MAIN CHALLENGES HYDROPROCESSING SHALE OIL FEEDS

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Abstract

With the increasing amount of shale oil in the worldwide market it becomes necessary to analyze, from the refinery point of view, what is the real impact of processing shale oil derived feeds on the catalytic system of hydrotreating units.

Compared with conventional oil, shale oil normally has higher content of contaminants like Arsenic (As), Vanadium (V), Nickel (Ni) and Silicon (Si). All those contaminants need to be trapped before entering the main catalyst bed were the Hydrodesulfuration (HDS) and Hydrodenitrogenation (HDN) take place. Particularly As is one of the most poisonous metals for hydrotreating catalyst, producing an activity loss of 30% with only 0.5 wt. % accumulation in the catalyst bed. This means that the grading or guard system of a hydrotreating reactor will have a more important role trapping all the contaminants, maintaining as high as possible the main catalyst activity.

Another challenge that faced when processing these types of feed is changing the perception of “the normal operation” of the unit. Shale oil contents different components like oxygen, chloride and different properties such as higher bromine numbers that can change dramatically the optimal operating point that the unit usually has.

An easy example is the higher bromine number that generates much more exotherm in the reactor that needs to be controlled by quench or by changing the loading scheme.

A more complex example could be the presence of oxygen that includes a new reaction that normally is discarded in the hydrotreating studies. In this case the organic oxygen will react mainly by Hydrodeoxygenation (HDO) to form water and also by Hydrodecarboxylation (HDCo) to form CO_2. Since the main reaction related to oxygen will be HDO, the presence of water will be the main factor to deal in the new reactor scheme, normally by treating it with a special layer at the top of the reactor. Another effect of the presence of oxygen is an increase of yields towards light products, since removing the oxygen from the molecule reduces significantly its boiling point. An example of this is the phenol (b.p. 182°C) that would produce benzene with 78°C.

The paper it concludes that more attention is needed in the analysis of the contaminants and general properties of the feed in order to make the best selection of the catalyst. The main challenge optimizing the operation of the unit processing shale oil derives is to take into account the higher amount of nitrogen, olefins and the presence of oxygen.

The optimal selection of the catalyst system for this type of feeds will derived in a longer cycle length of the unit and a more stable operation.

1. Shale Oil overview

Shale oils are heavy, viscous crude deposits. Heavy crude oils usually contain high concentrations of sulfur and a number of metals, particularly arsenic, nickel and vanadium. These properties make them difficult to pump out of the ground or through a pipeline and interfere with refining. These properties also create serious environmental challenges. The best-known reserve of shale oils is Venezuela's Orinoco heavy oil belt, which contains an estimated 1.2 trillion barrels.

The global impact of shale oil could revolutionize the world's energy markets over the next couple of decades, resulting in significantly lower oil prices, higher global GDP, changing geopolitics and shifting business models for oil and gas companies.

Shale oil has the potential to reshape the global economy, increasing energy security, independence and affordability in the long term. However, these benefits need to be squared with broader environmental objectives.

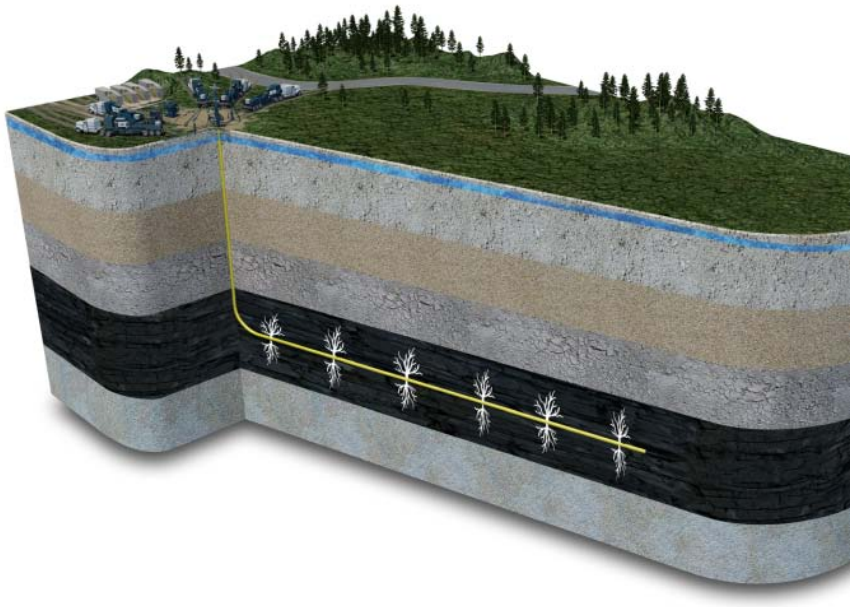

Figure 1 – Extracting Shale Oil

The US is not the only country in America to undergo the shale oil revolution as Uncle Sam's neighbors in South America are also poised to be future shale oil producers as well.

Argentina, Brazil, Venezuela, Uruguay and several other South American countries are beginning to find shale oil deposits and are already being explored by super majors and North American independents.

Argentina has emerged as a potential shale oil superpower as it now has the second-largest shale gas reserves (behind China with 1,115 trillion cubic feet) and the fourth-largest oil reserves. Argentina has the shale oil potential of 27 billion barrels of oil and 802 trillion cubic feet of recoverable shale gas.

According to the US Energy Information Administration, or EIA, Venezuela holds the sixth-largest shale oil

reserves with 13.4 billion barrels along with 167 trillion cubic feet of shale gas reserves. The low oil prices have made it nearly impossible for Venezuela to explore and produce shale oil gas due to the high production costs.

Brazil has for decades been focused on offshore drilling, which make up about 90 per cent of its oil production coming from offshore drilling in 2013. According to the EIA, Brazil has one of the largest proven and recoverable shale oil reserves in the world with a potential of 82 billion barrels. Brazil also holds a potential of 245 trillion cubic feet in shale gas reserves which gives it the potential to be one of the largest exporters of natural gas in the future.

