading of Shale Oil

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1. EXECUTIVE SUMMARY

In the 11th quarter considerable progress was made. The DoE funded program will end next quarter but the development program will continue with private funding. A new lab space was selected for installing the new reactor. The new reactor will feature a new sodium addition system expected to improve product yield and quality. Some very encouraging experimental results were obtained during the quarter where diluted Athabasca bitumen went from black to translucent yellow with sulfur and metals removal and partial residue shifting to lighter fractions. Also a very high sulfur (13%) oil shale was processed where essentially all of the sulfur was removed. The technology was showcased at the Offshore Technical Conference in Houston in early May and at the Jordanian Oil Shale Symposium in May as well.

2. PROGRESS, RESULTS AND DISCUSSION

2.1 Task 1.0 -- Project Management Plan

The PMP was updated within 30 days and submitted to the Project Manager (Quarter 1).

2.2 Task 2.0 -- Upgrading Development

It is explained in detail in 6th Quarterly report.

2.3 Task 3.0 -- Electrolysis Development

It is explained in detail in 6th Quarterly report.

2.4 Task 4.0 -- Analysis

It is explained in detail in 6th Quarterly report.

Budget Period 2

2.5 Task 5.0 – Upgrading Development

This task is related to developing the process of treating shale oil, or heavy oil at elevated temperature and pressure in the presence of an alkali metal, either sodium or lithium and also a hydrogen source, either hydrogen gas or methane (natural gas) to form an oil stream with reduced levels of sulfur, nitrogen and heavy metals and also in the process reducing the viscosity and increasing the API gravity. The object here is to determine the impact of various reaction parameters on product quality.

2.5.1 Subtask 5.1 – Analytical Capability

Analytical laboratory set up

There are no major changes in analytical capability.

2.5.2 Subtask 5.2: Upgrading Reactor and Separation setup

A detailed Hazard Review process was begun to finalize the installation of the larger reactor with an electromagnetic sodium pump to enable slow controlled addition of the sodium to the oil.

With most of the new lab's remodel work complete, the large reactor was moved into its desired location. The electrical and pneumatic utilities were connected and reactor operation was verified.

The sodium pump, flow meter, and reservoir were received and work was started for their installation. This included the mounting and wiring of the control box to the wall, procurement of an environmental chamber to house the reservoir and cart to support and hold the other items.

The new lab space for the continuous reactor was remodeled during this quarter, which included new paint, lighting, and installation of a sink and drain. Other necessary items were installed, which included a fume hood, the necessary electrical outlets for the various equipment, exhaust hoods, and cylinder racks. Work to remodel the adjacent lab for the separation and electrolysis processes has not been started due to the current tenants project demands.

2.5.3 Subtask 5.3 – Process runs

The Recipient shall obtain at least two samples of Shale Oil in sufficient quantity for the various runs planned and obtain permission to use the samples for the present study. Preferably the Recipient shall obtain samples with different origin which can be evaluated. Shale Oil shall be processed systematically according to the approved testing plan provided in the PMP.

Composition of shale oil shall be determined before and after the process. Up to 16 select runs shall also be characterized in terms of the oil character and chemistry.

Several experiments were performed with the following feed stocks: diluted bitumen (dilbit), a heavy oil, and two oil shale samples. These were all evaluated using both hydrogen and methane as capping gases and at varying levels of sodium stoichiometry. Target temperature and pressure for these runs were all 380 C and 1500 psi respectively and reaction time was set at 2 hrs. The individual runs may have varied from these values slightly due to exothermic reactions during testing causing temperature and pressure spikes, but all attempts were made to maintain these conditions.

The diluted bitumen was evaluated at different levels of sodium stoichiometry ranging from deficient Na at 0.64 to excess Na at 1.29. Results showed that 100% of the sulfur and metals could be removed with sufficient Na and that this upgrading is independent of capping gas. Increases in API correlated with sulfur removal and thus with Na stoichiometry, but liquid yields would drop with increasing Na. This is likely due to large exotherms triggered by the rapid addition of sodium promoting thermal cracking. The oil residual fraction (>530 C) was also significantly reduced from 42% to less than 10% during the upgrading process.

Two runs DB 5 and DB 6 were run step wise. That is adding a portion of the Na required in one run, then analyzing it, then running the previously run sample again with additional Na. The overall result for the two step runs were very similar to their one step counter parts. Please see Table 1 and Table 2 below for results of the runs.

