

# Oil & Natural Gas Technology

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## Post Retort, Pre Hydro-treat Upgrading of Shale Oil



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## **Abstract**

Various oil feedstocks, including oil from oil shale, bitumen from tar sands, heavy oil, and refinery streams were reacted with the alkali metals lithium or sodium in the presence of hydrogen or methane at elevated temperature and pressure in a reactor. The products were liquids with substantially reduced metals, sulfur and nitrogen content. The API gravity typically increased. Sodium was found to be more effective than lithium in effectiveness. The solids formed when sodium was utilized contained sodium sulfide which could be regenerated electrochemically back to sodium and a sulfur product using a "Nasicon", sodium ion conducting membrane. In addition, the process was found to be effective reducing total acid number (TAN) to zero, dramatically reducing the asphaltene content and vacuum residual fraction in the product liquid. The process has promise as a means of eliminating sulfur oxide and carbon monoxide emissions. The process also opens the possibility of eliminating the coking process from upgrading schemes and upgrading without using hydrogen.

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## EXECUTIVE SUMMARY

Ceramatec was awarded a grant by the National Energy Technology Laboratory (NETL), Department of Energy (DOE) to conduct a project titled: *Post Retort, Pre Hydro-treat Upgrading of Shale Oil*. The program began October 2009, and was completed September 2012. There were 2 primary areas of the technology development. In the first primary area, a process was developed which utilized an alkali metal in combination with limited hydrogen or methane to promote desulfurization, denitrogenation, and demetallization of shale oil or heavy oil streams not suitable for refining prior to treatment. In the second primary area an electrolysis process was developed to regenerate the alkali metal and separate sulfur and metals. Alkali metal conductive ceramic membranes were utilized in the electrolytic process.

After extensive testing, utilizing 3 different feedstocks, 2 shale oils from Uintah Basin oil shale and heavy oil from California, and using either sodium or lithium as the alkali metal. The conclusion was reached at the end of the 6<sup>th</sup> quarter that sodium is the preferred alkali metal over lithium for several reasons. 1) Sulfur removed relative to moles of alkali metal was substantially greater with sodium, 2) Sodium regeneration from sodium sulfide using the sodium ion conductive Nasicon membrane requires less voltage and is therefore economically favored over lithium. 3) Nasicon membrane is more mature and stronger than the lithium ion conductive Lisicon membrane, therefore the membrane cost is expected to be more favorable and 4) Sodium is less costly and more readily available compared to lithium. The fact that sodium specific gravity is very close to the specific gravity of the various oil feedstocks compared to lithium which is much more buoyant is a probable reason why sodium interacted with the oil more effectively for sulfur removal compared to lithium. Also, sodium melting at a relatively low temperature compared to lithium enabled operation of electrolysis for a long duration, almost 6000 hours without any degradation of the Nasicon membrane at a temperature above the melting temperature of sodium but well below the boiling temperature of organic solvents which were used to dissolve sodium sulfide, sodium polysulfide, and to some extent sulfur over the course of electrolysis. In the electrolysis cells, molten sodium was in direct contact with the membrane, reducing cell resistance.

While, the testing clearly favored sodium over lithium, hydrogen was only slightly preferred over methane as the gas mixed with the alkali metal and oil feedstock so both hydrogen and methane were evaluated for the remainder of the program. With everything equal, methane is preferred over hydrogen because of lower cost and lower carbon dioxide emission. Additional feedstocks were evaluated including several samples of bitumen and bitumen derivatives from Alberta, including two neat, one diluted, and a bitumen bottom from a different upgrading process. Also, another heavy oil from Mexico was tested, coker diesel, and three more oil shale samples; one from Australia, one from Jordan and one from Colorado's Piceance Basin. Regardless of the feedstock type, which varied considerably from one another in terms of sulfur, nitrogen and metals content, API Gravity, asphaltene and boiling curves, the reaction process with sodium had very similar effects. With either hydrogen or methane, sulfur removal was nearly directly proportional to the amount of sodium added. Heavy metals consistently are removed from the oil before the sulfur is removed. Nitrogen is also removed to a large extent but not to the same degree as sulfur and the correlation between nitrogen removal and sodium addition is weaker than with sul-

fur. Nitrogen removal was sporadic and occurred at a greater extent after most of the sulfur was removed. Very consistently, Total Acid Number (TAN) was reduced to “0”, regardless of the starting TAN value which was over 5 in some cases. API Gravity increased (which means the specific gravity decreased) as the amount of sodium utilized increased, nearly in the same way regardless of whether hydrogen or methane was used. The degree to which the API Gravity increases, to a large extent, can be predicted by a simple model. The increase in API Gravity can be very beneficial because it can reduce how much diluent is needed to meet the specifications for transport in a pipeline.

The process had additional benefits if the feedstock contained asphaltene or a high boiling fraction. For example, neat bitumen with 17% asphaltene, where the asphaltene contained 8.6% sulfur before, after sodium treatment had <0.3% asphaltene. The reduction in asphaltene cannot be explained merely by assuming the asphaltene turned into coke because the liquid yield was high enough to indicate asphaltene is transformed through the reaction with sodium, also the organic material still classified as asphaltene is sweet after treatment, nearly free of sulfur and metals. Likewise, feedstocks with a significant high boiling fraction are transformed. For example, a bitumen or heavy oil with 50% of the boiling fraction over 525C and 20% over 720C before treatment would have only 25% boil above 525C and less than 0.5% over 720C after treatment. The reduction in asphaltene content and downward shift in the boiling distribution dramatically increase the value of the material after treatment since in many cases a fraction which would be considered of low value could be considered for conversion to lighter liquids, for example by using Fluidized Catalytic Cracking Process.

Treatment of the feedstocks with sodium have the potential to increase their value considerably. Reduction of TAN alone can increase the value by \$10 per barrel for many high TAN feedstocks, and reduction of the high boiling fractions to lower boiling fractions can increase the value by over \$30 per barrel because coking is avoided. In addition, reduction of sulfur, metals, and nitrogen bring additional value.

If sulfur is removed without hydrogen then the carbon dioxide footprint is reduced by avoiding emission from steam methane reforming. Also sulfur oxide emissions are eliminated because the Claus plants required for conventional sulfur recovery from hydro-desulfurization are eliminated with the new process.

Data and results were presented on many occasions, domestically and internationally. There were three consecutive presentations at the Oil Shale Symposium in Colorado held in October 2010, '11, and '12, also at the Gas and Oil Expo in Calgary, June 1011, Jordan International Oil Shale Symposium, May 2012, at the Oil Sands & Heavy Oil Technologies conference July 2012, and the Oilsands 2012 conference August 2012 in Edmonton.

Before the program concluded, Western Hydrogen (WH) out of Calgary licensed the technology for upgrading bitumen or heavy oil from Canada and currently is investing in the continued development and scale up of the technology. WH has now transferred rights to a newly formed company dedicated to the technology called “Field Upgrading.”([www.fieldupgrading.com](http://www.fieldupgrading.com)) Alberta Innovates, also based in Calgary is also providing funding for the same purpose.

## **Experimental Methods**

### *Laboratory*

Experimental capability started from scratch. A lab space was cleared out, cleaned and painted. Extra ventilation was installed with redundant systems and back-up power for safety with hydrogen sulfide. Glove boxes and dry boxes were installed for handling of sodium and sodium sulfide solids.

### *Analytical*

Analytical capability was established through equipment purchases, training, and comparative testing against outside lab results. In house analytical capability developed as part of the program included: C, H, N, S composition; Ni, Fe, V, As, Hg composition (ICP); Total Acid Number (TAN); API Gravity; Gas composition (Gas Chromatography); Liquid boiling distribution (Gas Chromatography coupled with “Simdist” software; Asphaltene content.

Outside laboratory analyses occasionally performed are, olefins, and viscosity.

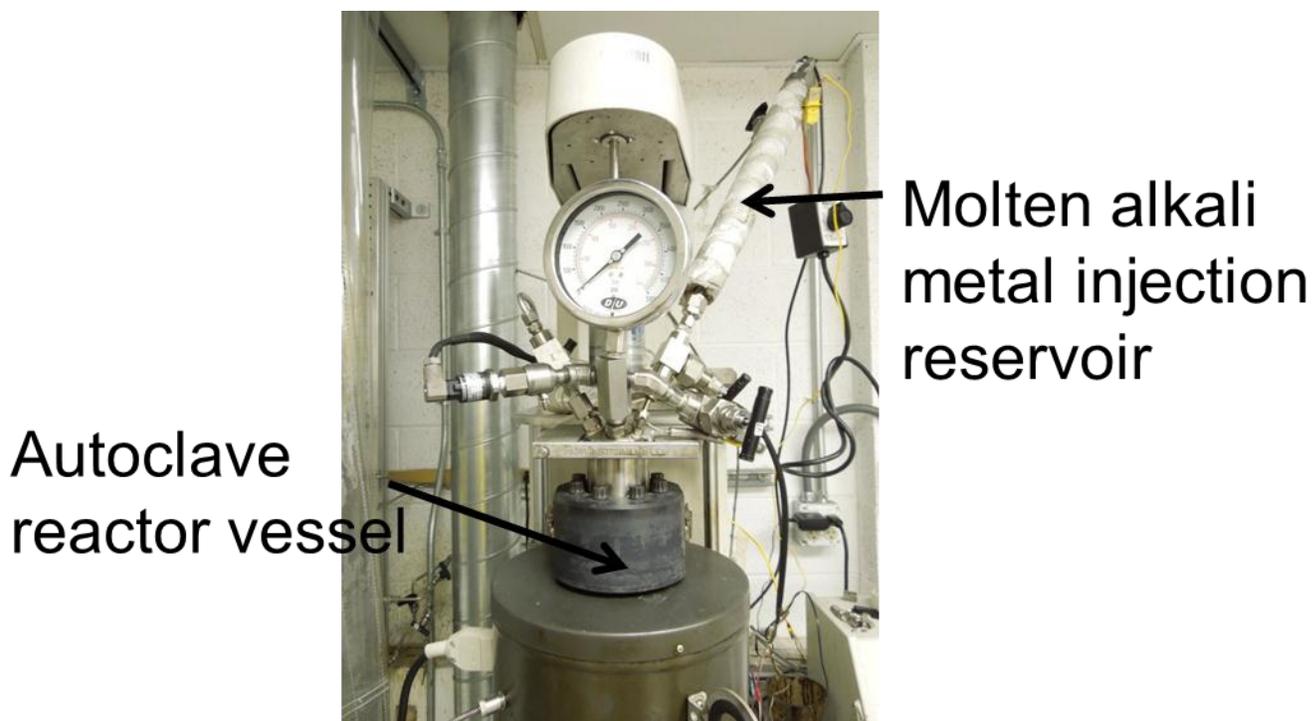
Before the program began, Ceramatec already had tools which were utilized for the program including, X-ray diffractometry, scanning electron microscopy, and kilns, grinders, tapecasters, powder presses, lamination presses, setters, and various tools and equipment needed to make ceramic membranes.

### *Reactor experiments*

Ceramatec also had a 500 cubic centimeter (cc) stirred autoclave reactor which was used for all of the experiments.

Initially sodium or lithium were charged directly into the reactor in the solid state with the liquid feedstock oil, then heated up to temperature but soon the equipment was modified to allow heated, molten sodium or lithium to be injected into the reactor liquid pneumatically under hydrogen or methane pressure. Once the molten alkali metal was injected, the contents of the reactor were held at temperature and pressure for a target period of time then quenched by dropping the heater

and bringing a bucket of water to dip the outside of the reactor into. Gases used in the experiments were high purity compressed gasses in cylinders. Gases entering the reactor were measured by mass flow meter, as well as gases leaving the reactor. Gases leaving the reactor were also analyzed by GC. After an experiment, solids and liquids were removed from the reactor and separated by centrifuge. If the feedstock did not have asphaltene, such as shale oil or coker diesel, the solids were washed with hexane to remove adhered liquids. The hexane was vaporized and the remaining liquid added to the liquid yield. If the feedstock contained asphaltene, such as Mexican heavy oil, or Alberta bitumen, the solids were rinsed with toluene to avoid precipitation of asphaltene, then toluene was vaporized from the wash and the remaining liquid added to the liquid yield.



