



Heavy Oil Upgrading Without Hydrogen

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Abstract

Standard upgrading of Heavy Oil using the hydro-treating process is well known. Oil is contacted with hydrogen in the presence of catalysts to form hydrogen sulfide, ammonia, and at the same time saturating to some extent aromatics and alkenes. Three issues with regard to upgrading with hydrogen include high utilization of hydrogen, undesirable saturation of organics to obtain a given level of heteroatom removal, and poisoning of catalysts can occur as heavy metals drop out. Alternatively, upgrading in the presence of hydrogen and molten sodium has been demonstrated with success over thirty years ago. One of the challenges, however, was the regeneration of alkali metal from the sulfides. The regeneration process currently is being developed electrochemically with a relatively low cost sodium conductive membrane called NASICON, sodium super ion conducting membrane. Concurrent with the regeneration effort, the upgrading process is being studied

anew. A remarkable discovery has shown that upgrading in the presence of sodium does not require hydrogen but instead can be achieved with other hydrogen donating sources such as methane. This discovery provides a gateway to using lower cost sources of hydrogen in the upgrading process, eliminating the need for steam methane reforming (SMR), and eliminating the emission of carbon dioxide associated with SMR. We will present results from our upgrading process where sulfur and nitrogen were substantially removed from shale oil, and from Heavy Oil, where heavy metals were substantially reduced, and where API gravity was improved. These results will be presented with and without the utilization of hydrogen.

Introduction

Oil feedstocks, in many cases, require removal of heteroatoms such as sulfur and nitrogen and also removal of heavy metals before they can be accepted at many refineries. In addition, increasing the API gravity and decreasing the

viscosity to increase the ability for the material to flow easily in pipelines is also desirable. The standard accepted process is hydrotreating the feedstock in the presence of heterogeneous catalyst. One of the primary difficulties of this approach is poisoning of the catalysts by metals and coke formed in the process. Utilization of sodium in combination with hydrogen was proposed and demonstrated by Beardon et al. and described in numerous patents.^{1,2,3} In Beardon's work, sodium is reacted with the feedstock at elevated temperature and pressure. Recent work at Ceramatec Inc has been focused in two areas, upgrading the feedstock and electrolytically regenerating the sodium from recovered sulfides and nitrides utilizing sodium ion conductive membranes which are conductive at relatively low temperature. With regard to upgrading we utilize two types of feedstock, shale oil and also heavy oil where the feedstock is reacted with an alkali metal, in particular sodium in the presence of hydrogen but alternatively in the presence of methane. Normally we would not expect methane to be of use for upgrading purposes but Gordon has proposed using methane and other light hydrocarbons for upgrading in the presence of molten sodium.⁴ As sodium reacts with organo-sulfur or organo-nitrogen to form sodium sulfide or sodium nitride, radicals formed as organo-sulfur or organo-nitrogen bonds are broken and reactive to hydrogen, methane, or other light organic species which may add to the organo molecules. Advantage of this approach is three fold: first, steam methane reforming is not required to provide hydrogen for the upgrading process; secondly, the carbon dioxide emission associated with steam methane reforming is avoided; third, the process provides a means for adding mass and volume to the original feedstock resulting in more product than when utilizing hydrogen. At the same time, while sodium is utilized as a reducing agent and scavenging agent to form sodium sulfide and sodium nitride, it also reduces the heavy metals bonded to organics allowing for them to be separated along with the sulfide and nitride from the product oil. Further benefit of such a process is reduction of Total Acid Number (TAN).

Model of Upgrading Process with Sodium: H₂ v CH₄

Feedstock chemistry is complex and varies depending on the material source and history but to make some initial comparisons between upgrading with sodium in the presence of hydrogen versus methane we can make some simplifying assumptions. We obtained 3 feedstock materials, 2 are shale oils derived from Uinta Basin oil shales. Shale Oil 1 was retorted slowly at relatively low temperature, and the second, Shale Oil 2, was retorted more quickly at a higher temperature. The third feedstock was a Heavy Oil crude from California. We measured API gravity, carbon, hydrogen, nitrogen, sulfur and heavy metals concentrations of the feedstock samples. For modeling purposes we also considered a Heavy Oil Compilation composition from 127 basins and 1199 deposits and Natural Bitumen Compilation composition from 50 basins and 305 deposits as reported by Meyer et al.⁵ The API Gravity, sulfur, and nitrogen concentrations of these various feedstocks are summarized in Table 1.