Table 1: Specifications of Dilbit

C %	H %	N %	S %	API	TAN	Ni (PPM)	V (PPM)
79.4	10.47	0.47	3.83	17.4	4.15	69.5	176.5

Table 2: Dilbit run data

Run Id	Capping Gas	Actual Na/ Theoretical Na	Sulfur Removed (%)	Vanadium Removed (%)	Nickel Removed (%)	API	Liquid Yield %
DB 1	H2	0.97	99.8	100.0	100.0	33.6	86.8
DB 2	H2	1.24	100.0	100.0	100.0	35.8	70.0
DB 5 P1	H2	0.64	76.2	94	79	23.0	98.1
DB 5 P2	H2	0.99	98.5	100.0	100.0	30.5	83.7
DB 5 P1&2	H2	1.07	99.5	100.0	100.0	30.5	82.1
DB 2B	CH4	0.96	98.6	100.0	100.0	34.3	69.0
DB 4	CH4	1.29	100.0	100.0	100.0	37.9	54.7
DB 6 P1	CH4	0.69	76.0	35	25	21.9	94.2
DB 6 P2	CH4	1.19	97.0	100.0	100.0	32.7	66.1
DB 6 P1&2	CH4	1.15	98.8	100.0	100.0	32.7	61.4

The heavy oil sample was from the upper Midwest and was evaluated at different stoichiometric levels of sodium between 0.81 and 1.11. The upgrading process was able to remove most of the sulfur and metals during the runs and followed the trend of higher sulfur removal with increased sodium content. The poorer liquid yields correlated with the sodium injection occurring all at once. Where the better yields had the sodium injected in multiple shots. With the current set up, the sodium injection rate is difficult to control. The use of hydrogen as a capping gas was preferred over methane but only marginally and there were good increases in API for all runs. The properties of the as received oil and run data are tabulated in Table 3 and Table 4

Table 3: Specifications of the heavy oil sample

C %	H %	N %	S %	API	TAN	Ni (PPM)	V (PPM)
81.37	10.57	0.44	5.0	14.2	0.4	54	257

Table 4: Heavy oil run data

Run Id	Capping Gas	Actual Na/ Theoretical Na	Sulfur Removed (%)	Vanadium Removed (%)	Nickel Removed (%)	API	Liquid Yield %
AHO 1	H2	0.81	87.6	97.4	66	21.9	97.8
AHO 3	H2	1.11	98.7	100	100	30.3	70.1
AHO 5	H2	0.94	94.4	100	90	23.9	89.7
AHO 2	CH4	1.07	96.3	93.3	83	26.5	66.0

The two oil shale samples were from different regions of the world. One was from the Middle East and the other from Colorado. The sample from the Middle east had a high sulfur content as compared to previous samples and was evaluated at sodium stoichiometries between very deficient at 0.17 to very excess at 2.44. It also had two runs where the same material was cycled twice with new sodium each time to upgrade in steps. The overall yields suffered for these runs do to doubling the losses during the multiple separations processes and that made it hard to determine if a two-step process was advantageous with respect to yield. Significant increase in API was obtained along with the high rate of sulfur removed. The percentage of sulfur removed correlated well with the sodium stoichiometry as seen in Figure 1 below. The properties of the as received oil and run data are tabulated in Table 5 and Table 6.

Table 5: Specifications of Middle Eastern shale oil

C %	H %	N %	S %	API	TAN
77.7	9.03	0.55	12.93	14.2	0.4

Table 6: Middle Eastern shale oil run data

Run Id	Capping Gas	Actual Na/ Theoretical Na	Sulfur Re- moved (%)	API	Liquid Yield %
MEOS 1	H2	0.91	98.0	32.0	72.0
MEOS 4 P1	H2	0.67	83.4	24.7	87.7
MEOS 4 P2	H2	2.44	97.1	40.	66.3
MEOS 4 P1&2	H2	1.14	99.2	40.0	58.2
MEOS 6 P1	H2	.70	87.6	27.2	85.2
MEOS 6 P2	H2	.94	70.6	30.1	89.3
MEOS 6 P1&2	H2	.84	95.2	30.1	76.1
MEOS 5 P1	CH4	0.17	40.5	12.8	92.8
MEOS 5 P2	CH4	0.45	58.5	17.5	82.3
MEOS 5 P1&2	CH4	0.47	66.7	17.5	76.4
MEOS 7	CH4	0.73	85.8	24.9	74.8