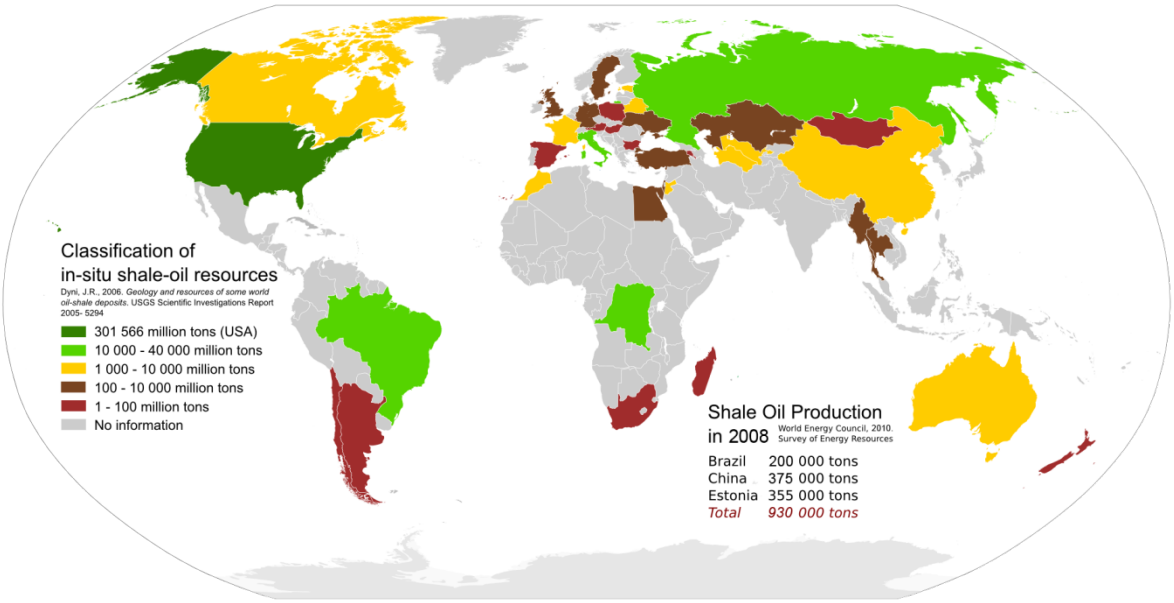

Figure 2 Shale oil in the world

As the demand for precursor fractions to fuels (such as gasoline and diesel) increases, there is much interest in developing economical methods for recovering liquid distillate fraction hydrocarbons from oil shale. However, these distillates are not yet economically competitive against petroleum crude. Furthermore, the value of hydrocarbons recovered from oil shale is lessened by the presence of undesirable contaminants. The major contaminants of concern are oxygen-containing, sulfur-containing, nitrogen-containing, and metallic (and organometallic) compounds that cause detrimental effects to the catalysts used in the subsequent refining processes.

Depending on the process, some oil shale distillates have a much higher concentration of higher boiling point compounds that would favor the production of middle distillates (such as diesel and jet fuels) rather than naphtha. Aboveground retorting processes tended to yield lower API gravity oil than the in situ processes, because the residence time in the underground retort encourages further cracking of the primary products. Thus, additional processing equivalent to hydrocracking would be required to convert oil shale distillates to a lighter range hydrocarbon (gasoline). Removal of sulfur and nitrogen would, however, require hydrotreating.

After fines removal, the shale oil is hydrotreated to reduce the nitrogen, sulfur, and arsenic content and

improve stability; the cetane index of the diesel and heater oil portion is also improved. The hydrotreating step is generally accomplished by a fixed catalyst bed processes at high hydrogen pressures, and hydrotreating conditions are slightly more severe than for comparable boiling range petroleum stocks because of the higher nitrogen content of shale oil.

2. Shale Oil Properties

Compared with conventional oil, shale oil is high in nitrogen and oxygen compounds and also has a higher specific gravity, owing to the presence of heavy nitrogen-, sulfur-, and oxygen-containing compounds. Shale oil also has a relatively high pour point, and some quantities of arsenic and iron are present.

Table 2.1 Properties of Shale Oil from Various Sources

Location	Sp gr (API)	Elemental analysis (%w/w wt. %)					Analysis of Distillate (%w/w) <350°C		
		C	H	O	N	S	Saturates	Olefins	Aromatic
Colorado, USA	0.943 (18.6)	84.90	11.50	0.80	2.19	0.61	27	44	29
Kukersite, Estonia	1.01 (8.6)	82.85	9.20	6.79	0.30	0.86	22	25	53
Stuart, Australia	-	82.70	12.40	3.34	0.91	0.65	-	-	-
Rundle, Australia	0.636 (90.8)	79.50	11.50	7.60	0.99	0.41	48	2	50
Irati, Brazil	0.919 (22.5)	84.30	12.00	1.96	1.06	0.68	23	41	36
Maoming, China	0.903 (25.2)	84.82	11.40	2.20	1.10	0.48	55	20	25
Fushun, China	0.912 (23.6)	85.39	12.09	0.71	1.27	0.54	38	37	25

Shale oil contains a large variety of hydrocarbon compounds (Table 2.1) but it also has higher nitrogen content than the 0.2 – 0.3% w/w of a conventional crude oil. In addition, shale oil also has a high olefin content and diolefin content — constituents which are not present in petroleum and which require attention during processing due to their tendency to polymerize and form gums and sediments. It is the presence of these olefins and diolefins, in conjunction with the high nitrogen content, which makes shale oil characteristically difficult to refine (Table 2.2). Crude shale oil also contains appreciable amounts of arsenic, iron, and nickel that also interfere with refining.

