HYDROCARBON
PROCESSING

Innovative solutions for processing shale oils

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New monitoring protocols can provide advance warning of any negative aspects of shale oil processing, thus enabling the refiner to take corrective measures early.

Keywords:

The refining of shale oil (also known as tight oil) extracted through fracturing from fields such as Eagle Ford, Utica and Bakken has become prevalent in many areas of the US. Although these oils are appealing as refinery feedstocks due to their availability and low cost, processing can be more difficult.

The quality of the shale oils is highly variable. These oils can be high in solids with high melting point waxes. The light paraffinic nature of shale oils can lead to asphaltene destabilization when blended with heavier crudes. These compositional factors have resulted in cold preheat train fouling, desalter upsets, and fouling of hot preheat exchangers and furnaces. Problems in transportation and storage, finished-product quality, as well as refinery corrosion, have also been reported. Operational issues have led to cases of reduced throughput and crude unit shutdowns. The problems encountered with shale oil processing and possible prediction and control strategies will be presented.

NEW RESOURCES

The production of shale gas and oils has increased rapidly due to significant advancements in drilling technology and hydraulic fracturing. Coupling chemical treatments to the mechanical drilling capabilities has enabled increased production efficiency.

In September 2012, shale oil production was reported to be nearly 1 million bpd (1 MMbpd). The most prolific production locations are in North Dakota (Bakken), Texas (Eagle Ford), Ohio, Pennsylvania (Marcellus and Utica), Colorado, Kansas, Nebraska and Wyoming (Niobrara). Other locations identified for probable shale oil production are in New Mexico, Oklahoma and Utah. By 2020, production will be at least 10 MMbpd, based on expanded drilling activity, as shown in **Fig. 1.**[1] The predictions are largely dependent on the volatility of oil prices, technical advancements, capital expenditure, infrastructure needs, and challenges associated with the processing of these abundant resources.

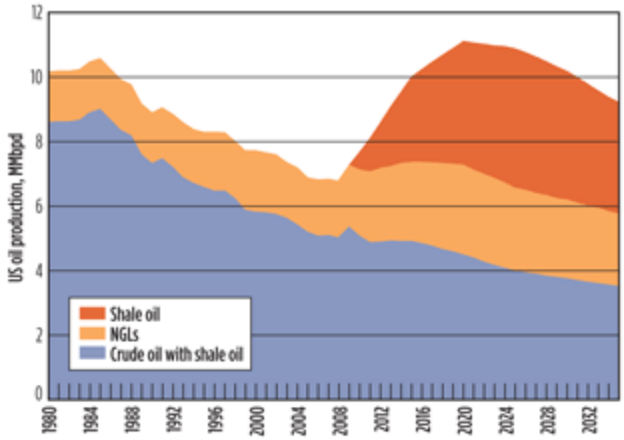

Fig. 1. Forecast prediction of US oil production. Source: EIA.

The properties of shale oils are significantly different than typical crude oils. As a result, a series of challenges needs to be solved to ensure uninterrupted transportation and refining of shale oils. The main challenges encountered with these feed streams will be discussed, including issues in storage, transportation, refining and finished fuel quality.

PHYSICAL AND CHEMICAL CHARACTERISTICS

Unlike most crude oils, shale oils are light, sweet oils, with a high paraffinic content and low acidity. They also have minimal asphaltenic content phase and varying contents of filterable solids, hydrogen sulfide (H_2S) and mercaptans. **Table 1** is a comparison of the oil characteristics typical for shale oil, and it includes data for Eagle Ford and Bakken shale oils.[2] There are significant differences in the sulfur content and the filterable solids loading. In addition, the streams from a shale oil production region can have significant variability, as shown in **Fig. 2.** These were shale oil samples from one field, with colors ranging from pale amber to black.