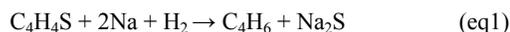
Table 1: Feedstock initial API, S & N concentration

	Shale Oil 1	Shale Oil 2	Heavy Oil 1	Heavy Oil comp.	Bitumen comp.
Initial API	32.8	44.2	13.4	16.3	5.4
%S	0.25	0.84	1.54	2.9	4.4
%N	1.48	0.47	0.76	0.4	0.6

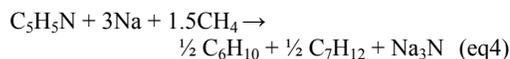
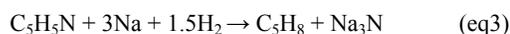
Modeling Methodology

Our approach assumes the composition of the oil remains unchanged except for molecules containing either sulfur or nitrogen and that all organic double bonds are retained. We assume that the sulfur and nitrogen are entirely contained in simple aromatic molecules and estimate the specific gravity and mass of the feedstock fraction that does not include these molecules. Then we estimate the specific gravity and mass of the organic fraction after the sulfur and nitrogen have been removed and then the estimate specific gravity and mass after the two fractions have been recombined. Also for simplification, we ignore presence of heavy metals.

In our modeling methodology we assume all sulfur content of the feedstocks is in the form of Thiophene, C₄H₄S and all nitrogen content is in the form of Pyridine, C₅H₅N. In our reaction process we assume sodium forms 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 we assume the remaining organic becomes 1, 3 Butadiene, C₄H₆ according to equation 1. If the process is conducted in the presence of methane then we assume the remaining organic becomes 1, 3 Pentadiene, C₅H₈ according to equation 2 because ·CH₃ and ·H are added to the two radicals formed with removal of S atom rather than two ·H atom radicals.



Likewise, in our modeling methodology, we assume all nitrogen content of the feedstocks to report in the form of Pyridene, C₅H₅N. In our reaction process we assume sodium forms 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 we assume the remaining organic becomes 1, 3 Pentadiene, C₅H₈ according to equation 3. If the process is conducted in the presence of methane then we assume half the remaining organic becomes Hexadiene, C₆H₁₀, and half becomes Heptadiene, C₇H₁₂, according to equation 4. We assume a split in products because there are three bonds with nitrogen which must be accommodated. We assume half of the bonds will receive ·CH₃ and half ·H. Thus half of the Pyridene molecules have two ·CH₃ and one ·H added to form Heptadiene and half have one ·CH₃ and two ·H added to form Hexadiene.



In reality, possibly none of these products are formed but this allows us a method of estimating some of the effects of replacing sulfur and nitrogen and replacing the corresponding bonds with methyl or hydrogen radicals.

Heavy Oil 1 Example

As noted above, Heavy Oil 1 has an initial API gravity of 13.4, 1.54% S, and 0.76%N. The modeling methodology described above to estimate the products when reacting with sodium and either hydrogen or methane is as follows.

With an API gravity of 13.4, the specific gravity can be calculated to be 0.976 g/cc. Thus 100g of the feedstock, would have a volume of 102.4cc. The sulfur and nitrogen we assume to be contained in Thiophene and Pyridene with combined mass of 8.43g and volume 8.22cc. Thus the sulfur and nitrogen free constituents have mass of 91.67g and volume of 94.20cc.

Reaction with Sodium and Hydrogen

After reaction with sodium and hydrogen, the Thiophene and Pyridene have become Butadiene and Pentadiene with combined mass of 6.29g and volume of 9.55cc. Combined with the sulfur and nitrogen free constituents we have a total of 97.96g with volume of 103.75cc. The product specific gravity is 0.944 and API gravity is 18.4. The sodium sulfide and sodium nitride form a salt second phase which is removed.

Reaction with Sodium and Methane

After reaction with sodium and methane, the Thiophene and Pyridene have become Pentadiene, Hexadiene and Heptadiene with combined mass of 8.11g and volume of 11.57cc. Combined with the sulfur and nitrogen free constituents we have a total of 99.78g with volume of 105.77cc. The product specific gravity is 0.943 and API gravity is 18.5. Again, the sodium sulfide and sodium nitride form a salt second phase which is removed.