Table 2.2 Major Compound Types in Shale Oil	
Saturates	Heteroatom Systems
Paraffins	Benzothiophenes
Cycloparaffins	Dibenzothiophenes
Olefins	Phenols
Aromatics	Carbazoles
Benzenes	Pyridines
Indans	Quinolines
Tetralins	Nitriles
Naphthalenes	Ketones
Bipenyls	Pyrroles
Phenanthrenes	
Chrysenes	

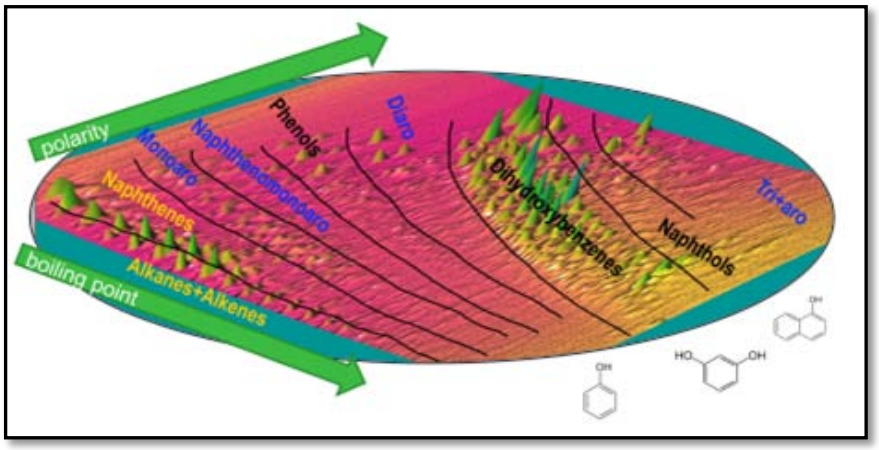

Figure 3 – Example of shale oil composition

Other characteristic properties of shale oils are:

1. High levels of aromatic compounds, deleterious to kerosene and diesel fractions.
2. The nitrogen content of the shale oil is higher than crude oil.
3. The oxygen content of shale oil is much higher than conventional petroleum.
4. Low hydrogen-to-carbon ratio.
5. Low sulfur levels, compared with most crudes available in the world (although for some shale oils from the retorting of marine oil shale, high sulfur compounds are present).
6. Suspended solids (finely divided rock) typically due to entrainment of the rock in the oil vapor during retorting.

7. Medium levels of metals.

Table 2.3 Challenges for Shale Oil Processing	
Parameters	Plugging on Processing
	Product quality
Arsenic content	Toxicity
	Catalyst poison
High pour point	Oil not pipeline quality
Nitrogen content	Catalyst activity inhibition
	Contributes to instability
	Toxicity
Diolefins	Contributes to instability
	Plugging on processing

3. Hydrotreating Shale Oil

3.1. Fines content

Most of shale ash fines will be found in the heavy raw shale oil stream. Particle size distributions are skewed toward the ultra-fine particle size range, with most shale ash particles under 2.5 microns and substantial ultra-fines under 0.3 microns in size. The shale ash fines are stabilized and kept in the oil suspension by the highly polar hetero-compounds in the aromatic shale oil.

The deposition of fines in catalyst beds operating in trickle bed flow are well studied due to the importance of Canadian oil sand liquid in petroleum refining. Literatures reported fines uptake in a trickle bed reactor is affected by catalyst size and shape, flow regime, vapor and liquid velocities, liquid hold-up in the catalyst bed, polar nature of the liquid and electrostatic interactions between the fines and catalyst. Ultra-fines in the colloidal range (<1 micron) tend to deposit evenly through the length of a catalyst bed. For larger non-colloidal fines, there is more likelihood of having non-uniform fines deposition in the bed with more fines at the top of the bed. The fines capturing efficiency of a clean catalyst bed is high initially and decreases rapidly as fines accumulate in the bed.

Even a few wtppm of fines in a hydrotreater feed can deposit enough fines to cause pressure drop problem after only months of operation. Commercial experience from shale oil and tar sand hydrotreaters shows fines deposition in the catalyst beds occurs when the hydrotreating severity is sufficient to reduce the polar nature of the oil, thus lowering its ability to suspend the fines in the oil. It is not uncommon to observe pressure drop built-up in the lower catalyst beds of a reactor processing shale oil or tar sand liquids.

The degree of fines disposition in a catalyst bed depends on the reactor operating conditions and the severity of hydrotreating. If hydrotreating is done at 60 barg, the hydrotreating severity will not be severe enough to reduce the polar nature of the hetero-compounds in the shale oil sufficiently to cause the fines to drop out of solution in the reactors of the hydrotreating section, so some fines will also deposit in hydrotreating beds in

higher pressure section. The strategy for avoiding premature pressure drop built-up is to spread out the fines deposition to all catalyst beds by using large size catalysts in the hydrotreating section and use multiple layers of grading to avoid sharp transition of size and void between bed layers.

3.1.1. Reactor cleaning considerations

Hydro-blasting is the cleaning method most often used to remove scales and fines from reactors. A hydro-blast rotor jet is inserted from the top reactor manway and moved vertical down towards to the bottom of the reactor with defined speed and positions for longer holding times. Hydro-blast cleaning is very effective for reactor wall and the hemispherical heads but supplemental cleaning is often required for reactor internals such as distribution tray, quench mixer, catalyst bed support, and outlet collector.

A scale catching tray on top of the first liquid distribution tray is often recommended and highly effective for trapping larger scale and particles. Some of the fines in the feed will be trapped by the scale catching tray, but some of the fines will be carried over to the distributor tray below and get trapped there. From a cleaning perspective, scale catching tray requires reactor entry for manual cleaning because it is more difficult to clean the distribution tray underneath.

When entry into reactors for manual cleaning must be minimized due hazardous substance such as As contaminated catalyst and fines, single-bed reactor allows for easier cleaning using hydro-blast rotor jet. To further reduce the need for entry into a dirty reactor, the distributor tray could be equipped with manway sections which are opened from the top reactor manway without requiring entry. Extra-large reactor top manway would give better access for cleaning and inspection. To overcome the difficulties in cleaning the distributors near the reactor wall, two or three horizontal nozzles above the distributor tray could be provided. Hydro-blast cleaning could then be performed using these nozzles to access the tray area next to the reactor wall.