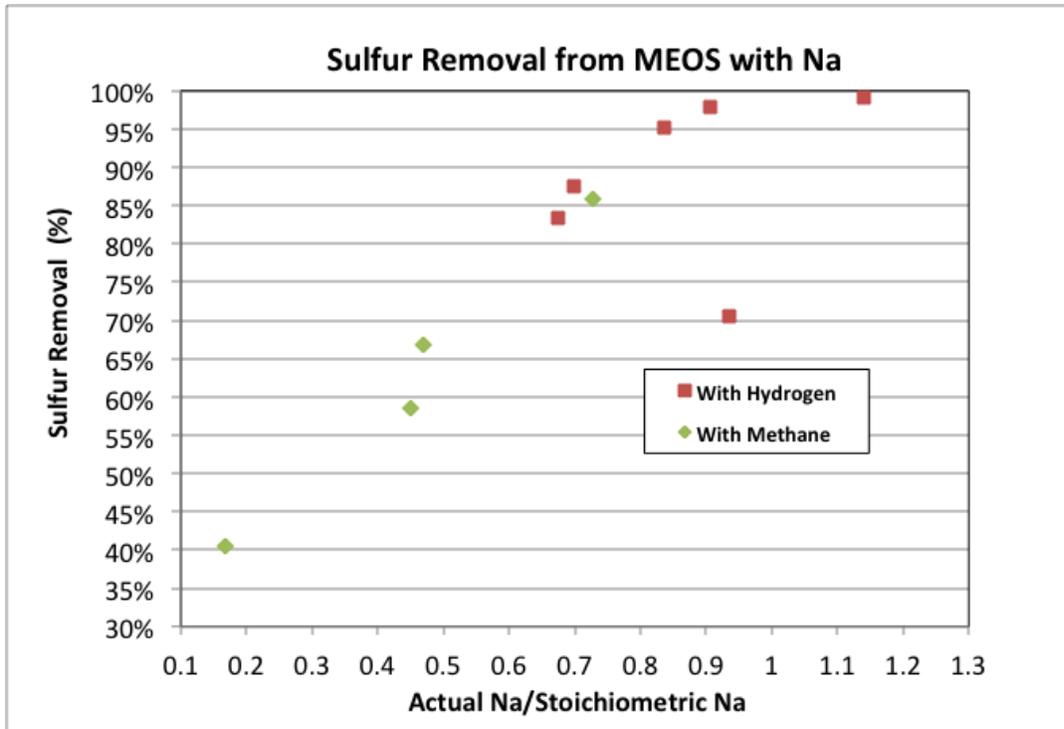


Figure 1: Sulfur removal with respect to Na concentration

The oil shale sample from Colorado had low sulfur and metal concentration as compared to previously run samples. The sulfur content was less than 1%. This was evaluated with sodium stoichiometry (based on sulfur and nitrogen content) between deficient at 0.55 and excess at 1.02. The runs with both high sulfur and nitrogen removal had poorer liquid yields, while the runs with good sulfur removal and moderate nitrogen removal had better liquid yields. Also the runs using the hydrogen capping gas had better overall liquid yields than those with the methane capping gas. However, sulfur and nitrogen removal were similar for runs of the two gases. Please see Table 7 and Table 8 below for the properties of the as received material and the run data.

Table 7: Specifications of Colorado shale oil

C %	H %	N %	S %	API
83.6	10.8	1.9	0.72	20.1

Table 8: Colorado shale oil run data

Run Id	Capping Gas	Actual Na/ Theoretical Na	Sulfur Removed (%)	Nitrogen Removed (%)	API	Liquid Yield %
CO 1	H2	0.55	73.4	2.8	22.0	97.5
CO 3	H2	1.02	99.8	96.6	38.7	49.8
CO 4	H2	0.76	99.5	94.3	36.6	58.0
CO 6	H2	0.57	98.0	49.8	25.4	75.3
CO 2	CH4	0.64	93.3	65.3	25.2	66.6
CO 5	CH4	0.71	99.4	91.5	33.6	50.7
CO7	CH4	0.60	96.7	72.1	27.7	59.7

2.6 Task 6.0 - Electrolysis development

To reduce the overall cost of the upgrading process, an electrolysis process will be developed to regenerate sodium or lithium from the respective polysulfide. The process will feature ceramic ion conductive membranes developed at Ceramatec. The energy cost to regenerate the alkali metals from the polysulfide is expected to be about half that of producing the metals from their respective chlorides.

2.6.1 Subtask 6.1 – Membrane fabrication

The Recipient shall fabricate and characterize sodium conductive and lithium conductive membranes.

2.6.2 Subtask 6.2 – Seal testing

Ceramatec shall evaluate various seal approaches for compatibility with the alkali metal and the metal polysulfide at various temperatures.

2.6.3 Subtask 6.3 – Cell design and set up

Ceramatec shall design benchtop cells for two types of operation, one where the alkali metal is molten and one where it plates onto a current collector. Reactors and catholyte transfer means will be provided to prepare alkali metal sulfide of differing composition and transfer to the cell. The cells will be designed to accommodate multiple reference electrodes, operate at various elevated temperatures. The cells will have features designed to facilitate sulfur removal and be designed to operate within a dry enclosure.