Comparison between Na & H₂ v Na & CH₄

Comparing the products from the two processes, product specific gravity and API gravity are nearly the same whether hydrogen or methane are used with a significant rise in API gravity of 5.0-5.1. With the loss of sulfur and nitrogen mass, only partially replaced by hydrogen and carbon, the product mass decreases in both cases but since the specific gravity decreases, the volume of the products is greater than the starting feedstock and in the case of upgrading with methane, the volume is 1.9% higher than when hydrogen is utilized. Without describing the calculation, an estimate of the heat of combustion of the products upgraded with methane are also about 1.9% higher than products upgraded with hydrogen.

Upgrading Other Feedstocks H₂ v CH₄

Using the same methodology, the API gravities were estimated for products using upgrading with sodium and hydrogen versus sodium and methane from the feedstocks shown in Table 1. The API gravities are summarized in Table 2. Also the ratio of the volume of product volume to

feedstock volume versus feedstock is presented in Table 3. The last row of Table 3 shows the percent volume increase that is obtained upon upgrading with methane versus hydrogen.

Table 2: Estimated API after upgrading Feedstocks

Process	Shale Oil 1	Shale Oil 2	Heavy Oil 1	Heavy Oil comp.	Bitumen comp.
Initial	32.8	44.2	13.4	16.3	5.4
Na + H ₂	38.1	47.4	18.4	22.5	14.5
Na + CH ₄	38.1	47.2	18.5	22.4	14.5

Table 3: Estimate of Volume Products / Volume Feedstock

Process	Shale Oil 1	Shale Oil 2	Heavy Oil 1	Heavy Oil comp.	Bitumen comp.
Na + H ₂	1.018	1.006	1.013	1.011	1.017
Na + CH ₄	1.042	1.016	1.033	1.029	1.048
CH ₄ /H ₂ -1	2.4%	1.1%	1.9%	1.9%	3.0%

These estimates predict there should be a significant increase in the API gravity of the heavier feedstocks regardless of whether hydrogen or methane are utilized without assuming any saturation of double bonds. Also, the volume of the products should be greater than the initial volume due to decreasing specific gravity and to a larger extent if the upgrading is with methane rather than hydrogen.

Experimental Results - Upgrading Process with Sodium: H₂ v CH₄

In the laboratory we have been utilizing a 500cc stirred reactor and conducting upgrading experiments. Initially we were testing with both sodium and lithium but have concluded sodium is the preferred alkali metal. Based on the sulfur and nitrogen content of the feedstock we calculate the theoretical mass of sodium needed to react fully to form sodium sulfide and sodium nitride according to equations 1-4 and add an amount of sodium relative to the theoretical amount then determine the effects.

Upgrading Experimental Procedure

Our test procedure briefly is the following. Weigh 180g feedstock, add to the reactor, add a predetermined amount of sodium, seal reactor, purge with nitrogen, fill with either hydrogen or methane to a base pressure. Heat to temperature above sodium melting point with low speed stirring then increase stir speed. Raise temperature to target value. Raise pressure of either hydrogen or methane to target value. Stir at high speed for set time period. Shut off hydrogen or methane. Cool down vessel. Open vent valve. Weigh products, measure API gravity, and TAN. Determine product composition with LECO CHNS analyzer and ICP (Perkin Elmer) to determine metals content.

Upgrading Experimental Results

Heavy Oil

Our work is still in progress. We have not determined the optimal conditions but have some very encouraging results with both sodium plus hydrogen and sodium plus methane.

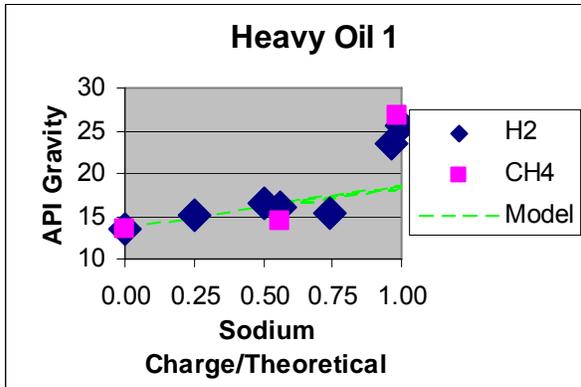


Figure 1: API Gravity versus Sodium Charge/Theoretical in the Presence of Hydrogen or with Methane for Heavy Oil 1 Feedstock