TABLE 1. Eagle Ford and Bakken shale oil property comparison

Parameter	Eagle Ford	Bakken
API	52	40.8
TAN, g KOH/g	< 0.05	0.09
Sulfur, wt%	< 0.2	0.304
Asphaltene, wt%	0.1	0.41
Resin, wt%	1.6	4.95
Filterable solids, PTB	225	76

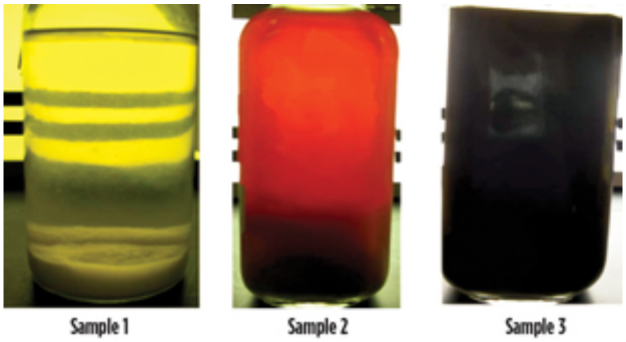

Fig. 2. Color variation of Eagle Ford shale oil.

Solids loading of samples from a single producing region can be highly variable and associated with the stage of fracturing and production from which the oil is produced. **Table 2** shows typical analytical results on the three shale oil samples from **Fig. 1.** Filterable solids ranged from 176 pounds per thousand barrels (PTB) to 295 PTB.

TABLE 2. Physical properties of Eagle Ford shale oil samples

Parameter	Yellow	Red	Black
API	55	44.6	52.3
TAN, g KOH/g	< 0.05	0.07	< 0.05
Sulfur, wt%	< 0.2	< 0.2	< 0.2
Na, ppm	1	1.6	1.6
K, ppm	0.3	0.4	0.5
Mg, ppm	3.4	2.9	3
Ca, ppm	2.6	2.8	3.8
Asphaltenes, wt%	0	0	0.1
Resin, wt%	0.5	3.2	1.6
Filterable solids, PTB	176	295	225

Paraffin. The paraffin content of shale oil is one of the main properties that contributes to downstream problems from transportation and storage to refinery processing. Analyses of one batch of shale oil revealed paraffin chains containing well over 50 carbons. Similar paraffin analyses have been observed from multiple shale oils. To understand fouling due to wax deposition, a carbon-chain profile analysis should be performed to document the molecular-weight distribution (MWD) and the melting points of the waxes in the system. **Fig. 3** illustrates the characterization of waxes from Eagle Ford and Bakken oil samples. Some samples of Eagle Ford shale oil contain over 70 carbon paraffins.

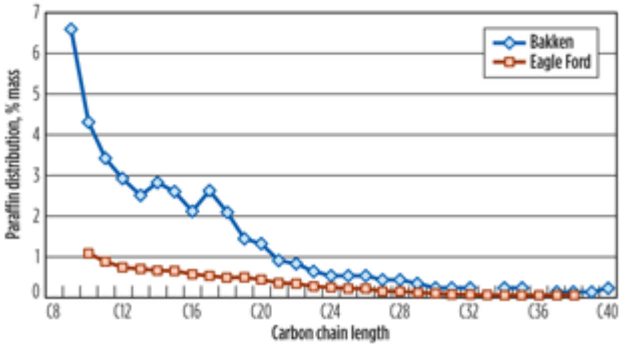

Fig. 3. Paraffin chain distribution for Bakken and Eagle Ford shale oils.

Due to their paraffinic nature, mixing shale oil with asphaltenic oil leads to destabilization of the asphaltene cores. Asphaltenes are polar compounds that influence emulsion stability. Once the asphaltenes destabilize, they can agglomerate, leading to larger macro-molecules. On hot surfaces, agglomerated asphaltenes easily crack or dehydrogenate and gradually form coke-like deposits.

Several shale oil production locations have high H_2S loading. To ensure worker safety, scavengers are often used to reduce H_2S concentrations. The scavengers are often amine-based products-—methyl triazine, for instance—that are converted into mono-ethanolamine (MEA) in the crude distillation unit (CDU). Unfortunately, these amines contribute to corrosion problems in the CDU. Once MEA forms, it rapidly reacts with chlorine to form chloride salts. These salts lose solubility in the hydrocarbon phase and become solids at the processing temperatures of the atmospheric CD towers and form deposits on the trays or overhead system. The deposits are hygroscopic, and, once water is absorbed, the deposits become very corrosive. These physical properties are responsible for the problems that are being experienced by refineries handling shale oils.