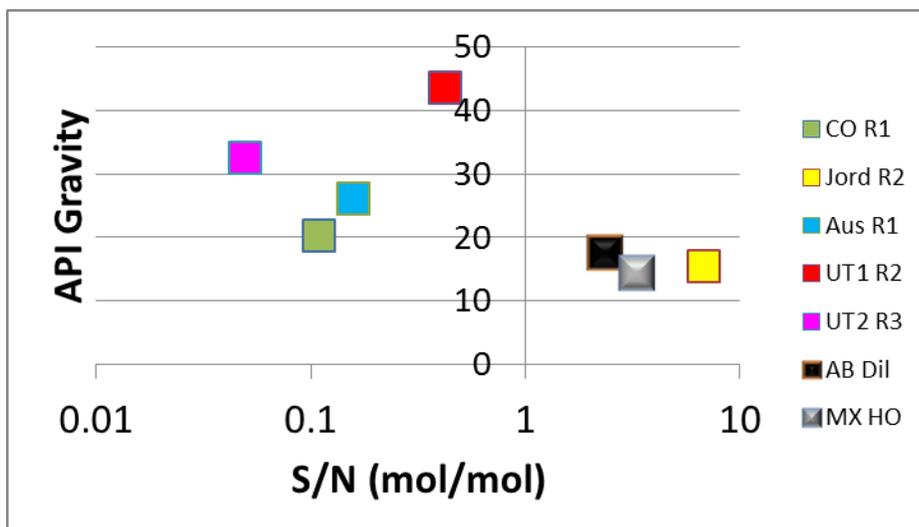
**Figure 1: Reaction vessel with molten alkali metal injection reservoir**

Table 1 Lists seven of the feedstocks tested, showing the C,H,N,S composition, hydrogen to carbon ratio and sulfur to nitrogen ratio. If the feedstock is shale oil, it is denoted with R1, R2 or R3 which represents three different retorting processes. Colorado R1 and Australian R1, for example were retorted with the same process and in this case in the same retort but the oil shale came from the different respective locations. Likewise, Jordanian R2 and Uintah 1 R2 were retorted in

the same retort process, R2, which was different from R1. Uintah 2 R3 was retorted in a retort different from either R1 or R2 and the oil shale Uintah 1 and Uintah 2 were from different locations but both locations were in the Uintah Basin. Alberta Dil is a sample of bitumen from the Athabasca tar sands that has been “diluted” with condensate, the light hydrocarbon liquid produced as a byproduct from natural gas production. The sample is about 22% condensate (or diluent) and about 78% bitumen. Mexican HO is a heavy oil sample from Mexico.

**Table 1: Composition, hydrogen to carbon ratio, sulfur to nitrogen ratio and API Gravity of seven of the feedstocks tested under similar conditions.**

Feed	C (%)	H (%)	N (%)	S (%)	H/C (mol)	S/N (mol)	API
Colorado R1	83.57	10.80	1.90	0.72	1.55	0.11	20.1
Jordanian R2	77.27	9.03	0.55	12.96	1.40	6.88	15.3
Australian R1	84.10	11.30	0.97	0.55	1.61	0.16	25.9
Uintah 1 R2	79.50	11.83	0.48	0.70	1.79	0.43	43.4
Uintah 2 R3	84.70	11.63	1.36	0.22	1.65	0.05	32.4
Alberta Dil	79.40	10.47	0.47	3.83	1.58	2.37	17.4
Mexican HO	81.37	10.58	0.44	5.00	1.56	3.31	14.2



**Figure 2: Plot of API Gravity versus the Sulfur to Nitrogen ratio (log scale)**

Figure 2 shows a plot of API Gravity versus Sulfur to Nitrogen ratio for seven of the feedstocks listed in Table 1. The figure shows the variety of feedstocks tested.

The sample diversity is broad where Jordanian R2 had sulfur content of 13%, with a S/N of 6.88 in contrast with Uintah 2 R3 that had considerably more nitrogen than sulfur on a molecular basis with S/N of 0.05. Also the API Gravity varied considerably with the Mexican HO on the low end with an API of 14.2 versus Uintah 1 R2 with a rather high API Gravity of 43.4.

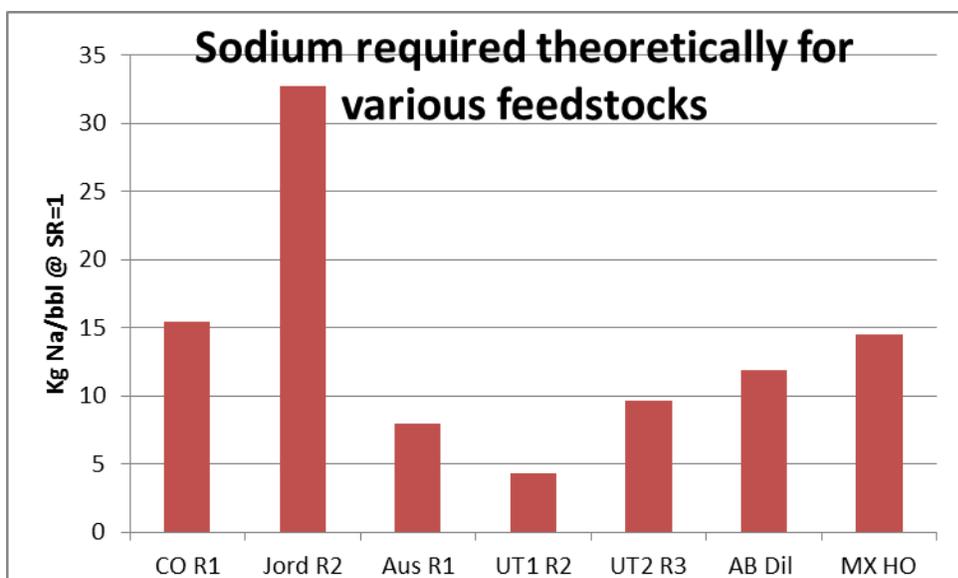
Solid liquid handling was performed in a nitrogen blanketed dry box to prevent oxidation or hydration of sulfides or in sealed containers. The weights of all the reactants and products were carefully tracked to enable mass balances and product yield determinations.

In the first 6 quarters the feedstocks were two shale oils from Uintah Basin oil shale and heavy oil from California. Later additional feedstocks were tested including several samples of bitumen and bitumen derivatives from Alberta, including two neat, one diluted, and a bitumen bottom from a different upgrading process. Also, another heavy oil from Mexico was tested, coker diesel, and three more oil shale samples; one from Australia, one from Jordan and one from Colorado's Piceance Basin.

### *Stoichiometry ratio*

Experiments were run where the amount of alkali metal for a given amount of feedstock charge varied. The theoretical amount of alkali metal was estimated based on the sulfur and nitrogen concentration where 2 moles of alkali metal were assumed to be theoretically required for every mole of sulfur and 3 moles of alkali metal required for every mole of nitrogen. The stoichiometric ratio was the actual amount of alkali metal used in the reaction divided by the theoretical amount.

Figure 3 shows the theoretical amount of sodium required for each of the feedstocks listed in Table 1.



**Figure 3: Sodium required for various feedstocks assuming theoretical amount to react with sulfur and nitrogen**

### *Electrolysis*

Another aspect of the experimentation was related to the electrolytic recovery of sodium from the reactor solids. Initially the experiments were conducted where sodium metal was produced electrochemically from sodium sulfide and where lithium metal was produced from lithium sulfide. Various organic polar solvents were evaluated, determining solubility of sulfur and alkali metal sulfide versus temperature, measuring conductivity, and evaluating stability. Two particular solvents were found to be the most effective for this application. Cells were constructed with anode in the compartment with dissolved alkali metal sulfide and on the cathode side there either was molten alkali metal or a polar solvent with an alkali metal salt dissolved for conductivity. Between anode and cathode compartment was a ceramic membrane, either Nasicon for the sodium system or Lisicon for the lithium system. The cells were operated at temperatures ranging from room temperature to 140C. Various anodes and cathodes were evaluated and sealing material for joining the ceramic membranes to alumina cell housings. Glasses were found to be suitable for the sealing purpose. All electrolysis experiments were conducted in dry boxes.

After preliminary tests, operation of sodium sulfide electrolysis at temperature near 130C was most promising. Two kinds of electrolysis experiments were run. In one case, alkali metal sul-

fides from actual reactor runs were used for the electrolysis to demonstrate recovery of sodium from actual oil feedstocks. In a second case, alkali metal sulfides were purchased and fed to the cells so that lifetime studies could be performed. The electrolysis cells were operated batch-wise. As sodium sulfide was converted electrochemically to sodium at the cathode, and higher polysulfide and eventually sulfur over time as electrical current passed, periodically the sodium was poured out of a closed end tube.

#### *Down-selection*

Based on the results, after the first 6 quarters, the experiments focused completely on sodium and lithium was no longer utilized.

#### *Improved reactor*

Based on the results of the initial runs, an improved reactor setup was determined necessary to further evaluate the technology in progress and ready to begin operation when the program ended. Most of the funding for the new reactor train was non-DoE sources. The key new feature of the new reactor train is an electromagnetic pump for controllably flowing sodium to the reactor and an electromagnetic flow meter for measuring and monitoring the flow rate. This improvement is expected to be very important for obtaining consistent results. Also, a gas compressor was added to the gas train to be able to better maintain the pressure in a narrower window. Installation of the new reactor began before the program was completed but the installation was not complete when the program ended.

## Results and discussions

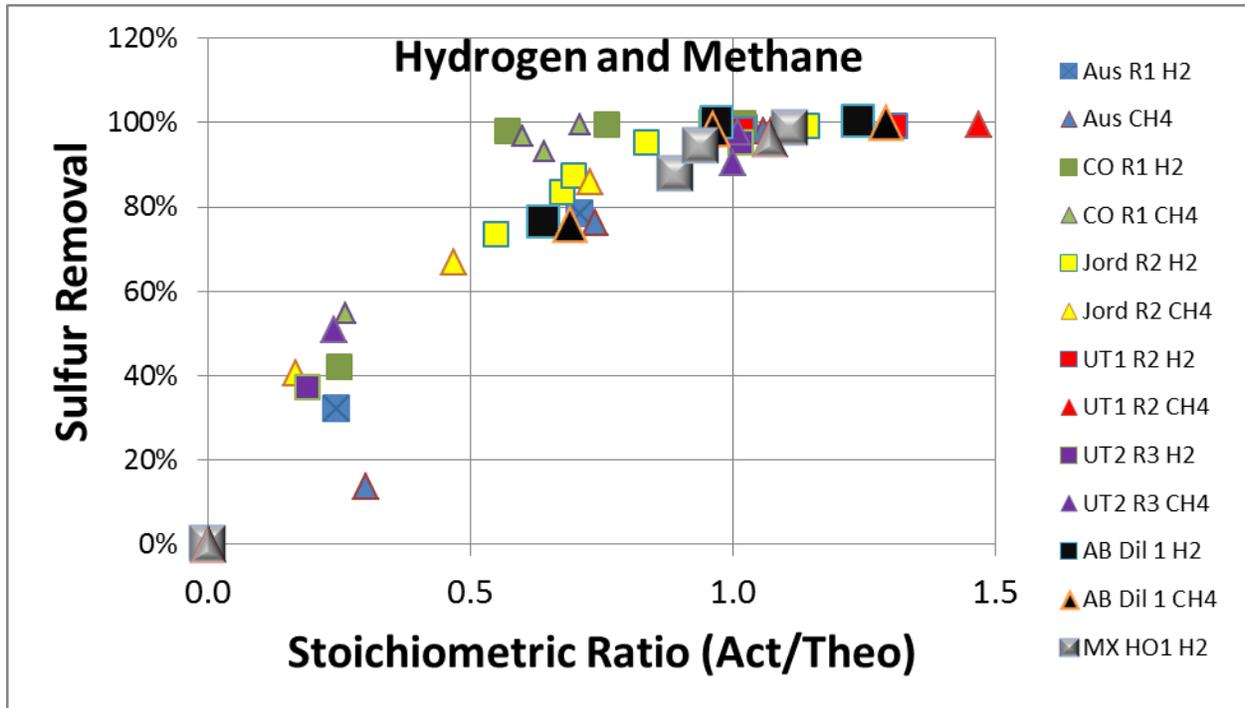
Table 2 lists many of the experiment performed over the first 6 quarters.

**Table 2: List of Experiments Performed Q1-6, CHNS Analysis, and Ratio of H, N, and S relative to C and the change of those ratios relative to the oil before treatment**