Figure 1 shows API gravity rising in Heavy Oil 1 as the sodium charge relative to theoretical rises. Also the API gravity rise when hydrogen is used is similar to the rise when methane is used which is consistent with the model prediction above. The model predicted the API gravity would rise to about 18.5 but the liquid fraction rose higher to about 25 when the theoretical amount of sodium was used. This can be explained because the operating conditions have not been optimized. At the lower charge ratios there was very little polymerization observed, but as the amount of sodium was increased toward the theoretical amount, polymerization increased resulting in a heavy organic fraction which separated from a lighter liquid fraction. We believe most of the polymerization can be eliminated by optimizing operation conditions and when that occurs, the API gravity of the liquid fraction is expected to be closer to the value predicted by the model.

Figure 2 shows the relative change in the sulfur/carbon ratio and nitrogen to carbon ratio of Heavy Oil 1 as the sodium charge relative to theoretical rises for both hydrogen and methane upgrading. Since the sulfur and nitrogen compositions decreased, these changes are negative. Sulfur drops more readily than nitrogen. As the amount of sodium relative to theoretical approaches 1, there is very little difference between whether hydrogen or methane were utilized.

Ultimately 98% of the sulfur was removed from the liquid phase whether hydrogen or methane were used and >80% of the nitrogen was removed when the theoretical amount of sodium was used to react with the sulfur and nitrogen.

Figure 2 also shows that about 20% of the sulfur was removed when either hydrogen or methane was used but no sodium, but very little nitrogen was removed.

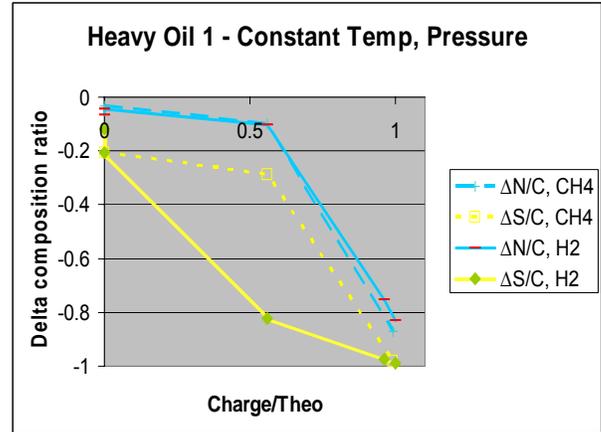


Figure 2: $\Delta S/C$ and $\Delta N/C$ versus Sodium Charge/Theoretical in the Presence of Hydrogen or with Methane with Heavy Oil 1 Feedstock

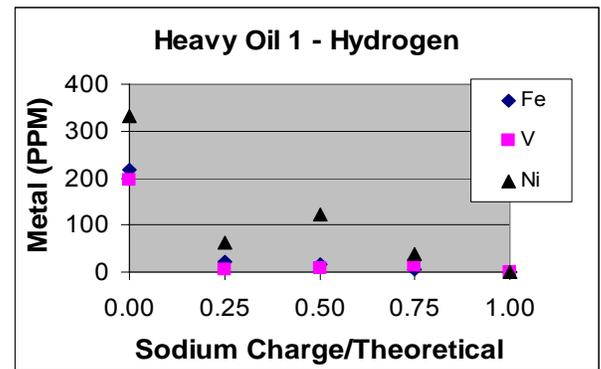


Figure 3: Concentrations of heavy metals in Heavy Oil 1 versus Sodium Charge/Theoretical in the Presence of Hydrogen

Figure 3 shows the concentrations of heavy metals in Heavy Oil 1 versus sodium charge/theoretical in the presence of hydrogen. The concentrations decline very significantly with as little as 25% of the amount needed for the sulfur and nitrogen.

The preference for removal appears to be metals>sulfur>nitrogen. Metals come out first, then sulfur, then nitrogen.

Total Acid Number (TAN)

Total Acid Number, TAN, was measured on the Heavy Oil 1 Feedstock with a value of 4.2. After upgrading process with the theoretical sodium charge and with hydrogen, the TAN value was 0 on three separate runs.

Aromaticity

Our model assumed that we do not saturate the double bonds during the upgrading process. Such saturation is not always desirable as it leads to high consumption of hydrogen. The Ceramtec process has been demonstrated to remove

only S and N while aromatics do not saturate. The portion of the Chromatogram shown in Figure 4 below indicates that the aromatics present prior to the upgrading process remain unchanged. For example, toluene and xylene peaks which appear in the feedstock remain in the post-treated product.