Extraction and production

The challenges associated with the production of shale oils are a function of their compositional complexities and the varied geological formations where they are found. These oils are light, but they are very waxy and reside in oil-wet formations. These properties create some of the main difficulties associated with shale oil extraction. Such problems include scale formation, salt deposition, paraffin wax deposits, destabilized asphaltenes, corrosion and bacteria growth. Multi-component chemical additives are added to the stimulation fluid to control these problems.

Shale oils are characterized by low-asphaltenic content, low-sulfur content and a significant MWD of the paraffinic wax content. Paraffin carbon chains of C10 to C60 have been found, with some shale oils containing carbon chains up to C72. To control deposition and plugging in formations due to paraffins, the dispersants are commonly used. In upstream applications, these paraffin dispersants are applied as part of multifunctional additive packages where asphaltene stability and corrosion control are also addressed simultaneously.

Scale deposits of calcite, carbonates and silicates must be controlled during production or plugging problems arise. A wide range of scale additives is available. These additives can be highly effective when selected appropriately. Depending on the nature of the well and the operational conditions, a specific chemistry is recommended or blends of products are used to address scale deposition.

Storage and transportation

Another challenge encountered with shale oil is the transportation infrastructure. Rapid distribution of shale oils to the refineries is necessary to maintain consistent plant throughput. Some pipelines are in use, and additional pipelines are being constructed to provide consistent supply. During the interim, barges and railcars are being used, along with a significant expansion in trucking to bring the various shale oils to the refineries. Eagle Ford production is estimated to increase by a factor of 6—from 350,000 bpd to nearly 2 MMbpd by 2017; more reliable infrastructures are needed to distribute this oil to multiple locations. Similar expansion is estimated for Bakken and other shale oil production fields.

The paraffin content of the shale oils is impacting all transportation systems. Wax deposits have been found to coat the walls of railroad tank cars, barges and trucks. Waxy deposits in pipelines regularly require pigging to maintain full throughput. Bakken shale oil is typically transported in railcar, although pipeline expansion projects are in progress to accommodate the long-term need. These railcars require regular steaming and cleaning for reuse. Similar deposits are being encountered in trucks being used for shale oil transportation. The wax deposits also create problems in transferring the shale oils to refinery tankage. **Fig. 4** shows samples of deposited wax collected from pigged pipelines in shale oil service.

Fig. 4. Waxy deposits removed from shale oil pipelines.

Multiple chemical and mechanical solutions are used to mitigate these deposit problems. A combination of chemical-additive treatment solutions involving paraffin dispersants and flow drag-reducer technologies has proven to be effective in pipeline applications. Wax dispersants and wash solvents have been used to clean transportation tanks and refinery storage vessels. In the case of pipeline fouling management, a combination of these technologies, coupled with frequent pigging, are the main means to mitigate wax deposition. Preventive fouling control programs have been developed to manage the wax deposition occurring in storage tanks. By injecting the proper chemical treatment to control wax buildup in storage tanks, the production field and refinery can handle and transfer larger quantities of oil without significant plugging issues.

One other problem encountered in storing and transporting shale oils is the concentrations of light ends that accumulate in the vapor spaces, requiring increased safety and relief systems. Shipping Bakken crude via barges was challenged by the increased levels of volatile organic compounds (VOCs). Vapor-control systems should be used to ensure a safe environment.

Due to the paraffinic nature of shale oils and their lack of heavy bottoms, most refineries mix crude oil with the shale oil. Unfortunately, the shale oils have low aromatic content, so mixing with conventional crude oil often leads to asphaltene destabilization. If blended oils are transported, the deposits can consist of waxes and precipitated asphaltenes. Dispersants specifically designed for both hydrocarbon types can control deposit formation during transportation. Until a proper transportation infrastructure is built, significant variation of shale oil shipments and potential for contamination are still possible. Refineries are already experiencing the impact of the quality variation of shale oil feeds, and of processing challenges.

REFINERY IMPACTS

Due to the variation in solids loading and their paraffinic nature, processing shale oils in refinery operations offers several challenges. Problems can be found from the tank farm to the desalter, preheat exchangers and furnace, and increased corrosion in the CDU. In the refinery tank farm, entrained solids can agglomerate and rapidly settle, adding to the sludge layer in the tank bottoms. Waxes crystalize and settle or coat the tank walls, thus reducing storage capacity. Waxes will stabilize emulsions and suspend solids in the storage tanks, leading to slugs of sludge entering the CDU. Waxes will also coat the transfer piping, resulting in increased pressure drop and hydraulic restrictions.