Oil	Temp	Metal	H source	Charge	Chg/Theo	Min	C	H	N	S	H/C	N/C	S/C	ΔH/C	ΔN/C	ΔS/C
Heavy 1	375	Li	CH4	1.8	0.56	60	84.99	11.39	0.70	1.28	0.134	0.008	0.015	0.019	-0.071	-0.162
Heavy 1	375	Li	CH4	1.8	0.56	60	84.35	12.14	0.14	0.02	0.144	0.002	0.000	0.094	-0.813	-0.987
Heavy 1	375	Li	H2	1.8	0.56	60	85.38	11.32	0.72	1.30	0.133	0.008	0.015	0.008	-0.049	-0.153
Heavy 1	275	Li	H2	1.8	0.56	60	85.33	11.60	0.70	1.50	0.136	0.008	0.018	0.034	-0.075	-0.022
Heavy 1	375	Li	H2	1.9	0.59	120	84.75	11.63	0.69	1.29	0.137	0.008	0.015	0.044	-0.082	-0.153
Heavy 1	375	Li	H2	3.2	0.99	120	84.34	11.51	0.67	1.21	0.136	0.008	0.014	0.038	-0.104	-0.202
Heavy 1	375	Li	H2	3.2	0.99	120	84.72	11.08	0.70	1.23	0.131	0.008	0.015	-0.005	-0.068	-0.192
Heavy 1	375	Na	CH4	0.0	0.00	120	86.17	11.31	0.74	1.23	0.131	0.009	0.014	-0.002	-0.032	-0.206
Heavy 1	375	Na	CH4	6.0	0.56	60	83.79	11.25	0.67	1.07	0.134	0.008	0.013	0.021	-0.098	-0.289
Heavy 1	375	Na	CH4	6.0	0.56	60	16.27	10.97	0.13	0.13	0.674	0.008	0.008	4.127	-0.099	-0.555
Heavy 1	375	Na	CH4	10.6	0.99	120	86.91	12.53	0.10	0.03	0.144	0.001	0.000	0.096	-0.870	-0.981
Heavy 1	375	Na	H2	0.0	0.00	60	85.70	11.46	0.71	1.36	0.134	0.008	0.016	0.017	-0.066	-0.117
Heavy 1	375	Na	H2	0.0	0.00	120	86.20	11.20	0.73	1.23	0.130	0.008	0.014	-0.012	-0.045	-0.206
Heavy 1	375	Na	H2	6.0	0.56	60	85.56	11.72	0.68	0.27	0.137	0.008	0.003	0.042	-0.104	-0.824
Heavy 1	375	Na	H2	10.3	0.96	120	86.18	12.50	0.19	0.04	0.145	0.002	0.000	0.103	-0.751	-0.974
Heavy 1	375	Na	H2	10.7	1.00	120	86.51	12.20	0.13	0.02	0.141	0.002	0.000	0.072	-0.831	-0.987
Heavy 1	375	Na	H2	10.7	1.00	120	15.00	11.33	0.03	0.01	0.755	0.002	0.001	4.744	-0.774	-0.963
Heavy 1	250	Na	H2	10.7	1.00	120	85.31	11.14	0.74	1.42	0.131	0.009	0.017	-0.007	-0.022	-0.074
Heavy 1	375	Na	H2	6.0	0.56	30	85.61	11.51	0.77	0.37	0.134	0.009	0.004	0.022	0.014	-0.759
Oil	Temp	Metal	H source	Charge	Chg/Theo	Min	C	H	N	S	H/C	N/C	S/C	ΔH/C	ΔN/C	ΔS/C
Shale 1	375	Li	CH4	1.8	0.43	60	85.59	12.40	1.29	0.17	0.145	0.015	0.002	-0.007	-0.140	-0.329
Shale 1	375	Li	H2	0.9	0.22	60	85.71	12.28	1.35	0.22	0.143	0.016	0.003	-0.018	-0.101	-0.133
Shale 1	375	Li	H2	1.8	0.43	60	85.15	12.49	1.23	0.10	0.147	0.014	0.001	0.005	-0.175	-0.603
Shale 1	275	Li	H2	1.8	0.43	60	84.88	12.33	1.35	0.18	0.145	0.016	0.002	-0.005	-0.092	-0.283
Shale 1	375	Li	H2	4.2	1.01	120	85.81	12.92	0.13	0.01	0.151	0.002	0.000	0.032	-0.914	-0.961
Shale 1	250	Li	H2	4.2	1.01	120	84.84	12.14	1.34	0.20	0.143	0.016	0.002	-0.020	-0.098	-0.203
Shale 1	150	Na	CH4	6.0	0.44	60	85.04	12.83	0.68	0.15	0.151	0.008	0.002	0.034	-0.544	-0.404
Shale 1	375	Na	CH4	6.0	0.44	60	85.72	12.51	0.71	0.06	0.146	0.008	0.001	0.000	-0.527	-0.763
Shale 1	375	Na	CH4	13.7	0.99	120	86.15	13.62	0.04	0.03	0.158	0.000	0.000	0.083	-0.973	-0.882
Shale 1	375	Na	H2	0.0	0.00	60	85.69	12.29	1.33	0.25	0.143	0.016	0.003	-0.017	-0.114	-0.014
Shale 1	375	Na	H2	1.6	0.11	60	85.55	12.21	1.27	0.19	0.143	0.015	0.002	-0.022	-0.153	-0.250
Shale 1	375	Na	H2	3.0	0.22	60	84.88	12.30	1.29	0.11	0.145	0.015	0.001	-0.007	-0.132	-0.562
Shale 1	375	Na	H2	5.9	0.43	30	85.79	12.33	1.48	0.25	0.144	0.017	0.003	-0.015	-0.015	-0.015
Shale 1	375	Na	H2	6.0	0.44	60	85.86	13.05	0.64	0.03	0.152	0.007	0.000	0.041	-0.575	-0.882
Shale 1	375	Na	H2	13.7	0.99	120	86.06	13.55	0.03	0.01	0.157	0.000	0.000	0.079	-0.980	-0.961
Shale 1	375	Na	H2	13.7	0.99	120	85.69	12.98	0.30	0.02	0.151	0.004	0.000	0.038	-0.800	-0.921
Shale 1	250	Na	H2	13.7	0.99	120	84.76	12.82	0.80	0.04	0.151	0.009	0.000	0.036	-0.461	-0.841
Oil	Temp	Metal	H source	Charge	Chg/Theo	Min	C	H	N	S	H/C	N/C	S/C	ΔH/C	ΔN/C	ΔS/C
Shale 2	375	Li	CH4	1.9	1.11	120	86.12	12.76	0.35	0.34	0.148	0.004	0.004	-0.002	-0.164	-0.573
Shale 2	375	Li	H2	1.8	1.06	60	85.36	12.69	0.38	0.40	0.149	0.004	0.005	0.001	-0.084	-0.493
Shale 2	275	Li	H2	1.8	1.06	60	84.59	12.62	0.40	0.66	0.149	0.005	0.008	0.005	-0.027	-0.156
Shale 2	375	Li	H2	1.8	1.06	60	86.04	12.92	0.33	0.37	0.150	0.004	0.004	0.011	-0.211	-0.535
Shale 2	375	Li	H2	1.9	1.11	120	86.06	13.08	0.37	0.39	0.152	0.004	0.005	0.024	-0.115	-0.510
Shale 2	250	Li	H2	1.9	1.11	120	85.25	12.65	0.42	0.65	0.148	0.005	0.008	-0.001	0.014	-0.175
Shale 2	375	Li	H2	6.0	3.52	60	80.10	11.64	0.21	0.76	0.145	0.003	0.009	-0.021	-0.460	0.026
Shale 2	375	Na	CH4	6.0	1.06	60	85.95	13.06	0.25	0.03	0.152	0.003	0.000	0.023	-0.401	-0.962
Shale 2	375	Na	CH4	6.3	1.12	120	86.37	12.96	0.24	0.03	0.150	0.003	0.000	0.010	-0.428	-0.962
Shale 2	375	Na	H2	0.0	0.00	60	85.38	12.77	0.39	0.77	0.150	0.005	0.009	0.007	-0.060	-0.024
Shale 2	375	Na	H2	1.5	0.27	60	85.33	12.81	0.40	0.62	0.150	0.005	0.007	0.011	-0.035	-0.214
Shale 2	375	Na	H2	3.0	0.53	60	85.77	12.99	0.39	0.51	0.151	0.005	0.006	0.020	-0.064	-0.357
Shale 2	375	Na	H2	6.0	1.06	60	86.41	13.36	0.16	0.02	0.155	0.002	0.000	0.041	-0.619	-0.975
Shale 2	375	Na	H2	6.3	1.12	120	86.37	13.53	0.18	0.03	0.157	0.002	0.000	0.055	-0.571	-0.962
Shale 2	375	Na	H2	6.3	1.12	120	86.34	13.16	0.24	0.12	0.152	0.003	0.001	0.026	-0.428	-0.850
Shale 2	250	Na	H2	6.3	1.12	120	84.62	13.00	0.25	0.07	0.154	0.003	0.001	0.035	-0.392	-0.911

Some of the initial runs were conducted at temperatures above 375C but at those temperatures there appeared to be considerable coking which would reduce the liquid yield. Table 1 only shows the results for runs at 375°C and below.

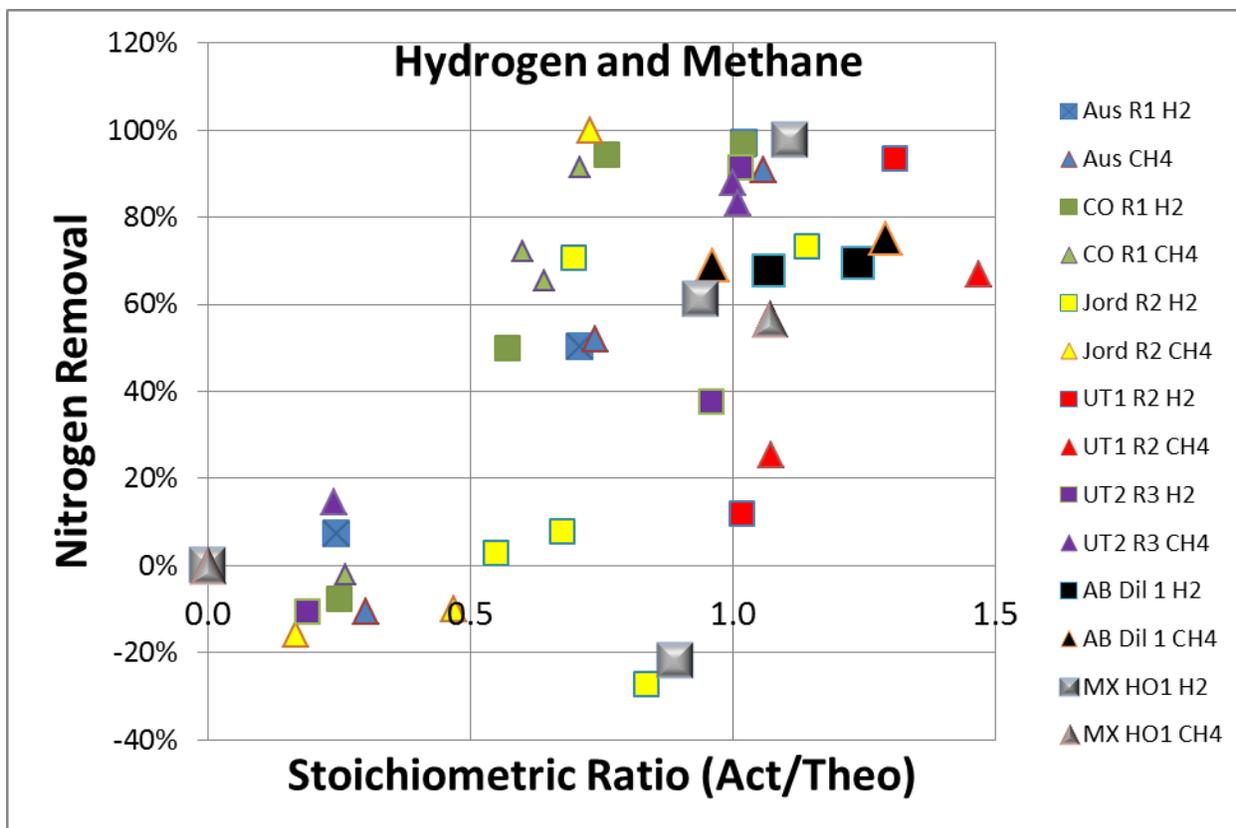
In general, the reduction of sulfur content decreased more with sodium than with lithium. Also in general, sulfur content reduction was greater than nitrogen content reduction for a given stoichiometric level. Heavy metals were reduced to a greater extent than sulfur and TAN level also reduced to zero in all of the experiments conducted where TAN was measured.



**Figure 4: Sulfur removal with sodium and either methane or hydrogen at various stoichiometric ratios and different feedstocks**

Figure 4 shows the sulfur removal from a variety of feedstocks with the properties shown in Table 1 and Figure 2 and with varying stoichiometric levels of sodium relative to the sulfur and nitrogen. One can see there is not much difference between the results with methane or hydrogen. All of the runs were conducted in the apparatus shown in Figure 1. Also, there is a strong relationship between the stoichiometric ratio and the amount of sulfur removed.

Figure 5 shows nitrogen removal from the same runs as Figure 4. Unlike the sulfur removal, the nitrogen removal is much more variable and erratic but still follows a general trend of more nitrogen is removed at higher stoichiometric ratios.



**Figure 5: Nitrogen removal with sodium and either methane or hydrogen at various stoichiometric ratios and different feedstocks**

Figure 6 and 7 both show plots of volumetric yield for the various feedstocks treated in the presence of hydrogen and methane versus stoichiometric ratio in the case of Figure 6 and sulfur removed in the case of Figure 7. In general, the highest yields occur at lower stoichiometric ratios and sulfur removal. The yield is expected to improve later when the new experimental set-up is used where sodium will be controllably added and cracking can be reduced, but these figures show in many cases, high yield is obtainable, even when the methane is used instead of hydrogen, when most of the sulfur has been removed and when there is a low Sulfur to Nitrogen ratio as in Utah 1 Retort 2.