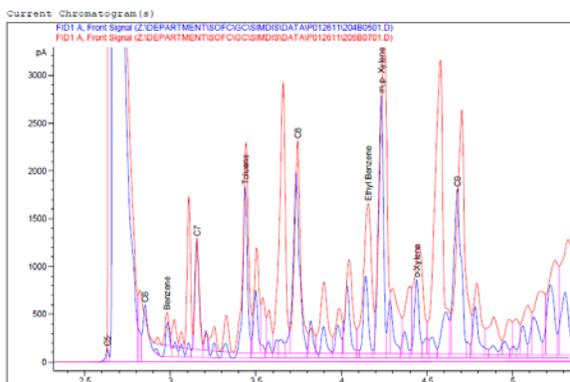


Figure 4: Partial chromatogram of shale oil before and after treatment with alkali metal upgrading, blue plot: before treatment, red plot: after treatment.

Shale oil

Figure 5 shows the relative change in the sulfur/carbon ratio and nitrogen to carbon ratio of Shale Oil 1 as the sodium charge relative to theoretical rises for both hydrogen and methane upgrading. For nitrogen there is very little difference between hydrogen or methane and the nitrogen removal was very high, about 98% when the theoretical amount of sodium was used. Sulfur removal was about 96% with hydrogen and a little lower when methane was used.

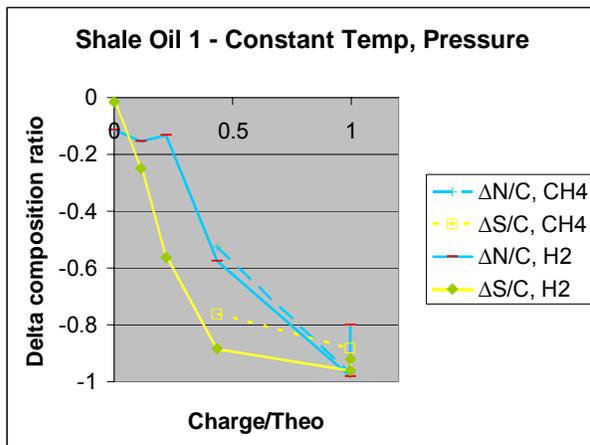


Figure 5: $\Delta S/C$ and $\Delta N/C$ versus Sodium Charge/Theoretical in the Presence of Hydrogen or with Methane with Shale Oil 1 Feedstock

Figure 6 shows the relative change in the sulfur/carbon ratio and nitrogen to carbon ratio of Shale Oil 2 as the sodium charge relative to theoretical rises for both hydrogen and methane upgrading. Data for methane upgrading for this feedstock was only conducted with a high ratio of sodium to theoretical. For sulfur, the removal was very high, about 96%

whether hydrogen or methane were utilized but nitrogen removal was much lower than when the other feedstocks were utilized. We have not determined yet why the removal was less effective for this feedstock.

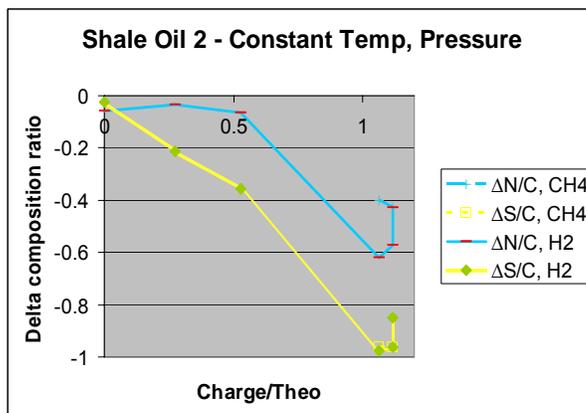


Figure 6: $\Delta S/C$ and $\Delta N/C$ versus Sodium Charge/Theoretical in the Presence of Hydrogen or with Methane with Shale Oil 2 Feedstock

Heavy Oil versus Shale Oil

While the nature and previous processing of Heavy Oil and Shale Oil were much different, the upgrading process using sodium and hydrogen and methane showed similar results in terms of ability to remove sulfur and nitrogen.