3.2. Organic chloride

Most of Cl will likely be converted into hydrochloric acid (HCl) in the hydrotreating section, but in the case of a hydrocracker, any unconverted organic Cl and dissolved HCl in oil feed could introduce HCl into that section.

The presence of HCl in the reactor effluent can cause severe corrosion/pitting of the reactor effluent cooler, its associated piping, and stripper/fractionator overhead system (if NH_4Cl passes through to the fractionation section). With just a few wtppm Cl in the feed, hydrotreaters have experienced severe corrosion in these systems, requiring high cost metallurgical upgrade to Incoloy 625 or even Hastelloy C-276. To effectively scrub out the HCl with water, long runs of piping or static mixer are used. NH_4Cl can also cause Cl Stress Corrosion Cracking (ClSCC) of low point drains in stainless piping.

3.2.1. Ammonium chloride salt deposition temperature

HCl can combine with ammonia (NH_3) to form ammonium chloride (NH_4Cl), a crystalline solid with a very high deposition temperature. NH_4Cl salt deposition must be avoided because it causes plugging and corrosion. The salt is hygroscopic (attracts water) so under-deposition corrosion and pitting are observed on affected equipment and piping. The estimated NH_4Cl salt deposition temperature of the reactor effluent in the LP (60 barg) hydrotreating section as a function of chloride feed content is shown below:

Table 3.1 Estimated NH_4CL deposition vs feed chloride content			
Feed chloride content, wtppm	40	5	1
Estimated NH_4Cl salt deposition temperature, °C	225	200	185

The above table shows it is necessary to inject wash water to the reactor effluent at relatively high temperature to avoid NH_4Cl salt deposition and the salt deposition temperature is relatively insensitive to feed chloride content. It should be noted that operating pressure will also slightly modifiy the NH_4Cl deposition temperature.

3.2.2. Vapor-liquid equilibrium for streams with hydrochloric acid

To assess the effect of HCl on corrosion and material selection, it is necessary to accurately predict the partitioning of HCl in the 2-phase hydrocarbon vapor/liquid system and 3-phase vapor/liquid/water system.

The solubility of a solute in a solvent in a dilute solution can be described by Henry's Law shown below:

$$X_i = \frac{f_i \times Y_i \times P}{K_h}$$

Where X_i is the mole fraction of the solute i, f_i is its vapor phase fugacity coefficient, Y_i is its vapor phase mole fraction, P is total pressure in bar, and K_h is Henry's constant in bar for the solute in the solvent of interest.

In non-polar systems, solubility follows unambiguous trends with the physical properties of the solute and solvent; solubility increases with solute boiling point and decreases with solvent solubility parameter. However, the solubility of polar gases such as HCl also depends on its dipole moment and Lewis acid-base interactions.

The accuracy of different process simulators for predicting the solubility of HCl in hydrocarbon liquid was checked by calculating the Henry's constants of HCl in n-C_{16} and comparing it against published data with temperature extrapolation. The Henry's constants predicted by PROII SRKM, PROII OLI (with full database), and ProMax Electrolyte are compared against publish data below.

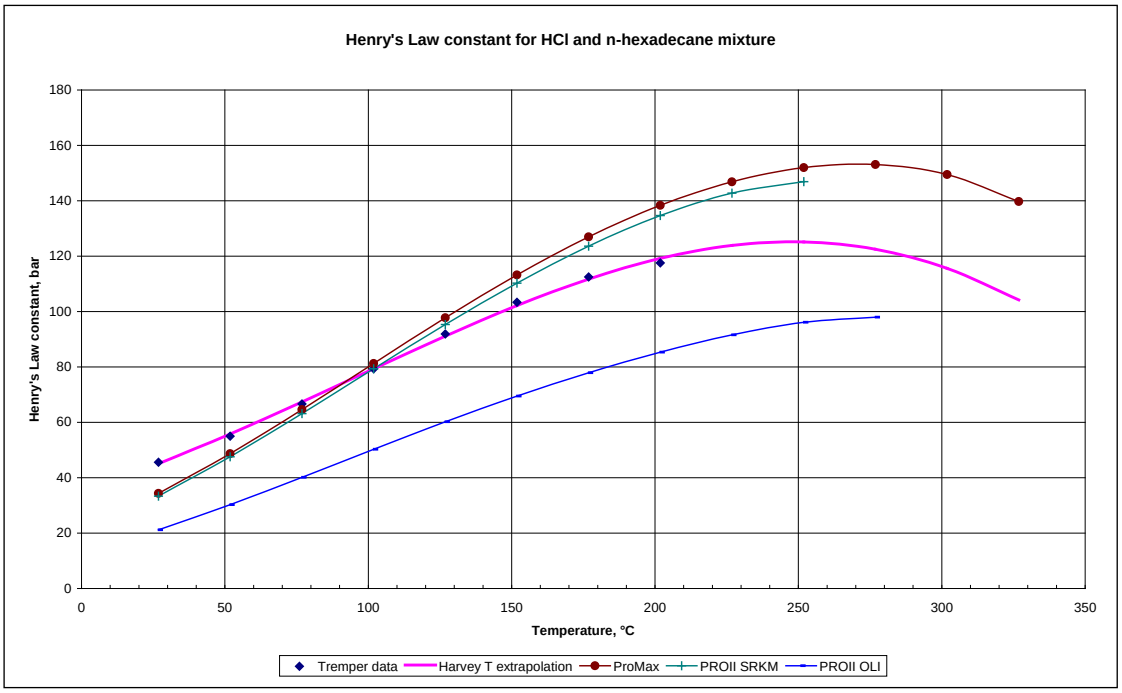

Figure 4 - Henry's law constant for HCl and n-hexadecane mixture

The plot shows that PROII SRKM and ProMax predicts similar K_h which are about 15% higher than the Tremper data with the Harvey temperature extrapolation. Surprisingly, the PROII OLI simulator predict K_h which is about 30% lower than the Tremper data near the hot separator operating temperatures of 250°C.