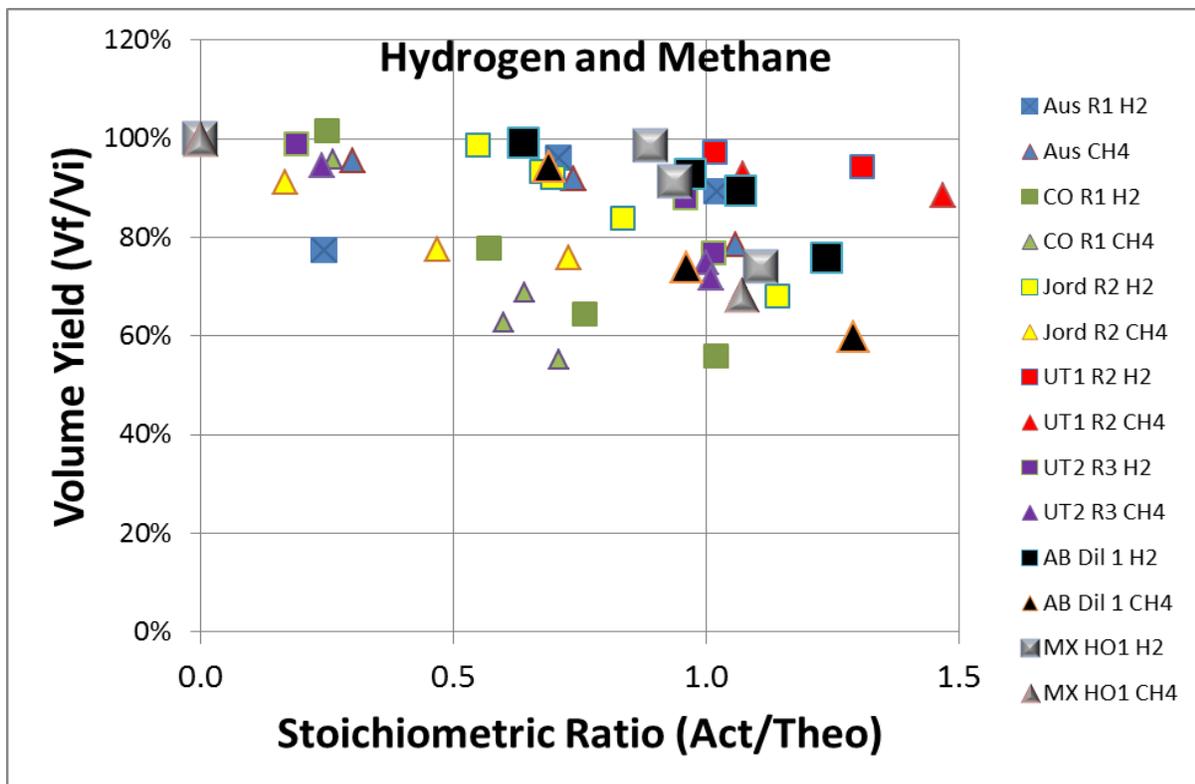


Figure 6: Volumetric yield with sodium and either methane or hydrogen at various stoichiometric ratios and different feedstocks

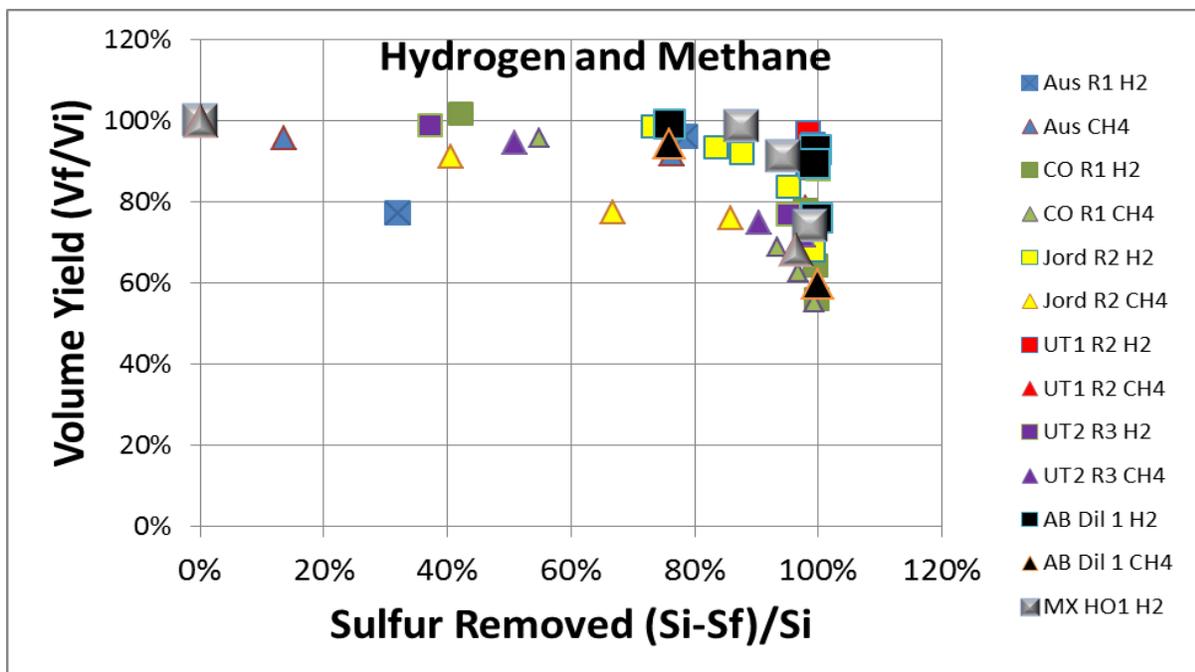
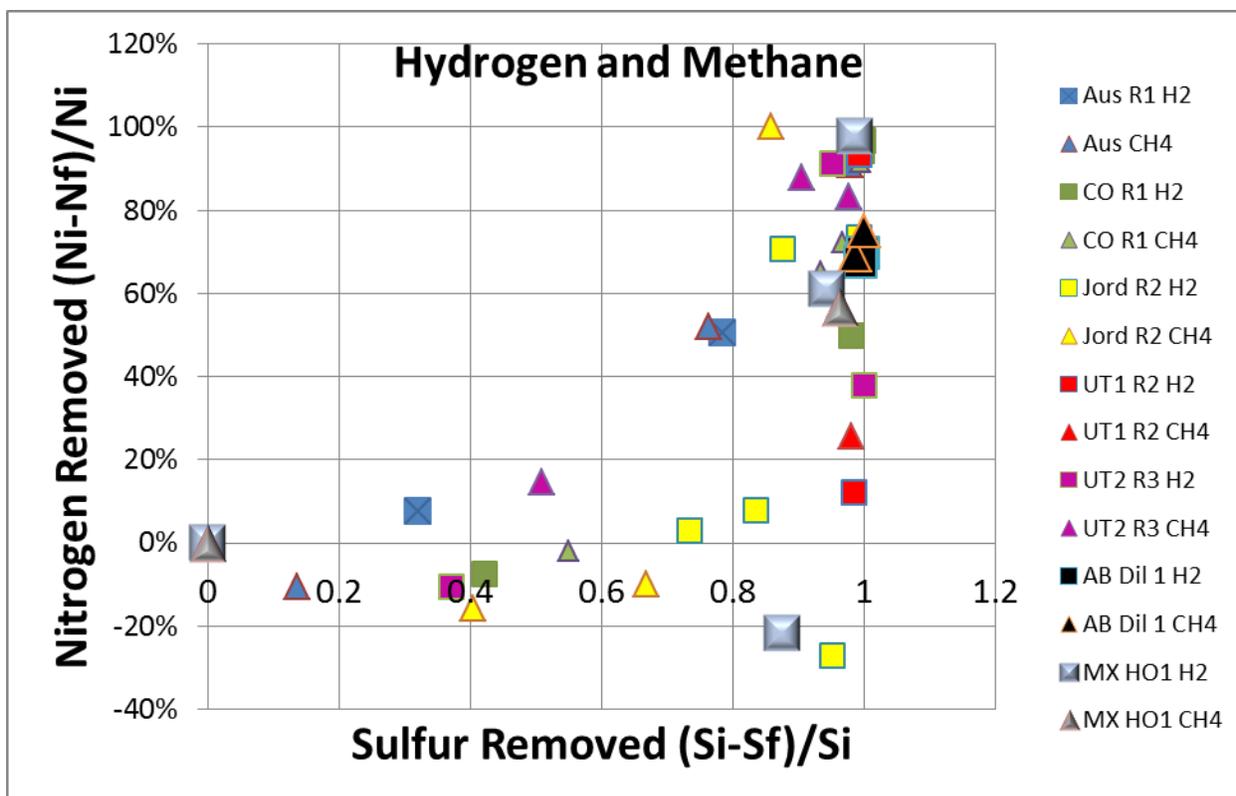


Figure 7: Volumetric yield with sodium and either methane or hydrogen versus different feedstocks



**Figure 8: Nitrogen removal versus sulfur removal with sodium and either hydrogen or methane versus different feedstocks**

In figure 8 the data is plotted in a different way where Nitrogen removal among the various feedstocks and methane versus hydrogen cover gas is plotted against sulfur removal. In general, nitrogen removal occurs less preferentially to sulfur so while it is possible to remove much of the sulfur with removing little nitrogen. The opposite is not true.

### *API Gravity*

Figures 9-15 show the how API Gravity generally rises according to the model proposed by Gordon and presented in Gordon, J. H.; Alvare, J.; Karanjikar, M.; Dear, T; “Heavy Oil Upgrading Without Hydrogen”, Gas & Oil Expo & Conference NorthAmerica 2011; June, 2011.

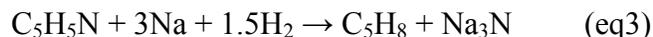
### Modeling Methodology

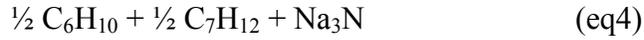
The model assumes the composition of the oil remains unchanged except for molecules containing either sulfur or nitrogen and that all organic double bonds are retained. Sulfur and nitrogen are assumed to be entirely contained in simple aromatic molecules and an estimate is made of the specific gravity and mass of the feedstock fraction that does not

include these molecules. The specific gravity and mass of the organic fraction after the sulfur and nitrogen have been removed is estimated then specific gravity and mass after the two fractions have been recombined. Also for simplification, presence of heavy metals is ignored. The modeling methodology assumes all sulfur content of the feedstocks is in the form of Thiophene, C<sub>4</sub>H<sub>4</sub>S and all nitrogen content is in the form of Pyridine, C<sub>5</sub>H<sub>5</sub>N. Sodium is assumed to form sulfides with the sulfur in the Thiophene and that two sodium atoms are required for every sulfur. If the reaction process is conducted in the presence of hydrogen then the remaining organic is assumed to become 1, 3 Butadiene, C<sub>4</sub>H<sub>6</sub> according to equation 1. If the process is conducted in the presence of methane then the remaining organic is assumed to become 1, 3 Pentadiene, C<sub>5</sub>H<sub>8</sub> according to equation 2 because •CH<sub>3</sub> and •H are added to the two radicals formed with removal of S atom rather than two •H atom radicals.



Likewise, the modeling methodology assumes all nitrogen content of the feedstocks reports in the form of Pyridene, C<sub>5</sub>H<sub>5</sub>N. Sodium is assumed to form nitrides with the nitrogen in the Pyridene and that three sodium atoms are required for every nitrogen atom. If the reaction process is conducted in the presence of hydrogen then the remaining organic becomes 1, 3 Pentadiene, C<sub>5</sub>H<sub>8</sub> according to equation 3. If the process is conducted in the presence of methane then half the remaining organic becomes Hexadiene, C<sub>6</sub>H<sub>10</sub>, and half becomes Heptadiene, C<sub>7</sub>H<sub>12</sub>, according to equation 4. A split in products is assumed because there are three bonds with nitrogen which must be accommodated. Half of the bonds will receive •CH<sub>3</sub> and half •H. Thus half of the Pyridene molecules have two •CH<sub>3</sub> and one •H added to form Heptadiene and half have one •CH<sub>3</sub> and two •H added to form Hexadiene.





In reality, possibly none of these products are formed but this provides a method of estimating some of the effects of replacing sulfur and nitrogen and replacing the corresponding bonds with methyl or hydrogen radicals which remarkably predicts very well in most cases provided there is insignificant thermal cracking.

According to the model, there is not expected to be much of a difference between the API Gravity of the oil when reacted in the presence of hydrogen versus methane and that data from a multitude of feedstocks bears that out.