Experimental Results – Regeneration of Sodium using NaSICON Membranes

NaSICON, sodium conductive membranes have been developed at Ceramtec Inc and are being used in multiple applications at increasingly larger scale. One of the largest applications has been for the production of sodium methylate from methanol and aqueous sodium hydroxide. The sodium methylate can then be used to produce biodiesel from organic waste. This membrane, which can be made in planar and tubular shapes, is very conductive to sodium ions even down to room temperature. This membrane is the enabling factor for electrolytic regeneration of sodium metal from sodium sulfide and sodium nitride.



Figure 7: Planar type NaSICON membrane electrolysis stack on left and Tubular NaSICON membrane bundle on right

Figure 7 shows two types of configurations in which we currently incorporate NaSICON membranes into electrolyzers. The electrolyzer stack on the left utilizes planar membranes and on the right is a bundle of tubular NaSICON membranes.

Membrane Background

The membrane has selective conductivity. It is non porous but allows sodium ions to conduct through the lattice structure. In addition to the high sodium selectivity of NaSICON, this ceramic material has also a large sodium ionic conductivity at low temperatures as shown in Figure 8. During our extensive lab testing, we have demonstrated the stability of the material in the presence of highly concentrated solutions of sodium sulfides in aprotic organic solvents and in the presence of molten sodium up to temperatures of 150C.

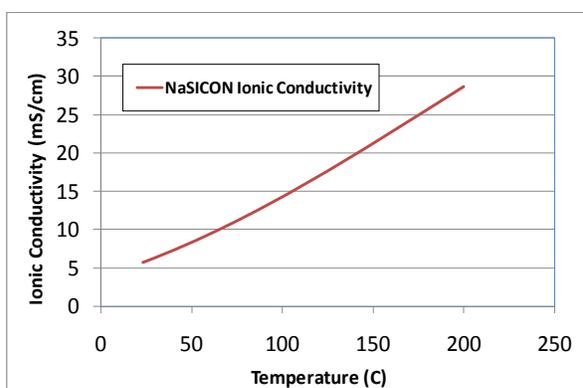


Figure 8: Sodium Ion Conductivity of Standard NaSICON and a new Process NaSICON versus temperature

Experiments with Sodium Sulfide

We have tested a number of electrolysis cells using sodium tetra sulfide (Na_2S_4), dissolved in an organic aprotic solvent, as anolyte system and molten sodium as catholyte. Cell operating temperatures within the range 120-150C and current densities up to 150 mA/cm^2 have been covered. Our lab test cells are operated in batch mode, where loads of Na_2S_4 periodically are added to the anolyte in the cell. In addition, the molten sodium is accumulated in the catholyte compartment and removed also in a batch fashion. Figure 9 shows the cell voltage and the cell Open Circuit Voltage (OCV) during 340 hours of operation at current densities of 50 and 60 mA/cm^2 and at a temperature of 130C. The low operating cell voltage and the stability of the NaSICON membrane, over two weeks of almost continuous operation proves the feasibility of the electrolytic sodium recovery process. The small voltage increase, observed in this period, is due to the increase in the OCV or Nernst Potential of the cell as the anolyte is enriched in higher order sodium polysulfides ($x > 4$ in Na_2S_x). This is displayed in Figure 10, where the cell Nernst Potential is plotted versus the number of sulfur atoms in the polysulfide molecule. It is expected that the polysulfide molecules will reach a maximum length in the sulfur chain, where eventually

will be oxidized to elemental sulfur (S_8). The data seems to indicate that the maximum x should be between 12 and 14.

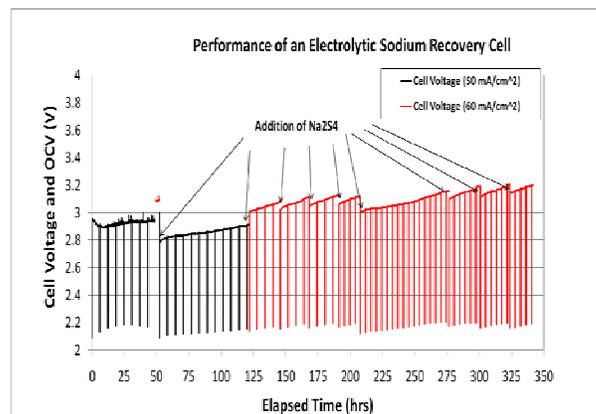


Figure 9: Cell voltage and Open Circuit Voltage (OCV) versus elapsed time for a lab test sodium recovery electrolytic cell operating at 50 and 60 mA/cm^2 current density and temperature of 130C.