The predicted HCl content in the hot separator liquid from the hydrotreating section is compared in the table below for PROII SRKM, PROII OLI with full database, and value calculated using the Harvey's correlation for HCl in n-C_{16}. (ProMax using pseudo-components at the LP hot separator conditions did not converge).

Table 3.2 HCl content of the hot separator

Hot Separator (60 barg, 270°C)	Units	Harvey correlation for K_h in n-C16	PROII SRKM	PROII OLI
Vapor flow	kg/h	NA	83,430	72,108
Liquid flow	kg/h	NA	85,688	97,010
HCl in vapor	vppm	25.9	25.9	21.8
HCl in liquid	**wtppm**	**2.3**	**1.2**	**10.0**
Henry's constant	**bar**	**123.7**	**233**	**23.9**

The table shows the predicted HCl content of the hot separator liquid ranges from 1.2 to 10 wtppm.

3.2.3. The impact of chloride on materials selection and process layout

The corrosion rate of a complex system of HCl, NH_3, H_2S, and water is affected by several inter-dependent variables. Corrosion rate is high at low pH of the aqueous phase (low NH_3/HCl ratio), high temperature, and high NH_4Cl concentration. To avoid severe corrosion, it is necessary to avoid NH_4Cl salt deposition and to ensure enough liquid water exists at the injection point to dilute the NH_4Cl concentration in the water phase.

NH_4Cl salt deposition and corrosion could occur on cold surfaces of small diameter instrument lines, no flow piping associated with reactors, relief values, and bypass lines. Small diameter instrument lines can be effectively purged with hydrogen, but an elaborate hydrogen purge system would be required to purge the reactors associated lines. For example, the reactor arrangement shown below would require 11 active hydrogen purge lines and 7 inactive purge lines (shown as dash lines).

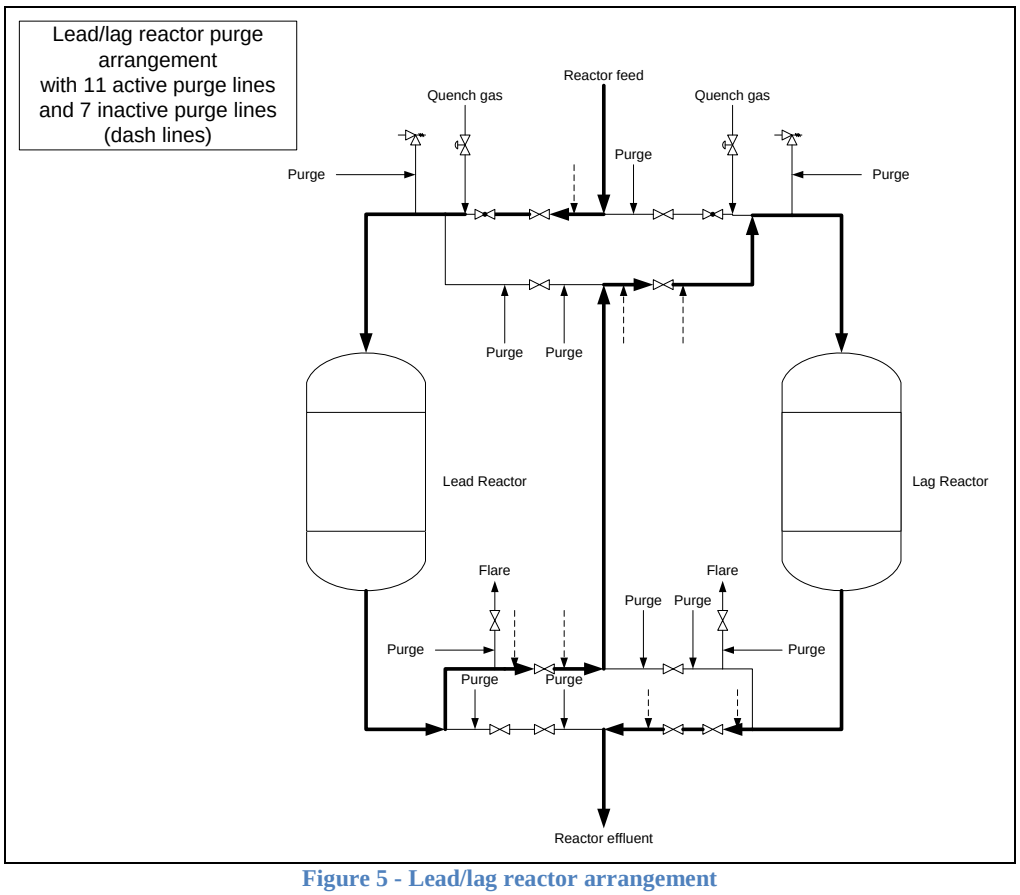

Figure 5 - Lead/lag reactor arrangement

But even with this elaborate hydrogen purging system, there is no certainty that NH_4Cl deposition would not occur in the larger diameter piping unless very large purge flow is used.

The need to inject wash water at a high reactor effluent temperature negatively impacts heat recovery from the reactor effluent. Heat exchanger downstream of the wash water injection point would require high cost material, so it is common to simply reject the heat in an alloy effluent aircooler. The highly unsaturated shale oil feed results in a high heat release. Since the heat release is in excess of what is required for feed preheating, full utilization of the reactor effluent heating value is not required.

The presence of chloride can cause Chloride Stress Corrosion Cracking (ClSCC) of stainless piping, especially small-diameter low-point drains. Material upgrade to Alloy 825 is an effective but costly solution. Rather than using Alloy 825, Topsoe design practice is to stress relief stainless welds and heat exchanger cold form U-bends. During turnaround, sensitized stainless equipment and piping should be thoroughly soda ash washed to remove Cl and polythionic acid before exposing to air.