Mixing asphaltenic crude with paraffinic shale oils leads to asphaltene destabilization that contributes to stable emulsions and sludge formation. To control these problems, wax-crystal modifiers or paraffin dispersants can be applied successfully. Wax-crystal modifiers must be added when the shale oil is still hot from the formation. When the paraffins begin to leave the liquid phase, wax modifiers are ineffective, and paraffin dispersants are required to control deposition.

Desalter operations may suffer from issues related to the shale oil properties. Solids loading can be highly variable, leading to large shifts in solids removal performance. Sludge layers from the tank farm may cause severe upsets, including growth of stable emulsion bands and intermittent increases of oil in the brine water. Agglomerated asphaltenes can enter from storage tanks or can flocculate in the desalter rag layer, leading to oil slugs in the effluent brine.

Solutions include using tank farm additives to control the formation of sludge layers, along with specially designed asphaltene dispersants and aggressive desalter treatments to ensure optimum operation. Pretreatment, coupled with high-performance desalter programs, have provided the best overall desalter performance and desalted crude quality; multiple treatment options for both areas can ensure maximum performance. **Fig. 5** is an example of applying a tank pretreatment. A crude-oil tank treatment program was initiated that broke waxy emulsions in tankage, enabling improved water resolution of the raw crude oil and minimizing sludge and solids entering the desalter. This program provided significant improvement of solids released into the desalter brine water compared to previous operations. Prior to initiating the pretreatment program, solids in the brine averaged 29 PTB, and the emulsion band control was sporadic. After the tank pretreatment program started, the desalter emulsion band could be controlled with the emulsion breaker program, and solids removal to the brine water increased by a factor of 8 to an average of 218 PTB.

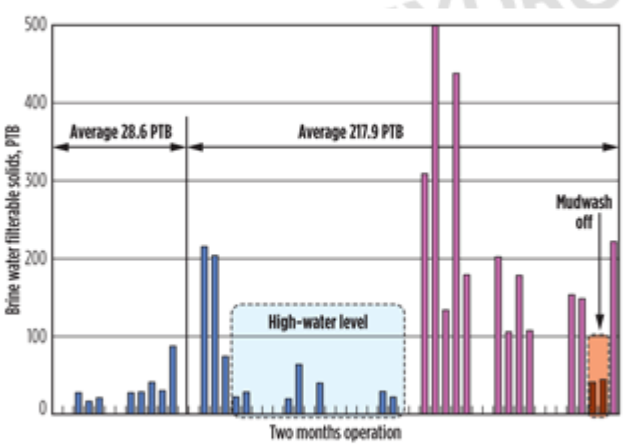

Fig. 5. Tank pretreatment impact on desalter filterable solids.

Preheat exchanger fouling has been observed in the cold train before the desalters and in the hot train after the desalters. Cold train fouling results from the deposition of insoluble paraffinic hydrocarbons, coupled with agglomerated inorganic solids. Solutions to cold train exchanger fouling include the addition of wax dispersants and other oil management best practices to ensure consistent solids loading with minimum sludge processing.[a] Crude oil management can include additives to stabilize asphaltenes and surfactants that resolve emulsions and improve water separation.[a] These practices also include proactive asphaltene stability testing to ensure that the crude blends to be processed retain an acceptable compatibility level.

Hot train fouling occurs from destabilized asphaltenes that agglomerate and form deposits. These materials entrain inorganics, such as iron sulfide and sediments from production formations, into the deposit matrix. Some deposits, including high molecular-weight paraffins, become complex with the asphaltene aggregates. Mixing shale oils with asphaltenic crude oils results in rapid asphaltene agglomeration. Rapid hot train exchanger fouling has been seen in units running crude blends with asphaltene concentrations of 1% or less. **Table 3** shows the analysis from a hot exchanger deposit that had to be shut down for cleaning after only a short time online. This hydrogen-to-carbon ratio is consistent with asphaltenic deposits.