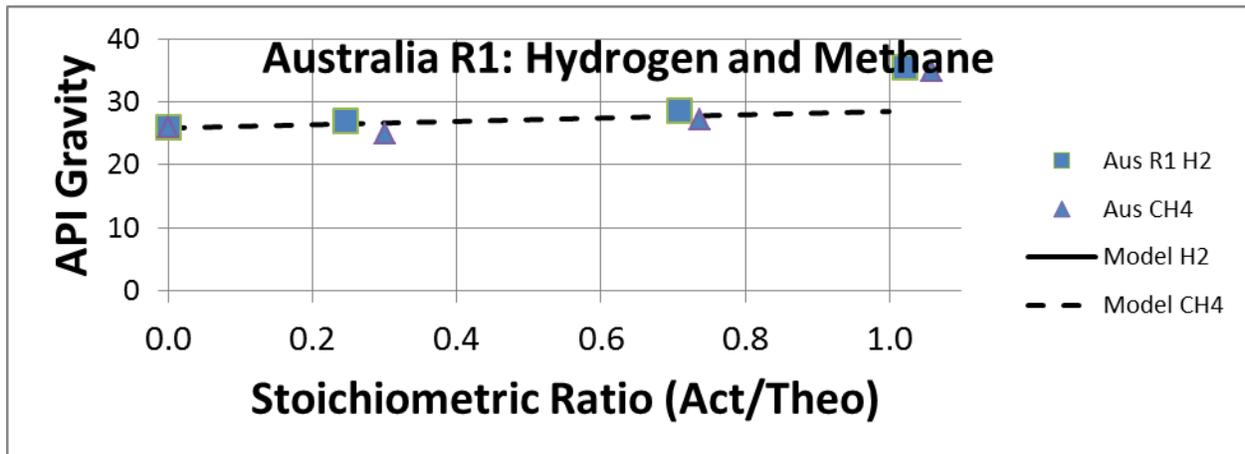


Figure 9: API Gravity versus Stoichiometric Ratio for an Australian Shale Oil for Hydrogen and Methane with the Model Prediction

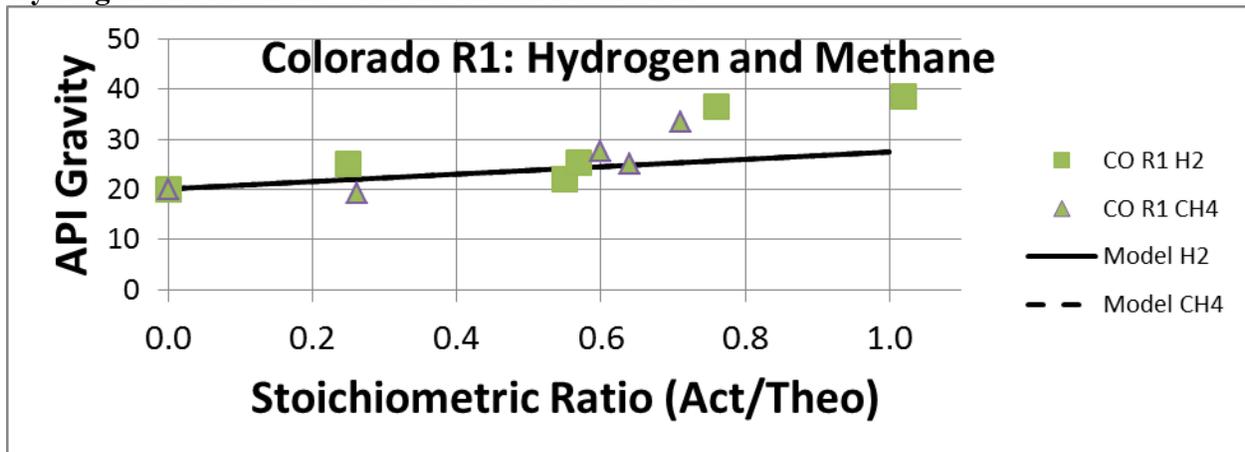


Figure 10: API Gravity versus Stoichiometric Ratio for a Colorado (Piceance Basin) Shale Oil for Hydrogen and Methane with the Model Prediction

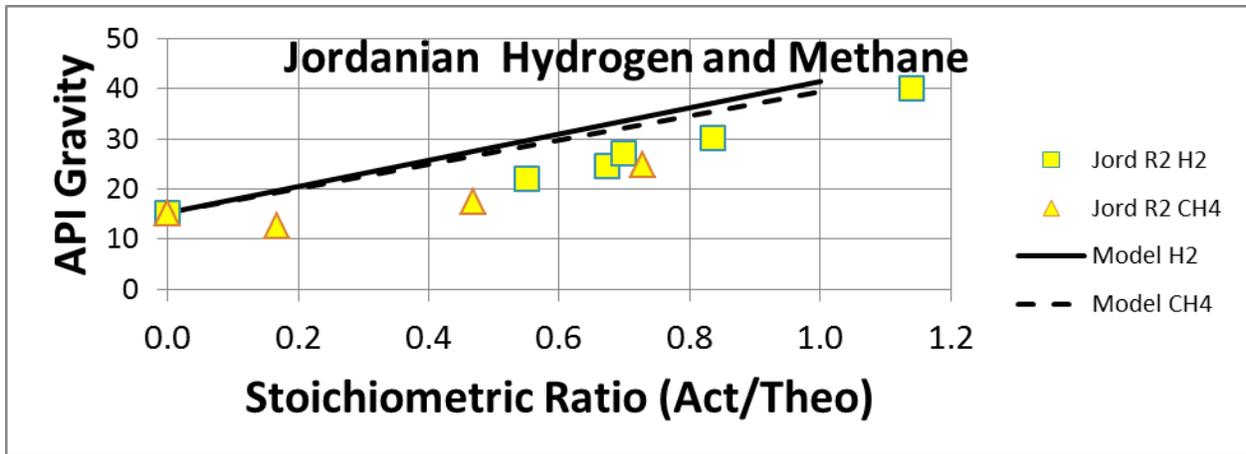


Figure 11: API Gravity versus Stoichiometric Ratio for a Jordanian Shale Oil for Hydrogen and Methane with the Model Prediction

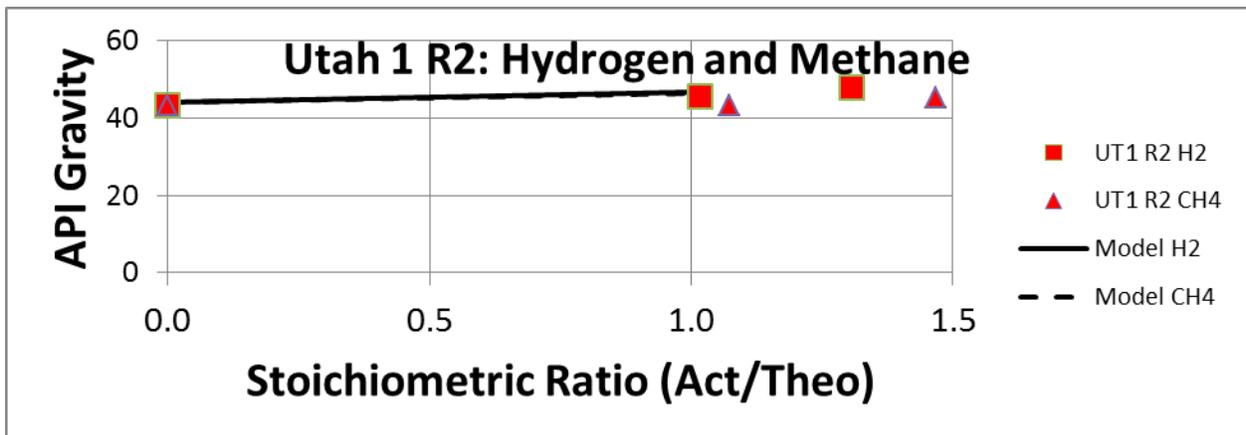


Figure 12: API Gravity versus Stoichiometric Ratio for a Utah (Uintah Basin) Shale Oil for Hydrogen and Methane with the Model Prediction

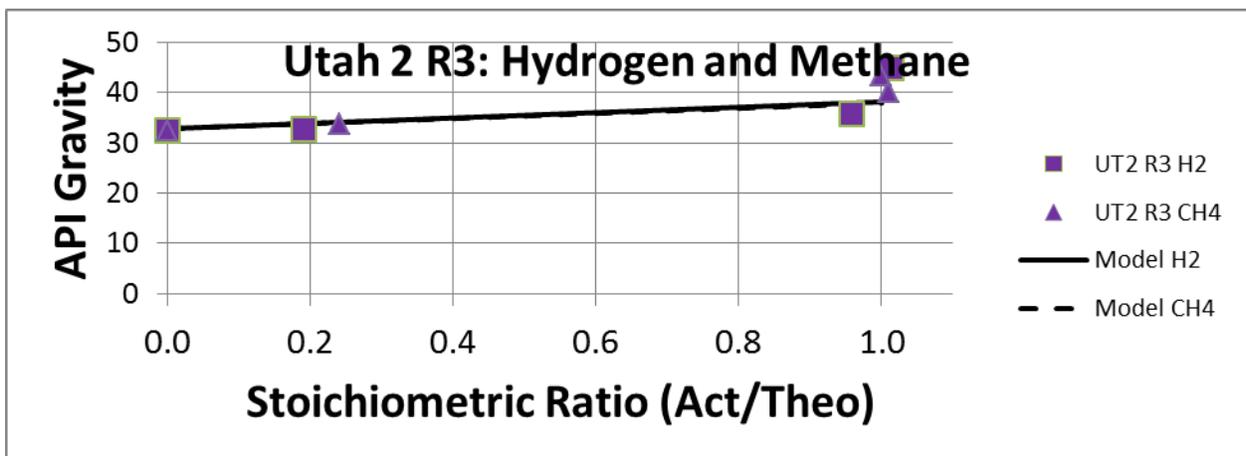
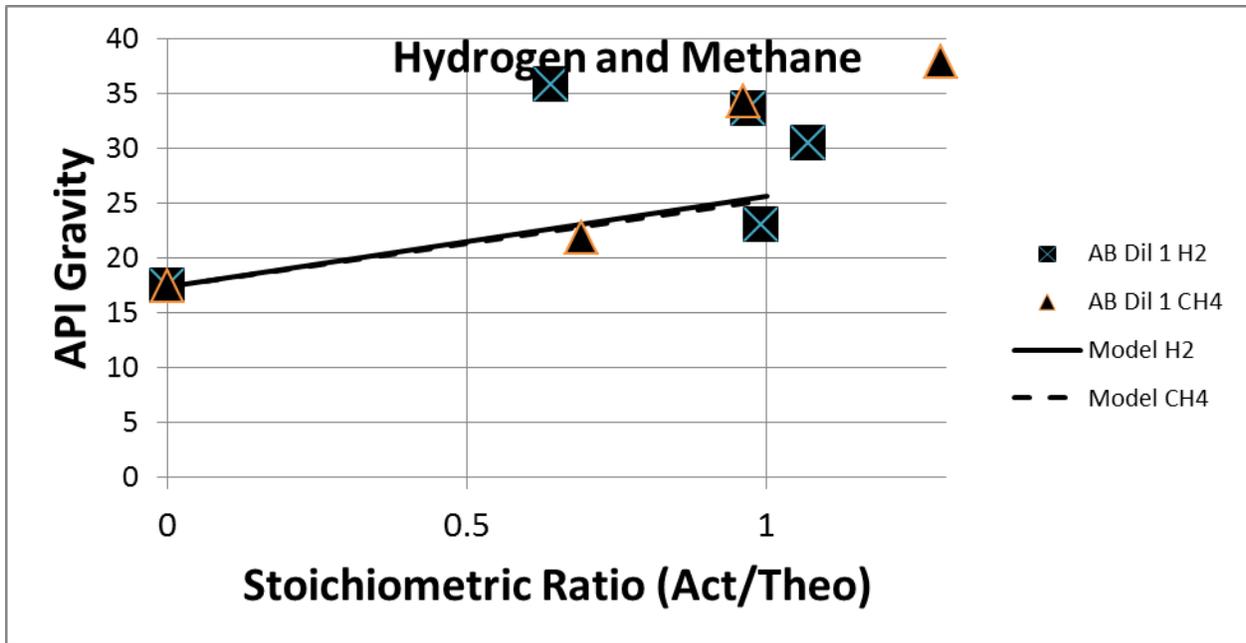
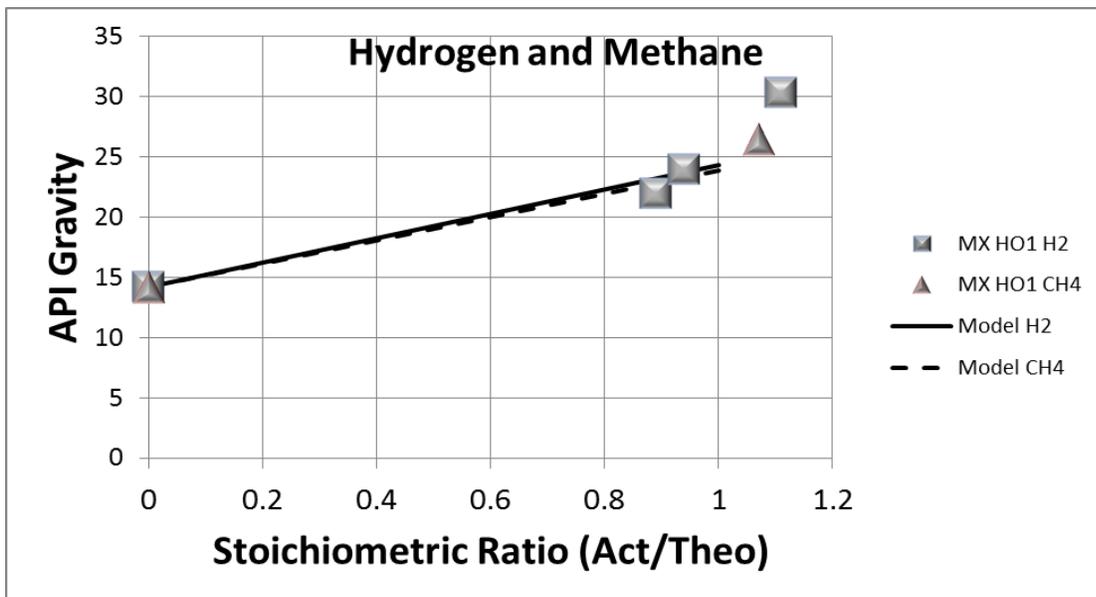


Figure 13: API Gravity versus Stoichiometric Ratio for a Utah (Uintah Basin) Shale Oil for Hydrogen and Methane with the Model Prediction

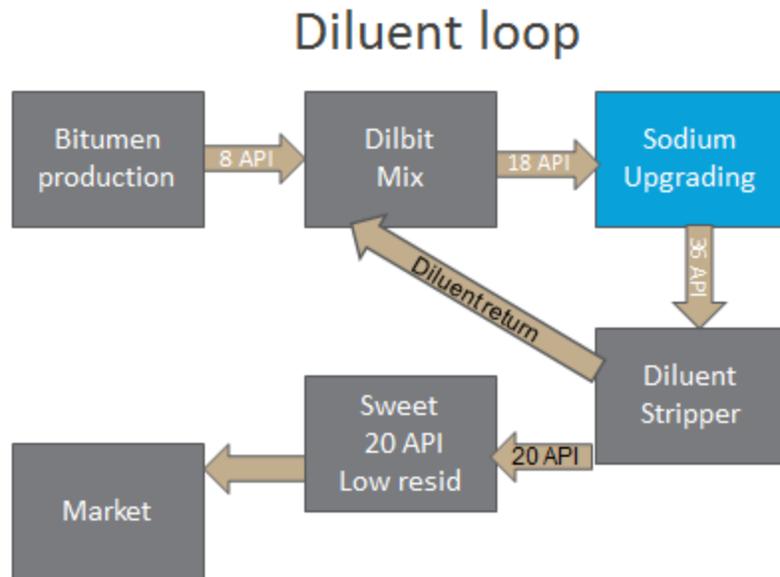


**Figure 14: API Gravity versus Stoichiometric Ratio for a Alberta diluted Bitumen for Hydrogen and Methane with the Model Prediction**

Figure 16 shows schematically how diluent could be stripped off of upgraded bitumen or heavy oil then utilized locally. Typically the API Gravity needs to be about 20 for pipeline shipment. Often, condensate is priced above sweet crude because it is needed to enable shipment of bitumen or heavy oil. But since the API Gravity of dilbit rises above pipeline specification, stripping off diluent may be considered.