The following corrosion prevention strategy can be adopted in the shale oil for hydrotreaters and hydrocrackers:

1. Wash water can be added at a location hot enough to avoid ammonium chloride salt deposition or the HCl aqueous dew point temperature. A 40°C margin can be added to the predicted ammonium chloride deposition temperature to account for the difference between bulk fluid and tube wall temperatures and localized cold spot in the upstream effluent heat exchangers.

2. After wash water injection, no additional heat recovery can be done using U-tube heat exchangers.

3. Wash water injection rate will be set to ensure at least 25% of the wash water exists in the water phase and an ammonium bisulfide (NH_4SH) concentration of less than 4 wt% in the cold separator sour water.

4. Sour water from the high pressure section is cascaded as wash water to the low pressure section to reduce water usage and pumping cost. A side benefit of cascading the wash water is the NH_3 in the water will raise the pH of the aqueous phase to reduce its corrosivity.

5. Good vapor/liquid/water contact is critical to scrub out the HCl and to allow the three phases to reach thermal and chemical equilibrium.

6. Minimize the Cl break-through to the HP section by considering the use of a cold separator only configuration so all the feed to the HP section is water washed.

7. Minimize dead legs and normally no flow bypass lines at locations where NH_4Cl salt deposition may occur. Small diameter instrument lines and dead legs such as PSV lines and bypass lines will be purged with hydrogen.

8. Water wash of cold separator vapor to ensure sour water droplets and residual HCl does not break through to downstream piping and recycle gas compressor

9. Tentative material selection for LP section effluent aircooler, static mixer, and aircooler inlet piping (after wash water injection) would be Incoloy 625. The LP effluent aircooler outlet piping and the HP effluent aircooler and its inlet and outlet piping would be CS.

3.3. Organic oxygen content

The organic oxygen contained in shale oil feeds will react to form water. Analysis has shown oxygenates in the feed usually are phenols, alkyl-oxybenzenes, resorcinols, aldehydes, ketones, ethers, and alcohols. The carboxylic acid content has also to be considered (acid number). Organic oxygen compounds can react either

by hydrodeoxygenation (HDO) to form H_2O or by decarboxylation to form CO_2. The oxygenates in the shale oil will react mainly by HDO and would not form a significant amount of CO_2.

HDO of the feed oxygenates produces products with a much lower boiling range, resulting in a high conversion to diesel and lighter. The types and distribution of oxygenates in the feed can have a large impact on light ends and naphtha yield. For example, HDO of phenol (b.p.=182°C) and resorcinol (b.p.=277°C) would produce benzene (b.p.=78°C), where as HDO of n-butyl alcohol (b.p.=118°C) would produce butane (b.p.=-0.5°C). In general, the boiling point down shift from HDO of oxygenates in the naphtha and kerosene boiling range is approximately minus 60°C to minus 100°C per oxygen atom removed; therefore, the HDO products from the oxygenates in the kerosene and naphtha boiling range would end up as gases, LPG, light naphtha, and heavy naphtha.

HDO of oxygenates in the light naphtha would produce only gases and LPG. This could have a large impact on the overall light ends yield in a hydrocracker. Similarly, the HDO of the heavy naphtha and kerosene would produce naphtha and lighter products, reducing the yield of the more valuable kerosene and diesel.

When considering the conversion of oxygen containing species, it is evident that these are much more reactive than refractory compounds, which must be removed to reach the specification. This means that the problem of industrial operation will typically not be to achieve full conversion, but rather to be able to control exothermic reactions. As the reactions also consume large amounts of hydrogen, higher make-up hydrogen and quench gas flows are needed.

The depletion of hydrogen combined with high temperatures may lead to accelerated catalyst deactivation and pressure drop build-up. Control of these factors would require the use of tailor-made catalysts and a careful selection of unit layout and reaction conditions. In this way, it is possible to achieve a gradual conversion without affecting the cycle length and still meeting product specifications.

In contrast to conventional hydrotreating, higher amounts of propane, water, carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4) are formed. These gases must be removed from the loop either through chemical transformation by a gas cleaning step such as an amine wash or, more simply, by increasing the purge gas rate. If not handled properly, the gases formed will give a decreased hydrogen partial pressure, which will reduce the catalyst activity. Further problems with CO and CO_2 may occur due to competitive adsorption of sulfur and nitrogen-containing molecules on the hydrotreating catalyst. The CO, which cannot be removed by an amine wash unit, will build up in the treat gas, requiring a high purge rate or another means of treat gas purification. In the reactor effluent train, liquid water and CO_2 may form carbonic acid, which must be handled properly to avoid increased corrosion rates.

Based on this information, special catalyst formulations have been developed and are currently running in industrial operation. These are designed to have a high activity and stability under the conditions prevailing in this operation.

Understanding and controlling selectivity by using the described reaction routes is a key to the design of optimum catalysts for this very demanding service.

3.4. Diolefins and olefins

Diolefins in the feed can cause polymerization reactions which leads to coking and fouling of equipment when the feed is heated. The fouling effect of diolefins it is normally neutralized by a high LHSV diolefins reactor

operating at about 200°C. The main design challenge of these cases is to properly design the reactor(s) and heat balance to account for the high heat release from olefins saturation.

Since the exothermic di-olefin saturation reactions produce large amounts of heat, it is necessary to operate at low temperatures and to use a selective catalyst to control the temperature increase. High selectivity means that the catalyst should saturate di-olefins only and not mono-olefins, which might lead to a too high temperature increase in the reactor.

Topsoe has carried out studies of catalyst selectivity by processing a model feed containing 1,3-hexadiene. The di-olefin to olefin reaction selectivity was studied as a function of diolefin conversion as shown in Figure 6A. As expected, the selectivity decreased with conversion, since the two reactions (saturation of 1,3-hexadiene to hexenes and saturation of hexenes to hexane) are consecutive.