TABLE 3. Hot train exchanger deposit analyses of shale oil with asphaltenic crudes in wt%

Sample	C	H	N	O	Cl	Fe	S	H/C atomic ratio	Ash	Summary
Exchanger 1-crude side	82	8	1	2	1		6	1.16	1	Asphaltenes
Exchanger 2-crude side	78	7	1	4	1	1	8	1.07	3	Asphaltenes
Exchanger 3-crude side	81	8	1	2	1		7	1.18	3	Asphaltenes

Feed analyses of the shale oil and crude blend being processed revealed poor stability of the asphaltenes. Asphaltene stability tests are used to measure the ability of a crude oil blend to hold asphaltenes in solution.[3, a] The method utilizes light scattering, coupled with automatic titration, to force asphaltene destabilization and agglomeration.

As titration begins, the oil becomes less opaque and the light intensity increases. When the destabilization point is reached and the asphaltenes rapidly agglomerate and flocculate, the fluid opacity suddenly increases. Inflection points on the curve show where asphaltenes become unstable: farther to the right indicates higher stability asphaltenes, while inflection points farther to the left suggest unstable asphaltenes. **Fig. 6** shows asphaltene stability results for several crude blends, along with a test on Eagle Ford shale oil. An inflection point was not achieved for the shale oil because it has no asphaltenes to flocculate. Typical crude oils are shown, with asphaltene stability index (ASI) results around 120. When the shale oil was blended with the typical crude oils at a ratio of 80/20, the measured asphaltene stability result was less than 30, indicating rapid and uncontrollable destabilization of the asphaltenes.

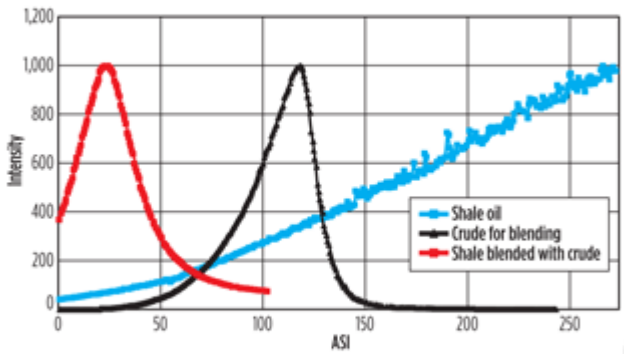

Fig. 6. Asphaltene stability index testing of shale oil and shale oil/crude blends.

If the asphaltenes in the crude blend were not being rapidly destabilized, the asphaltene stability would have been well above 120. This data shows that mixing certain crude oils with shale oil can result in rapid asphaltene deposition. New technology can provide the capability to rapidly perform asphaltene stability measurements onsite with a high degree of accuracy.[4, a]

Hot-train exchanger fouling can be controlled through antifoulant additives designed to control the agglomeration and deposition of asphaltenes and entrained inorganic solids. Another fouling control strategy is to do regular analysis of the stability of the asphaltenes in the crude oil blend under consideration for processing. This information can guide operations to minimize fouling problems.

CDU atmospheric furnace fouling has also been observed at several refineries processing shale oils, especially those processing a blend of asphaltenic crude and shale oils. In some cases, the fouling rate was so severe that the crude unit had to be shut down for furnace pigging. CDU furnace operations with conventional crude oils experience little to no fouling, and these furnaces can easily run for 5 to 6 years between turnarounds. **Fig. 7** shows the rate of fouling in a unit processing a mixture of shale oil with crude vs. the rate of fouling with more typical crude feeds.

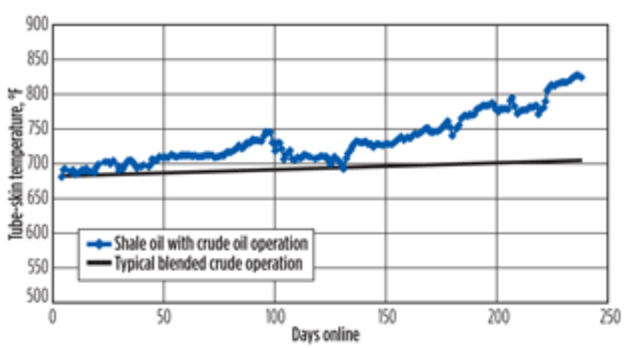

Fig. 7. Atmospheric furnace skin temperature trends.