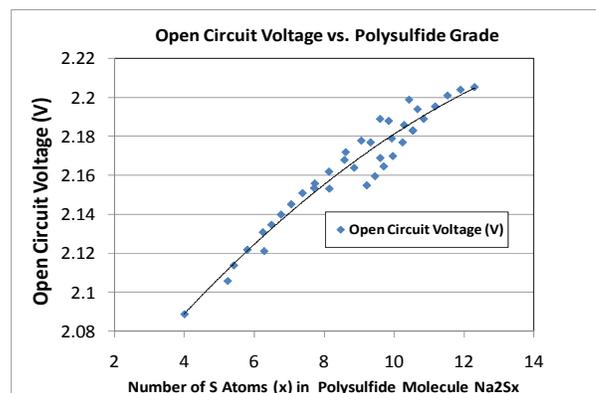


Figure 10: Open Circuit Voltage or Nernst Potential versus number of Sulfur atoms (x) in the sodium polysulfide molecule (Na_2S_x) present in the anolyte.

Experiments with Salts from Upgrading

Salts separated from a shale oil feedstock after upgrading were dissolved in our preferred aprotic organic solvent. Figure 11 shows the ionic conductivity versus temperature of a 20% wt. solution of the salts. The large increase in ionic conductivity of the solution, as compared to the pure solvent, indicates the presence of sodium, sulfides and nitride ions in solution. Initial trials using sodium sulfide and nitride salts separated from the upgrading process are showing good recovery of sodium.

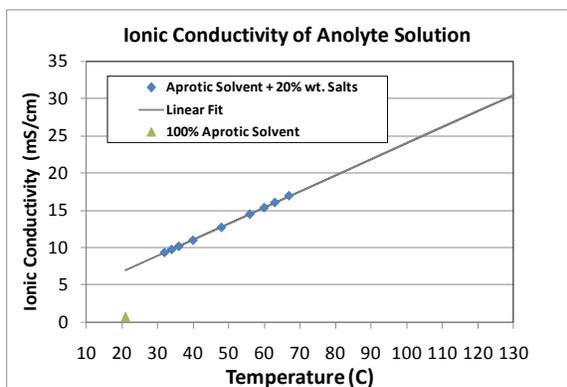


Figure 11 Ionic conductivity (mS/cm) of a 20% wt. solution of sodium sulfide and sodium nitride organic salts dissolved in our preferred organic aprotic solvent

Look at Costs

An early stage cost estimate has been prepared where capital and operating costs were estimated for Heavy Oil 1 upgraded at the full theoretical amount of sodium required to react with the sulfur and nitrogen. The costs include current costs for hydrogen, methane, and grid power. The sodium was assumed to be regenerated in NaSICON cells with a 5% loss and the makeup was assumed to be generated on-site electrolytically with associated costs included. The total costs amounted about \$6 per barrel. Reducing the sulfur, nitrogen, and metals concentration and increasing the API gravity are expected to increase the value of the product oil to justify the process cost. In addition the model predicts an oil volume increase by as much as 3.3% if methane is utilized which partially offsets the upgrading cost. There also is a possibility that the heavy metals removed from the oil can be recovered in the reduced form. Their value exceeds \$6 per barrel and also may justify the upgrading expense.

Conclusion

Upgrading Heavy Oil utilizing sodium and either hydrogen or methane offer benefits of lower impurities, increased API gravity, low TAN, and retained aromaticity. Methane as an upgradant is feasible and provides a way to increase the volume and value of the oil without the need for steam methane reforming and the associated carbon dioxide emission. A critical aspect of the upgrading process, regeneration of sodium from sulfides and nitrides appears to be feasible using a low cost NaSICON material produced by Ceramatec Inc.

Acknowledgement

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Nomenclature

NaSICON =	Sodium super ion conductor
SMR =	Steam Methane Reforming
API =	American Petroleum Institute
TAN =	Total Acid Number
Comp. =	Compilation
g =	gram(s)
cc =	cubic centimeter(s)
ICP =	Inductive Coupled Plasma Analyzer
Δ =	Change (Delta)
mS/cm =	milli Siemen per centimeter
C =	Celsius, Centigrade
V =	Voltage
OCV =	Open Circuit Voltage (Potential)
mA/cm^2 =	milli Amp per square centimeter
wt. =	by weight

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