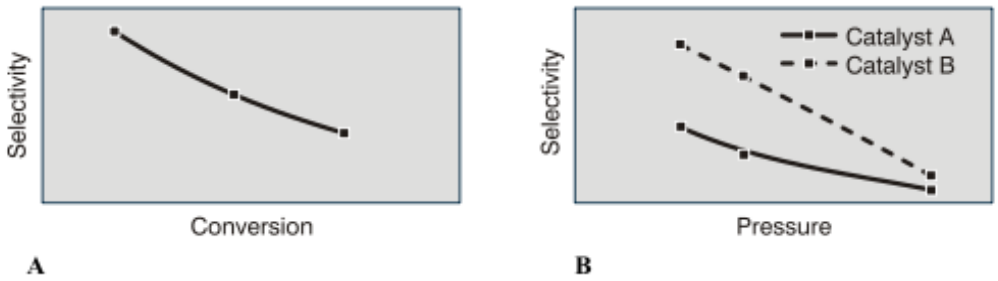

Figure 6: Selectivity of di-olefins saturation reaction

The effect of pressure was also investigated. In Figure 6B, the selectivity is shown as a function of the reactor pressure for two different catalysts. At all conditions, the hexadiene is completely converted, but as can be seen, the selectivity towards hexene increases with decreasing pressure. Furthermore, the two catalysts tested have different selectivity and slightly different responses to changes in pressure. This means that even though the saturation reactions are very fast, there are still a number of knobs that can be turned to control the reactions to ensure that both complete saturation of di-olefins and high selectivity towards olefins are achieved. Topsoe uses this knowledge to optimize the selection of catalyst and process conditions to maximize the run length.

3.4.1. The impact of diolefins and olefins on catalyst selection

The high olefin content increases the risk of coking on the catalyst, and good grading becomes more important in order to avoid excessive pressure drop build-up. Typically, a hard crust layer leading to rapid pressure drop build-up would be experienced in the top part of the catalyst bed if the grading and reactor dimensions were not designed to handle the higher amount of olefins. The solution to the problem comes from a fundamental understanding of crust formation with respect to the following:

- Graded catalytic activity
- Heat transfer
- Bed void size
- Rate of olefin saturation versus temperature

Typically, in the past, part of the solution was to grade the top of the catalyst bed by catalytic activity only, i.e. gradually increasing catalytic activity from the inert top layer down to the main bed by several increments instead of having one step from inert to maximum activity.

This is, however, not sufficient for high olefinic feedstocks since only very small activation energy is required, resulting in a high temperature increase in the topmost part of the catalyst bed even when utilizing low activity catalysts. The key to solving this challenge, in combination with the activity grading, is to design the reactors and the rate of treat gas to allow a sufficient heat transfer in the axial direction thereby avoiding hot spots and resulting crust formation. This problem has typically been overlooked in the past but is becoming more important as the amount of olefins in feeds increases.

However, even with the best activity grading, some crust and coke formation will still occur in combination with contaminants introduced with the feedstock. This call for additional protection to make sure that there is a sufficient void for these types of contaminants.

Typically, this is done by controlling the bed void size. Controlling the bed void size is done by loading the reactor with different sizes and shapes of grading material: high void topping material followed by larger rings on top of smaller rings and underneath these, the bulk catalyst. The reason for using rings of different sizes is to create a loading, which has a differentiated filtering effect, so that the largest contaminants introduced with the feed, are trapped in the upper layers, and the smaller particles are deposited in the lower layers.

3.5. Iron

This can cause major fouling problems in the catalyst bed. If the feed Fe content is indeed high, then more consideration would be given to the use of parallel diolefins reactor and bypassable dearseniting reactors to allow on line catalyst change out, despite the risk of NH_4Cl deposition and corrosion in dead legs.

An example of the fouling caused by a few wtppm of Fe in the feed is illustrated in the photo below.

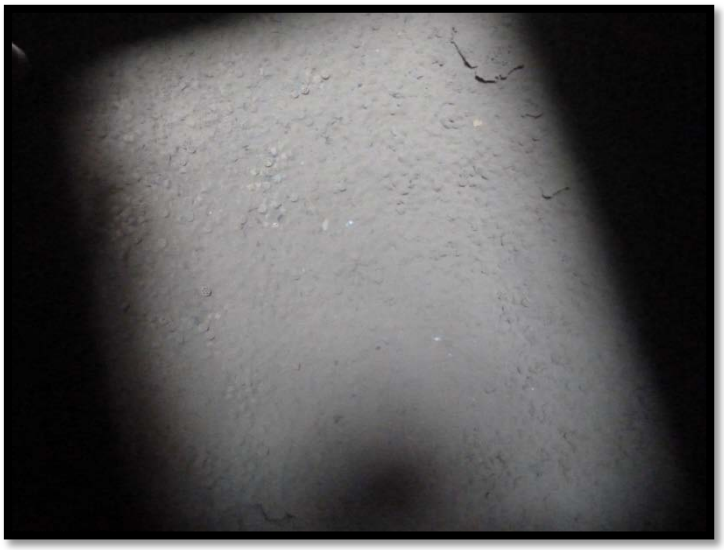

Figure 7 - The photo shows a layer of FeS dust covering the top of the first catalyst bed in a kerosene/diesel hydrotreater which shuts down every 3 to 12 months due to pressure drop built-up. The refinery runs high acid crude so corrosion produces soluble Fe in the kerosene

3.6. Arsenic

Shale oil feedstocks contain arsenic (As) in the tens to hundreds of wtppb range. Arsenic must be removed by sorbent because it is a severe poison of hydrotreating catalyst. Topsoe has a high nickel content sorbent specifically designed for As removal. The catalyst at 300°C achieved As/Ni molar uptake can be higher than 0.7 (equivalent to 15 wt% As uptake on fresh catalyst).