**Figure 15: API Gravity versus Stoichiometric Ratio for a Mexican Heavy Oil for Hydrogen and Methane with the Model Prediction**



**Figure 16. Flow chart of diluent flow loop**

*Simulated distillation*

Figures 17 and 18 show plots of simdist temperature versus fraction boiloff for treated and as-received shale oils, Uintah 1 R2 and Jordanian R2, respectively. The simdist plot is generated from gas chromatograph data and represents what would be expected from actual distillation. Notice there is very little difference in the boiling curves even though API Gravity has increased and in the case of the Jordanian sample, about 13% sulfur was removed. In contrast, Figure 19 shows the simdist curve for treated and as received Alberta diluted bitumen. Here there is a large shift downward after treatment.

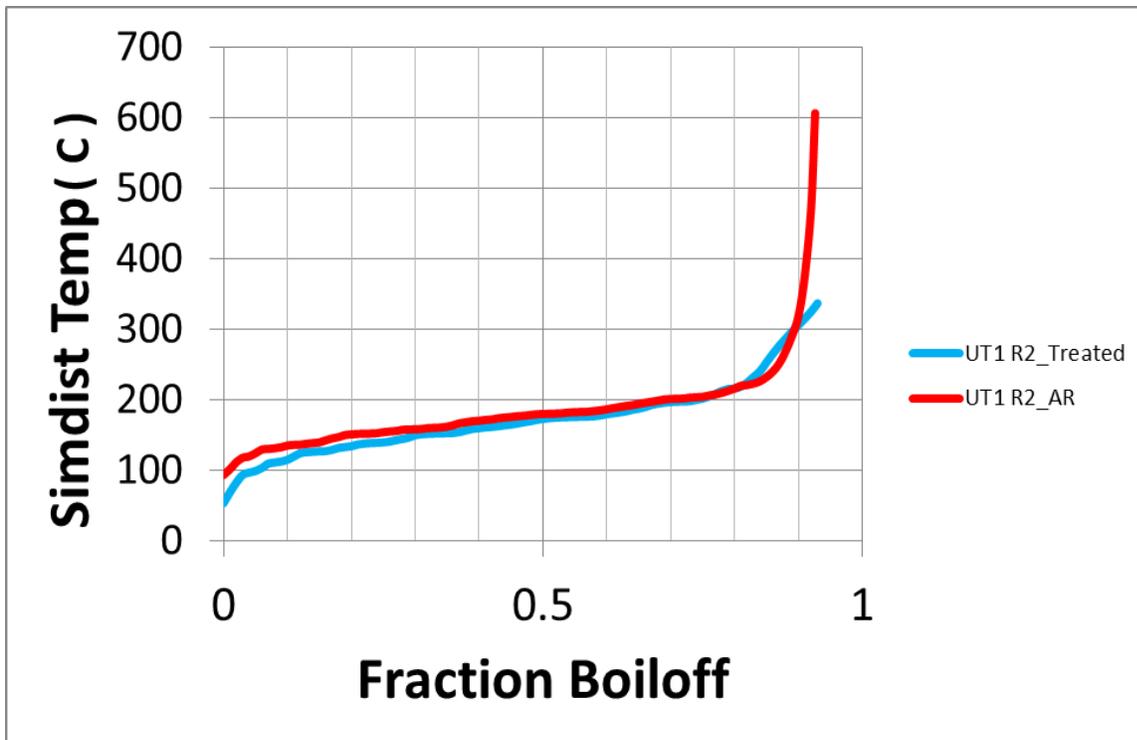


Figure 17: Simdist temperature versus fraction boiloff for As Received and Treated Uintah 1 Shale Oil, where the treatment was with sodium and hydrogen

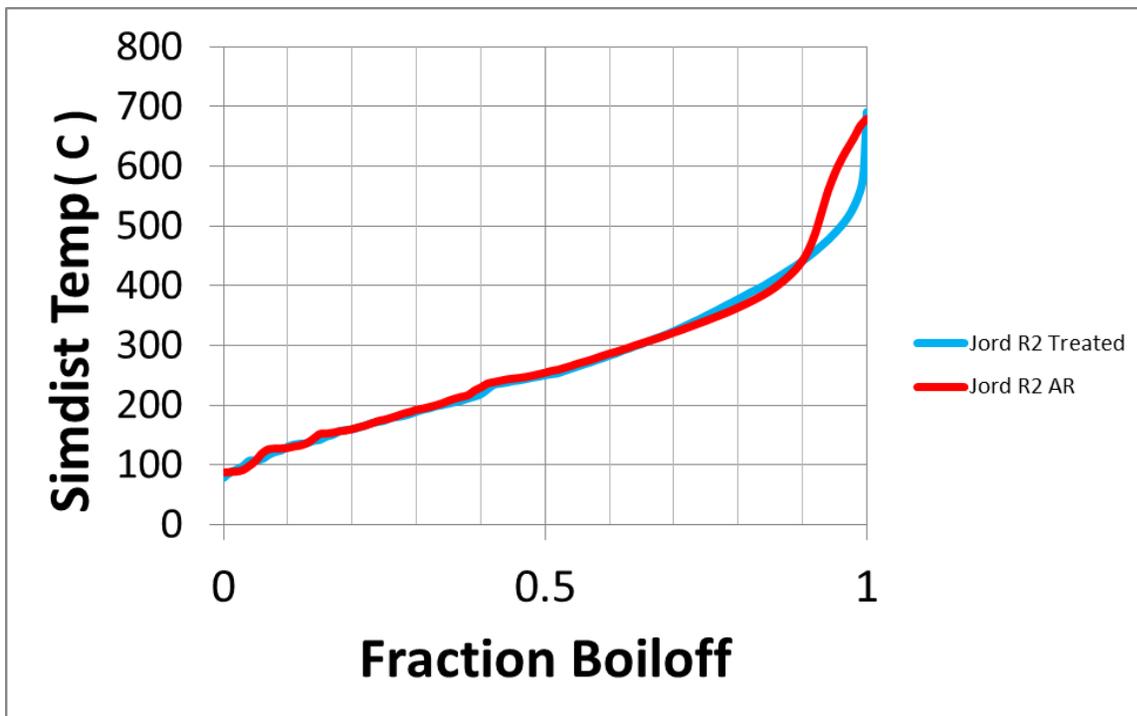
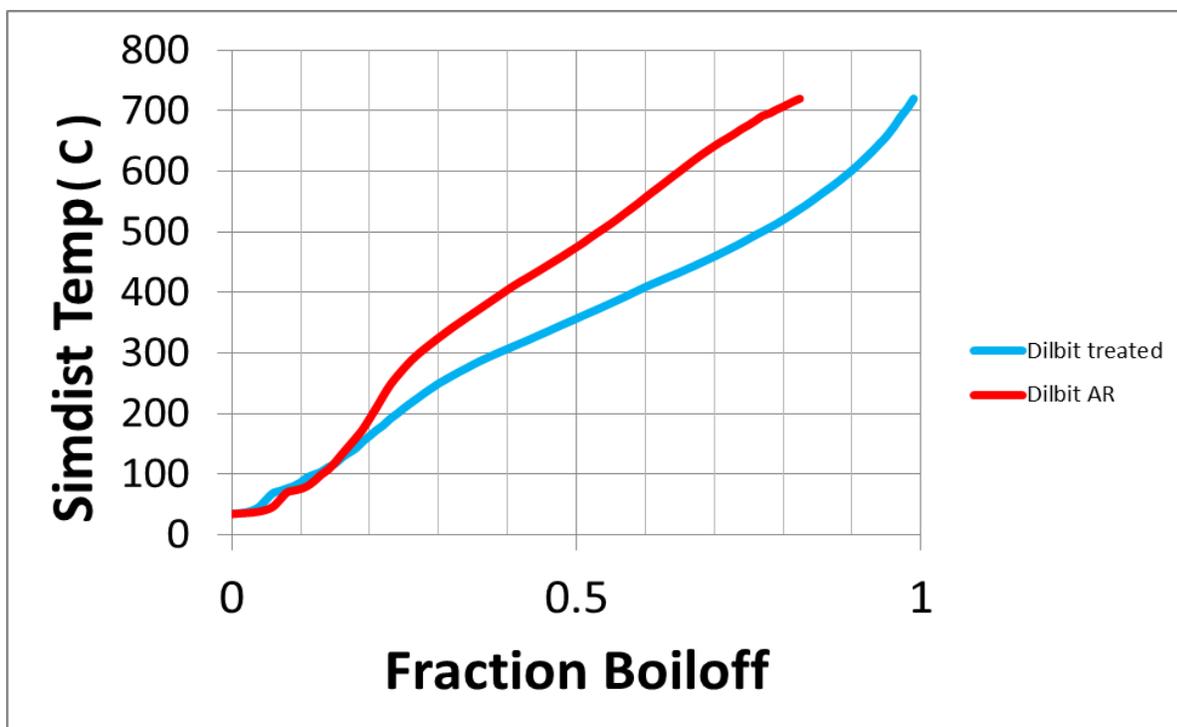


Figure 18: Simdist temperature versus fraction boiloff for As Received and Treated Jordanian Shale Oil, where the treatment was with sodium and hydrogen

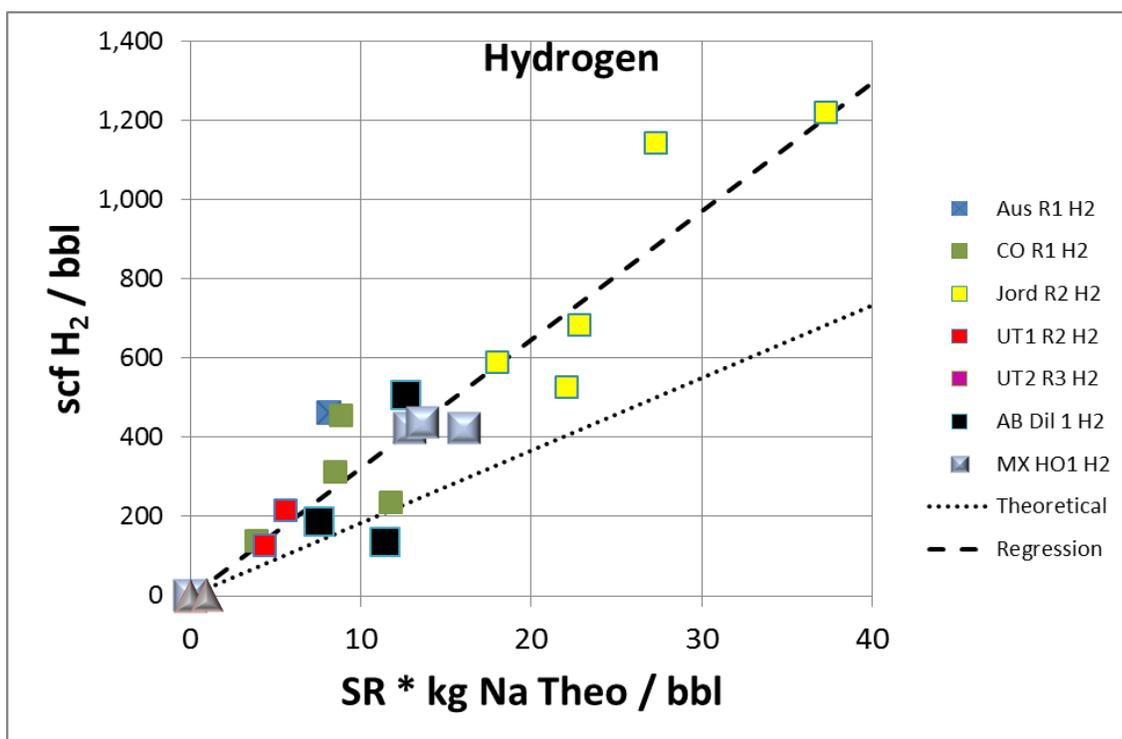


**Figure 19: Simdist temperature versus fraction boiloff for As Received and Treated Alberta diluted Bitumen where the treatment was with sodium and hydrogen**

A very important aspect of the shift in simdist curves after treatment is the reduction of the  $>538^{\circ}\text{C}$  fraction and the almost complete elimination of the  $>720^{\circ}\text{C}$  fraction. The  $>538^{\circ}\text{C}$  fraction is generally known as vacuum residue (or “resid”) fraction and has very little value compared to the other fractions because typically in a refinery this fraction is sent to a coker after distillation. What was seen very regularly was the feedstocks with a large resid fractions would typically see that fraction cut in half or more where the lighter boiling fractions increased. This boiling curve shift increases the value of the product about 50%, simply by decreasing the resid fraction. But in addition, the  $>720^{\circ}\text{C}$  portion of the resid fraction is almost completely eliminated and the resid fraction has very little sulfur or heavy metals. Thus rather than send the treated resid fraction to the coker, the material may be suitable for the Fluidized Catalytic Cracker (FCC) where it can be converted to liquid fuel. In this way the value of the product increase another 50% because the material instead of being valued as 50% coker feed is valued as 100% to be utilized for liquid fuels.