2.6.4 Subtask 6.4 – Cell operation

The Recipient shall operate cells under various conditions including variation of the current density, electrode gap, temperature, electrolyte, polysulfide order, and alkali metal. Current will be measured as a function of applied voltage. Periodically cell operation will be interrupted and cell contents analyzed to determine current efficiency. In Phase 1 the alkali metal polysulfide will be synthesized from alkali metal and sulfur and will not contain appreciable impurities which may flow through from an actual upgrading process as will occur in Phase 2.

Long term test cell results

Sodium recovery cell *Na Recovery Cell 20120213* has been operated for 2435 hours at current densities of 60, 70, and 80 mA/cm². The properties of the cell are listed in Table 9. Figure 2 shows the total operating voltage and the cell open circuit potential versus total elapsed time for the cell. Table 10 displays the average voltage and average open circuit potential of the cell during the test.

Table 9: Summary of sodium recovery test cells run in long-term mode during reporting period

Cell ID#	Anolyte	Anode Electrode	Membrane	Catholyte	Cathode Electrode	Seal Type	Operating Conditions
Na Recovery 20120213	Na2S4 in MF	Platinized Ti mesh (1.1" diam.)	NaSICON GY (1 mm thick, 1.67 cm ² active area)	Molten Na	Molten Na, Ti rod current collector	Silica-Boria Glass	Temperature=130C Anolyte Agitation Cte Current=60-80 mA/cm ²

Table 10: Summary of performance of sodium recovery test cells run in long-term mode

Cell ID	Total Run Time	Current Density	Avg. Voltage	Avg. OCV	Status
	Hours (days)	mA/cm ²	V	V	
Na Recovery Cell 20120213	2435* (101*)	60-80	3.26	2.19	Cell still in operation

* Total time includes short time periods to measure the cell OCV

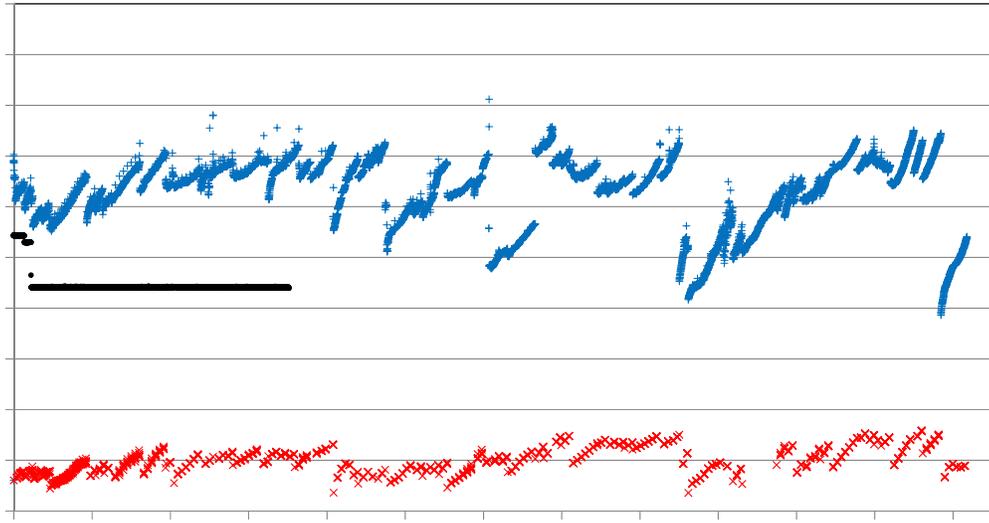


Figure 2: Cell voltage and Open Circuit Voltage (OCV) versus run time for long term cell *Na Recovery Cell 20120213*. Run time includes time periods for OCV measurements (no DC current applied)

2.7 Task 7.0 – Analysis

2.7.1 Subtask 7.1 – Develop electrolysis process model

Ceramatec shall analyze data from Task 3 and a performance model will be developed. Various factors such as membrane thickness, type of alkali metal, electrode configuration and cell design would be included in the model considerations.

2.7.2 Subtask 7.2 – Preliminary cost analysis

The Recipient shall incorporate the models from Subtasks 4.1 and 4.2 into a preliminary cost model. Based on the preliminary cost analysis, a selection will be made between sodium and lithium as the most promising alkali metal for further pursuit in Phase 2. Sodium was selected because of higher efficiency of removing sulfur and lower cell voltage in electrolysis compared to Lithium.