3.6.1. The impact of arsenic on catalyst selection

Arsenic must be removed by sorbent because it is a severe poison of hydrotreating catalyst. Approximately 0.5 wt % of As on the catalyst results in 30% loss in activity. Even though nickel is known to effectively capture the arsenic present in the feed by forming NiAs, the challenge with this type of catalyst is primarily to let the oil have access to all the nickel through the catalyst pore system

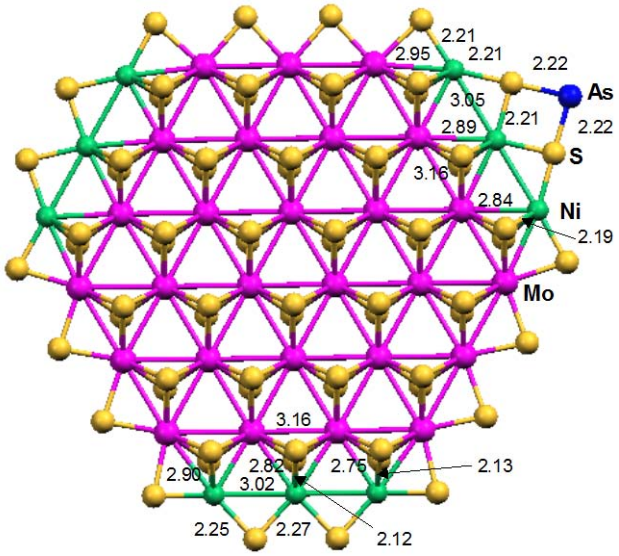

Figure 8: Titrates the active catalyst sites by forming NiAs or CoAs

This is why the refinery needs to have an effective guard on the top of the reactor in order to protect the downstream catalyst from premature As poisoning. Normally As sorbent at 300°C achieved As/Ni molar uptake can be higher than 15 wt% As uptake on fresh catalyst.

3.7. Aromatics and micro-concarbon value

Hydrotreating and hydrocracking of highly aromatic feeds with high concarbon require relatively high pressure, especially at high level of hydrocracking conversion. Higher pressure improves the aromatic saturation rate, shifts the aromatics saturation equilibrium to allow higher aromatics conversion, and decrease catalyst deactivation rate by suppressing heavy polyaromatics (HPNA) formation. A feed with a high aromatics content will consume more hydrogen, thus requiring a large recycle gas circulation rate.

3.8. Nitrogen

Organic nitrogen is a strong inhibitor for hydrotreating and hydrocracking catalyst activity and can increase catalyst deactivation rate. When the organic nitrogen is converted to NH3, the NH3 also inhibits hydrocracking catalyst activity but not to the same degree as organic nitrogen and it will not cause permanent deactivation (the activity recovers when NH3 is stripped from the catalyst).

The problem of nitrogen compound inhibition has received considerable attention because the effects influence both process and catalyst development. Organic nitrogen compounds have a significantly negative kinetic effect on hydrotreating reactions like hydrodesulfurization (HDS), on other hydrogenolysis reactions and on hydrogenation reactions.

The nitrogen compounds present in the oil can be divided into basic and non-basic compounds. Basic nitrogen compounds are unfortunately strong inhibitors for the HDS reaction.

The consequence of introducing organic nitrogen to the catalyst is a reduction in conversion and liquid volume yields. The increase in operating temperature to maintain conversion reduces the cycle length and may affect the product quality in a negative way, mainly by increasing the products density.

There are two different reaction pathways, both of which are important for the removal of S compounds: the direct sulfur extraction pathway and the hydrogenation pathway.

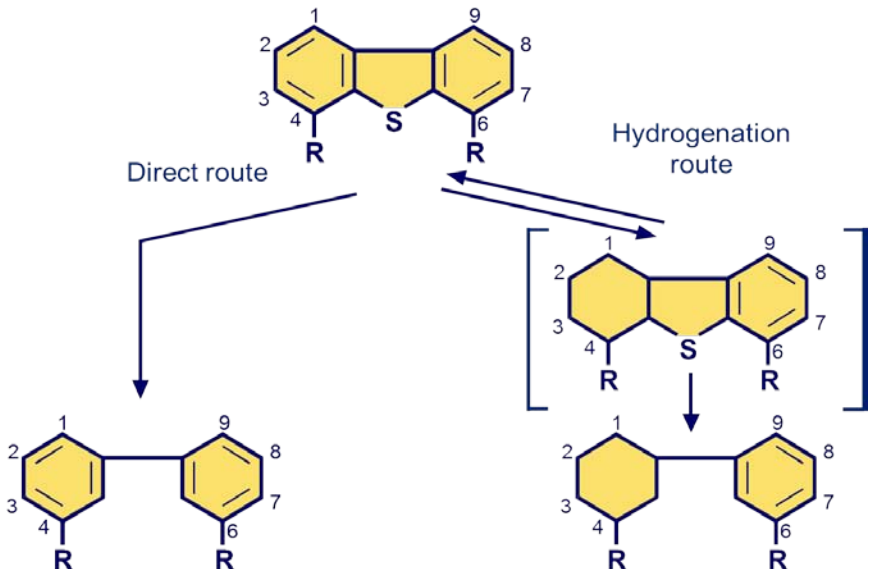

Figure 9: HDS Reaction pathways

Nitrogen is a strong inhibitor of the desulfurization reactions, and therefore the nitrogen content in the feed is a very important parameter.

The hydrogenation route is inhibited by nitrogen compounds (and in particular basic nitrogen compounds). So when the specific basic nitrogen compounds are removed, the fast hydrogenation route will predominate.

In the presence of specific basic nitrogen compounds, the slow direct route will predominate.

The inhibition effect was found to correlate with the proton affinity of the nitrogen compounds; this result also suggests that different sites are involved in the hydrogenation route and the direct route.

4. Conclusions

It can be concluded that more attention is needed in the analysis of the contaminants and general properties of the feed in order to make the best selection of the catalyst when processing shale oil feeds. The main challenge optimizing the operation of the unit is to take into account the higher amount of nitrogen, olefins and the presence of oxygen that include a new reaction to pay attention in the hydroprocessing reactor. As developed above, this means that catalyst systems to process shale oil feeds should have more focus in trapping contaminants and controlling the exotherm.

The optimal selection of the catalyst system for this type of feeds will derived in a longer cycle length of the unit and a more stable operation which means higher margins for the refinery.

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