## Asphaltenes

Asphaltenes were measured on the bitumen and heavy oil samples. A typical bitumen sample would have about 17% asphaltene as determined by considering only the insoluble portion when subjecting the feedstock to pentane. Sulfur content in the asphaltene was 8.6% by weight, much higher than the overall sulfur content. After treatment with sodium, the asphaltene content dropped dramatically to <0.3% and the sulfur content of the asphaltene was about the same as the overall treated oil. The decline in asphaltene may be part of the reason for the shift in boiling point distribution from high boiling fractions to lower boiling fractions.



**Figure 20: Plot of Hydrogen consumed per barrel for various feedstocks versus the sodium charged**

A mass balance of each reactor run was used to determine the hydrogen consumed. The amount of hydrogen theoretically consumed would be 1 H<sub>2</sub> molecule for every 2 Na atoms charged assuming the H capped off a radical formed when Na<sub>2</sub>S was formed or Na<sub>3</sub>N. The stoichiometric ratio (SR) multiplied by the theoretical amount of sodium needed per barrel is the x-axis of the Figure 20 plot while the standard cubic feet of hydrogen per barrel consumed is the y-axis. Shown in Figure 20 is the data from various runs with different feedstocks. The fine dotted line

represents the theoretical expectation where 1 H per Na charge. The coarse dotted line is a regression of the data where 1.77H was consumed for every Na charged overall on average. While there was considerable scatter in the data, the overall trend was consistent over such a diverse set of feedstocks, widely ranging sodium requirements and stoichiometric ratios.

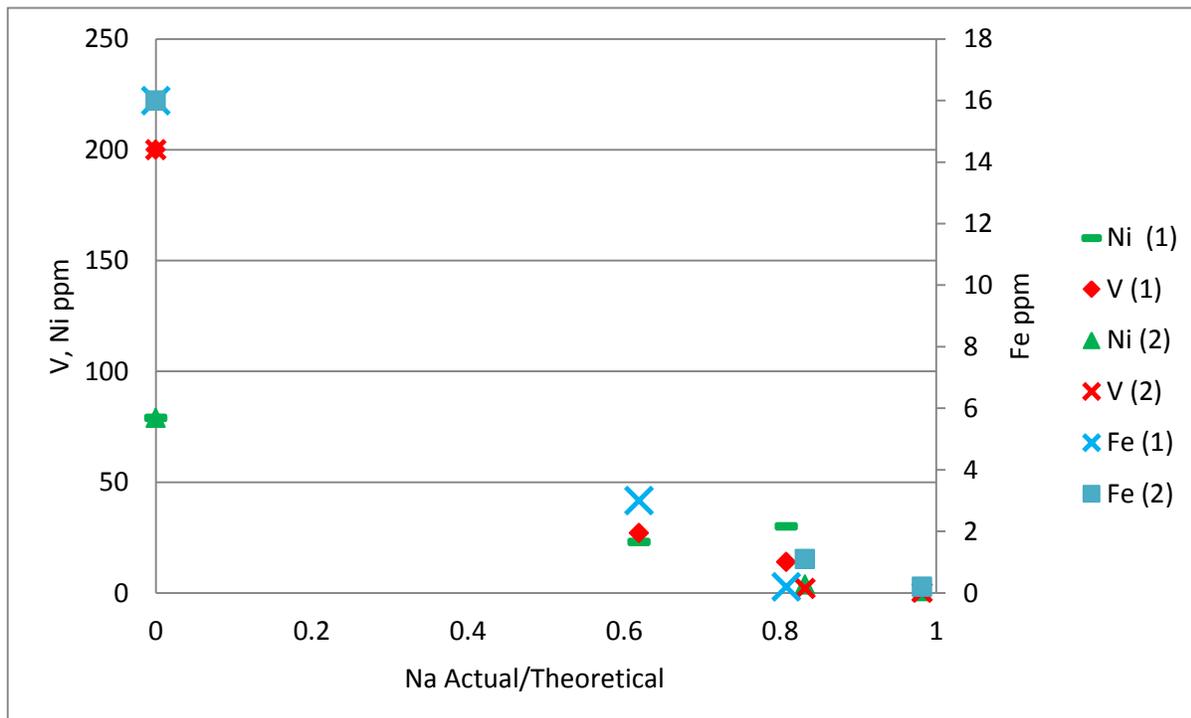
With regard to runs where methane was used, no hydrogen was consumed at all. In most cases rather than consuming methane, in general there was slight methane production.

#### *Total Acid Number (TAN)*

TAN can be a problem for many feedstocks. The price producers may receive for their product may be discounted if the TAN is above “1” and may be significantly discounted if the TAN is above “3”. Whenever TAN was measured after treatment with molten sodium, the TAN was found to be “0” which would not be discounted at all. Also, in cases where sodium was added with low stoichiometric ratios 0.25 – 0.5, the TAN still went to “0”. In one experiment an upgraded heavy oil was acidified using dilute strong acid to determine whether the acid group was merely converted to the “salt” form, exchanging a proton ion for example with a sodium ion and perhaps reducing the protons to hydrogen gas with sodium metal. But the TAN remained very low, indicating the the acid groups originally in the oil, for example carboxylic groups on Napthenic acid, were likely eliminated.

#### *Metals Removal*

Figure 21 below shows the effect of Na treatment on metals in bitumen. As observed, V, Ni and Fe drop below detectable levels after processing with stoichiometric levels of sodium and decrease considerably as the sodium stoichiometric level rises.



**Figure 21: Metals concentration in Bitumen versus stoichiometric level of sodium**

Table 3 shows the metals removal from a California Heavy Oil with sodium and hydrogen and with sodium and methane where the sodium was near the stoichiometric level required for sulfur and nitrogen removal. From the table it can be seen that the metals drop to very low levels.

**Table 3: ICP measurement of products in Heavy Oil and Conversion with Sodium and either hydrogen or methane**

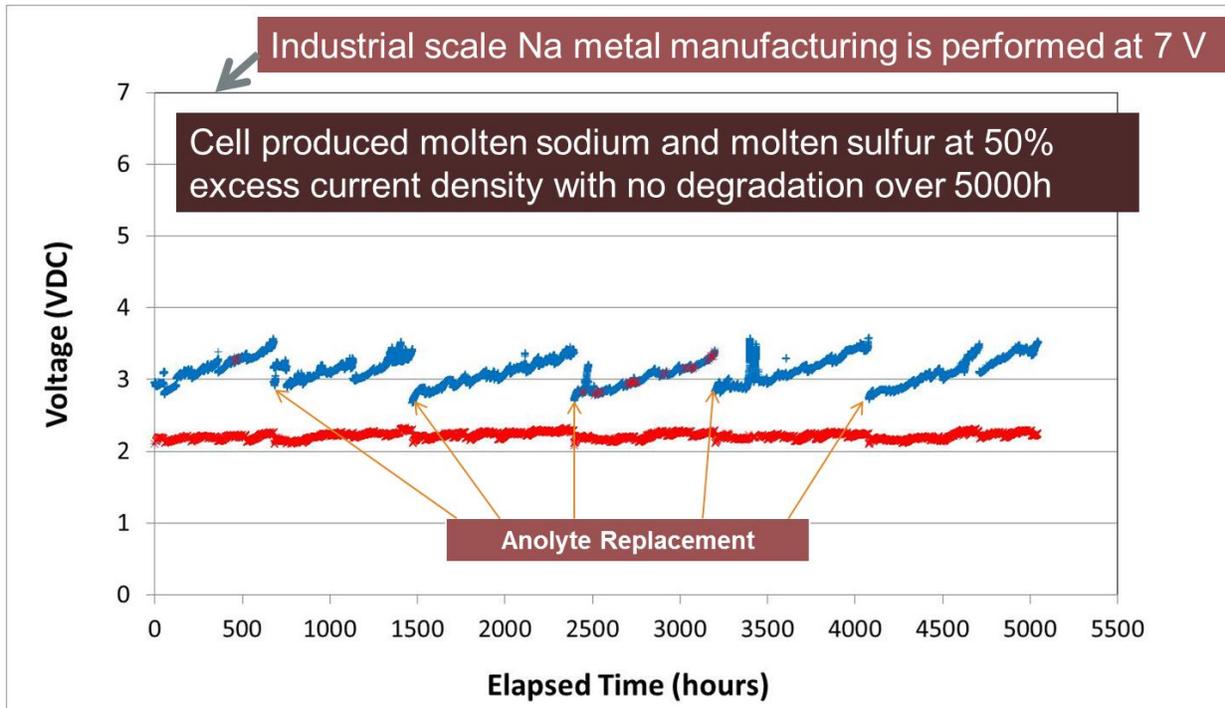
	Heavy Oil with H <sub>2</sub> & Na			Heavy Oil with CH <sub>4</sub> & Na		
	In	Out	Convers.	In	Out	Convers.
<b>Fe ppm</b>	218.0	0	100%	218	2.39	99%
<b>V ppm</b>	197.0	0	100%	197	1.31	99%
<b>Ni ppm</b>	331.4	0	100%	331.4	0.85	100%

### *Electrolysis*

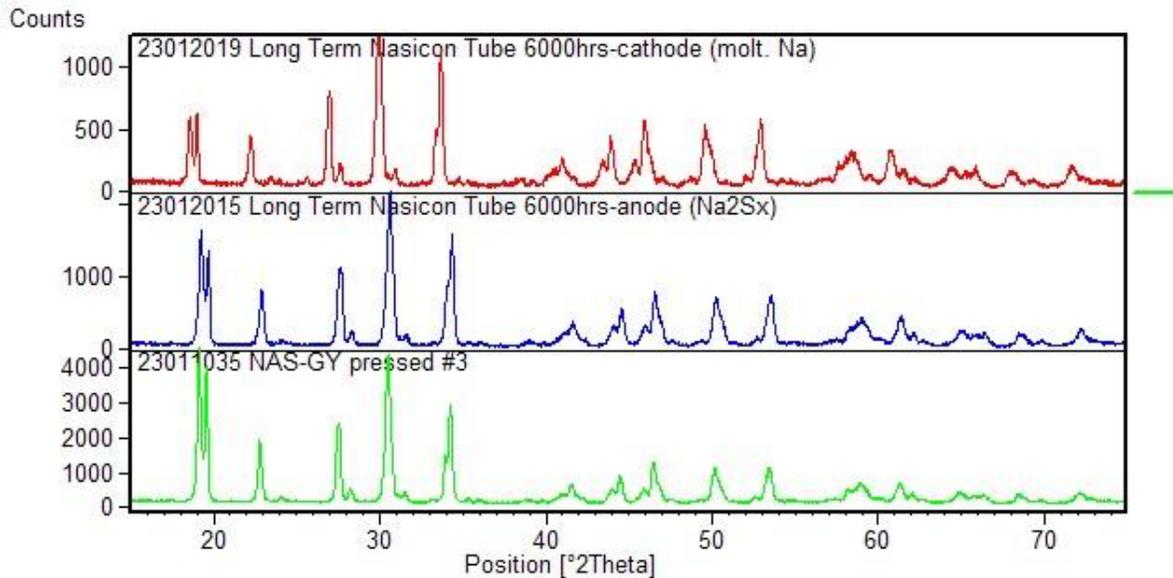
Extensive work was performed on the electrolysis which will be required to regenerate sodium metal from sodium sulfide. Figure 22 shows a plot of cell voltage and open-circuit voltage of a

cell using Nasion membrane conducted at 130°C – above the melting temperature of both sodium and sulfur. The current density was around 95 milliamps per square centimeter (mA/cm<sup>2</sup>) through the test which is about 50% higher than what we believe will be an economical operating current density. Sodium sulfide was added regularly to the anolyte bath to maintain concentration. The membrane was glass sealed to an alumina tube. Periodically the tube was pulled out of the anolyte bath and sodium poured out partially. There were two indications the cell system was stable. The open circuit voltage, indicated in red in Figure 22 was stable throughout the test. Also, when the membrane was pulled out of the bath the membrane was examined and found to appear unchanged, without corrosion or discoloration. Eventually when the test was concluded, then membrane cross-section was examined by scanning electron microscopy and by X-ray diffraction analysis (XRD). As shown in Figure 23, the XRD indicated the material diffraction pattern, crystal structure, was unchanged for both anode side and cathode side in comparison to an unused sample. The blue curve, in Figure 22, representing the cell voltage steadily increased over time. When the anolyte was replaced periodically, the cell voltage returned to its initial value. Which means, membrane and electrodes were stable. The rise in cell voltage was attributed to operation in batch mode so sulfur content increased and also impurities contained in the purchased sodium sulfide accumulated. Eventually the test was concluded when a mishap occurred in the lab and someone accidentally unplugged the cell heater, allowing the contents to freeze while the power was still on. The membrane appears to be very stable in contact with molten sodium but there is risk of dendrite formation when the temperature is below sodium freezing during electrolysis.

Also noted on Figure 22 is the approximate voltage required to operate typical sodium production cells, 7V, is approximately double the voltage required from this process. Two major differences exist between the cells, the source material and presence of membrane. In the case of production cells, sodium chloride is the source which requires almost double decomposition voltage compared to sodium sulfide. The membrane in the present technology allows the electrodes to be placed much closer together with loss of current efficiency. The closer placement reduces cell resistance.

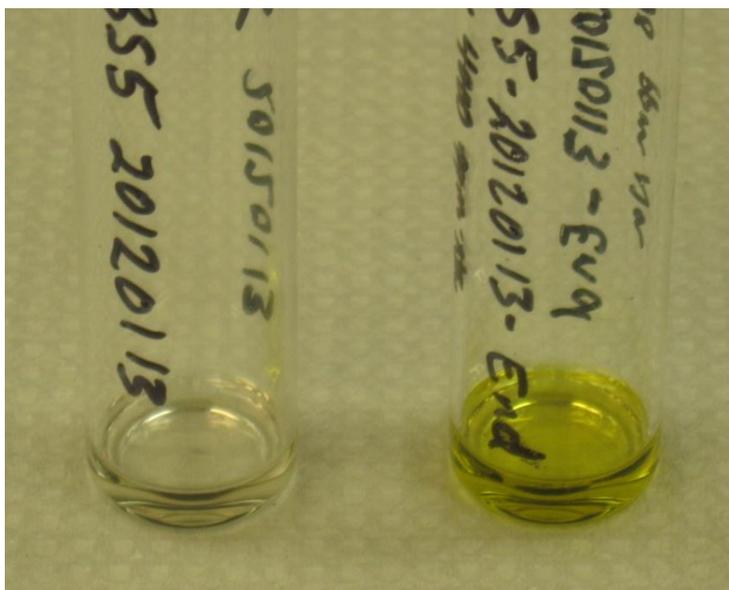


**Figure 22: Plot of sodium sulfide electrolysis cell voltage (blue) and open circuit voltage (red) over time**



**Figure 23: Comparison of X-Ray Diffraction (XRD) scans of the cathode and anode sides of the NaSICON membrane, recovered from long term sodium recovery test, with pristine NaSICON material.**

In addition to the longevity tests performed with purchased sodium sulfide as shown in Figure 22, numerous electrolysis tests were conducted with the solids separated from actual treatment runs with various feedstocks. Initially there was concern the solvent we identified, one that can dissolve sodium sulfide and have good conductivity, and have relatively high boiling temperature, would also suspend or dissolve constituents other than just sodium sulfide, leading to polarization. A simple processing step was identified which when taking solids from any feedstock treated with sodium, regardless of whether hydrogen or methane were cover gas, the solvent would preferentially only dissolve sodium sulfide, leaving all else behind. This was evaluated with solids from various shale oil, heavy oil, bitumen, and residue feedstocks



**Figure 24: Photos of anolyte solution using dissolved sodium sulfide generated in the treatment of bitumen with sodium – On left is anolyte with dissolved sodium sulfide generated from bitumen, on right is the anolyte after most of the sodium has been removed and the sulfide has been converted into sodium polysulfide.**

Figure 24 shows anolyte prepared from Athabasca bitumen treated with sodium and hydrogen. Sodium sulfide dissolves preferentially leaving all the coke and metals contained in the post reaction solids behind. The anolyte prepared in this way has good conductivity. On the right is

the same anolyte that has been electrolyzed such that nearly all of the sodium has been removed and the sodium sulfide has converted to sodium polysulfide.

### *Economics*

Table 4 lists the major equipment for two alternative upgrading pathways. In the left column is the Molten Sodium Upgrading (MSU) pathway and on the right is the Delayed Coking / Hydrotreating pathway. Cokers are difficult to scale down and must be very large to be practical. The solid coke has very little value compared to liquid fuels. Liquids coming off of a coker must be fractionated, then each fraction has a dedicated hydrotreater for removing sulfur since each fraction requires a different catalyst, then each hydrotreater requires associated sulfur recovery units.

The reduced equipment requirement is expected to dramatically reduce capital costs of the MSU process compared to upgrading with coking and hydrotreating. Preliminary scoping level capital cost estimates place the capital cost of the proposed technology at about half (\$30,000 USD/Bbl/day) compared to coking with hydrotreating (\$60,000 USD/Bbl/day) for a 25,000 bpd (bitumen feed basis) plant in the Edmonton area.

Based on the data generated from the “Alberta Dil” sample, a consultant in Calgary familiar with bitumen pricing and valuation and based on early stage capital cost estimates prepared the following table comparing the costs of the “Molten Sodium Upgrading” (MSU) process versus delayed coking process; a currently practiced technology for heavy crudes and bitumen. Largely because of the shift in boiling point distribution and increase in API Gravity, the value of the upgraded bitumen is dramatic, over \$30/bbl. Given the higher yield of MSU compared to coking, the margin per barrel is expected higher. Table 5 compares the upgraded product price, margin, operating cost, net margin, capital cost, IRR, and NPV. While electricity is required to regenerate sodium metal from the sulfide in the MSU case, delayed coking / hydrotreating is expected to have higher operating costs because of the need for hydrogen and all the equipment that must be operated and maintained. Based on the estimates, MSU has favorable economics and is more favorable than the alternative.

**Table 4. Major Equipment Comparison**

<b>Molten Sodium Upgrading</b>	<b>Delayed Coking / Hydrotreating Upgrader</b>
Reactor	Atmospheric Unit
Solids Separator 1	Vacuum Unit
Diluent Stripper	Cokers
Solids Dryer	Coker Fractionator
Solids Separator 2	Gas Recovery Unit
Electrolysis Unit	Hydrogen Plant
Tank Farm	Naphtha Hydrotreater
Utilities	Distillate Hydrotreater
	Gasoil Hydrotreater
	Amine and SRU
	Tank Farm
	Utilities

**Table 5. Estimate comparison between Molten Sodium Upgrading (MSU) Potential and Conventional Delayed Coking Upgrading**

<b>Edmonton Basis, 25,000 bpd bitumen</b>	<b>MSU Product Potential</b>	<b>Delayed Coking Sweet SCO</b>
Feedstock Price, US\$/bbl	\$42.76	\$42.76
Product Price, US\$/bbl	\$75.65	\$80.01
Product Yield, LV%	95%	82%
Gross Margin, US\$/bbl	\$29.93	\$23.67
Operating Cost, US\$/bbl	\$8.85	\$16.30
Net Margin, US\$/bbl	\$21.08	\$7.37
Capital Cost, US\$/bbl	\$30,000	\$60,000
Capital Cost, US\$MM	\$750	\$1,500
IRR, %	18.4%	1.1%
NPV (10%), US\$MM	\$602	(\$835)

Notes:

- 1) Gross margin, operating cost, net margin and capital cost on per barrel of bitumen feed basis
- 2) Bitumen Feedstock and Product prices assume long-term pricing at (real \$US/bbl) of \$56.65 for WCS at Hardisty Athabasca Diluted Bitumen blend, \$76.48 for MSW at Edmonton and \$89.05 for condensate at Edmonton
- 3) Power cost assumption is \$75/MW-hr using a gas fired cogeneration unit

- 4)Gross margin includes sulphur sales at \$100/MT at Edmonton. Solids (including metals) assumed to have no value nor cost
- 5) Opex, capex and price assumptions are scoping level preliminary estimates at this time for a 25,000 bpd plant (bitumen basis) at Edmonton
- 6)IRR and NPV assume 25% tax beginning in first year of operation

### *New Reactor Runs*

The new reactor was not ready for experiments by the end of the program. Tests began December 2012.

## Conclusions

Sodium is preferred over lithium for upgrading oil feedstocks because it is more effective in sulfur removal and less expensive to regenerate from the sulfide.

The upgrading method effectively removes heavy metals, TAN, sulfur, a large portion of the nitrogen and increases the API Gravity.

If the feedstock has asphaltene or a vacuum residue fraction, both are considerably reduced by the upgrading process and the fraction which boils above 525°C, since the metals and sulfur are substantially removed and the fraction boiling above 720°C is almost non-existent, the +525°C fraction may be suitable for FCC feed rather than coker feed.

The value of the oil increases considerably for certain types of feedstocks after treatment with sodium.

The regeneration of sodium from the sulfides generated by the process appears to be feasible at this stage of development using Ceramatec's Nasicon ceramic sodium ion conducting membrane as a separator between molten sodium at the cathode and an organic solvent mixture of sodium sulfide dissolved from solids separated from the upgraded oil after treatment with sodium. In addition, the economics look favorable in the case of bitumen which should be similar to the case of heavy oil.

## References

### Patents

Number	Inventor	Status	Date	Title
7,897,028	Gordon , et al.	Issued	March 1, 2011	Process for the recovery of materials from a desulfurization reaction
8,088,270	Gordon , et al.	Issued	January 3, 2012	Process for recovering alkali metals and sulfur from alkali metal sulfides and polysulfides
20110100874	Gordon	Published	May 5, 2011	Upgrading of petroleum oil feedstocks using alkali metals and hydrocarbons
20100089762	Gordon	Published	April 15, 2010	Apparatus and Method For Reducing an Alkali Metal Electrochemically at a Temperature Below
1000.2.209	Gordon	Converted	July 16, 2012	<i>(Not Public)</i>
1000.2.211	Gordon , et al.	Converted	November 16, 2012	<i>(Not Public)</i>
1000.2.212	Gordon	Provisional	February 3, 2012	<i>(Not Public)</i>
1000.2.215	Gordon	Provisional	July 13, 2012	<i>(Not Public)</i>

### Conference Presentations

Oil Shale Symposium, Golden, CO, October 2010,

Gas and Oil Expo in Calgary, AB, June 1011

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Jordan International Oil Shale Symposium, Dead Sea, May 2012  
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## **Articles**

### **GOEXPO Paper**

Gordon, J. H.; Alvare, J.; Karanjikar, M.; Dear, T; “Heavy Oil Upgrading Without Hydrogen”, June, 2011.Gas & Oil Expo & Conference NorthAmerica 2011.

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## **Quarterly Reports**

Q1	October 2009 –	December 2009
Q2	January 2010 –	March 2010
Q3	April 2010 -	June 2010
Q4	July 2010 -	September 2010
Q5	October 2010 -	December 2010
Q6	January 2011 –	March 2011
Q7	April 2011 -	June 2011
Q8	July 2011 -	September 2011
Q9	October 2011 -	December 2011
Q10	January 2012 –	March 2012
Q11	April 2012 -	June 2012
Q12	July 2012 -	September 2012

## List of Acronyms and Abbreviations

AB	Alberta
Act	Actual
API Gravity	American Petroleum Institute Specific Gravity
AR	As received
Aus	Australian
bbl	Blue barrels (oil barrel)
bpd	Barrel per day
C	Centigrade
Capex	Capital expense
cc	Cubic centimeter
Chg	Charge
cm	centimeter
CO	Colorado
Convers.	Conversion
Dil	Diluted bitumen
DOE	Department of Energy
FCC	Fluidized Catalytic Cracking
GC	Gas Chromatograph
h	hour
HO	Heavy Oil
ICP	Inductance Coupled Plasma (Elemental Analysis)
IRR	Internal rate of return
Jord	Jordanian
Kg	Kilogram
LV	Left volume
mA	milliamp
Min	Minute
MM	Million

Mol	Mole
Molt	Molten
MSU	Molten Sodium Upgrading (Upgrader)
MSW	Mixed Sweet Blend (MSW) is the benchmark conventionally produced light sweet crude for western Canada.
MT	Metric tonne
MW	Mega Watt
MX	Mexico
Na	Sodium
Nasicon	Sodium (Na) super (S) ion (I) conductor (con)
NAS-GY	Nasicon-GY (This is an internal code for a particular formulation)
NETL	National Energy Technology Laboratory
NPV	Net present value
Opex	Operating expense
ppm	part per million
Q	Quarter
R	Retort
Resid	Residue
Scf	Standard cubic feet
Si	Sulfur initial
Simdist	Simulated Distillation
Sf	Sulfur final
SR	Stoichiometric ratio
TAN	Total Acid Number
Theo	Theoretical
Temp	Temperature
US	United States
USD	United States dollars
V	Volt
VDC	Volt Direct Current
Vi	Volume initial

Vf	Volume final
Vol	Volume
WCS	Western Canadian Select
WH	Western Hydrogen
XRD	X-Ray Diffraction
$\Delta$	Delta (Difference)

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