Depending on the asphaltene stability of the shale oil/crude oil blend, the furnace skin temperatures can climb by 0.5°F/day to 2°F/day vs. more typical operations of 0.1°F or less. To control furnace fouling when processing shale oils blended with various crude oils, constant monitoring of the asphaltene destabilization potential is required.

Setting a minimum limit on the ASI ensures that the majority of the asphaltenes stay in solution. This limit should be developed for each unit, based on correlations between the rate of furnace fouling being experienced and the stability index. Using appropriate antifoulant additives can control agglomeration of asphaltenes and disperse offending materials into the bulk oil phase.

Shale oils often contain high concentrations of H_2S that require treatment with scavengers due to safety purposes. Amine-based scavengers often decompose as the crude oil is preheated through the hot preheat train and furnace, forming amine fragments. MEA, one of the most commonly used amines, readily forms an amine-chloride salt in the atmospheric tower. These salts deposit in the upper sections. Often, under-deposit corrosion is the major cause of failures in process systems because CDU tower under-salt corrosion rates can be 10 to 100 times faster than a general acidic attack. Mitigation strategies include controlling chloride to minimize the chloride traffic in the tower top and overhead, increasing the overhead operating temperature so that the salts move further downstream in the overhead system, and acidifying the desalter brine water to increase removal of amines into the water phase.

Finished fuels

The quality of the finished fuels from refining shale oils has changed significantly. As the shale oils have higher light-ends content, one benefit is increased production of naphtha for gasoline, and stable diesel and jet distillates. These increased volumes can boost refinery margins. However, due to the chemical nature of these shale oil feeds, several challenges can be encountered. The streams are more paraffinic—thus, they suffer from poor pour and cloud-point properties. In addition, shale oils are lower in sulfur content, so the need for lubricity additives is anticipated. Effective additives can be used to improve all distillate stream properties. Conductivity can also be off-spec; a combination of lubricity/conductivity improvers can raise the quality of the distillate. To optimize chemical treatment program, testing on specific product streams is required and suitable product selection should be customized. **Table 4** summarizes the main issues identified for different distillate cuts that a refiner can experience as well as chemical and mechanical solutions that can mitigate these challenges.

TABLE 4. Possible problems and solutions for finished fuels from shale-oil processing

Distillate	Challenge	Solutions
Light ends (C_3–C_4)	Copper strip corrosion	Corrosion inhibitors
Naphtha	Water shedding, corrosion	Corrosion inhibitors, microbial control
Jet fuel	Lubricity, conductivity, water shedding, stability	Various lubricity additives, filtration devices, dry solid systems, microbial control
Diesel	Lubricity, conductivity, stability, water shedding	Various lubricity additives, de-hazers, microbial control
Residual fuel oil	Asphaltene instability, gum deposits	Blending and compatibility monitoring Asphaltene stabilizers Paraffin dispersants

Preparing to process shale oils. The risks that shale oils present can be successfully managed. The first step is to identify the onset of all concerns. To be prepared for processing shale oils, monitoring protocols can provide advance warning of any negative aspects of shale oil processing and the impacts on product quality, thus enabling the refiner to take corrective measures early. **HP**

ACKNOWLEDGMENT

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NOTES

[a] CRUDE OIL MANAGEMENT, ASIT and FIELD ASIT SERVICES are trademarks of Baker Hughes Incorporated.

LITERATURE CITED

[1] US Energy Information Administration, *Shale Plays Report,* May 9, 2011.
[2] Kremer, L., "Shale Oil and Solutions," COQA Meeting, November 2012.
[3] Stark, J. L. and S. Asomaning, "Crude Oil Blending Effects on Asphaltene Stability in Refinery Fouling," *Petroleum Science and Technology,* Vol. 21, Nos. 3 & 4, 2003.
[4] Sandu, C. and T. Falkler, "New Field Tool Helps Refiners Detect Incompatible Feedstocks, Prevent Operational Problems," ERTC 2012.

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Charles Harry
07.19.2013

The addition of mbp needs or usage would be useful relative to Fig.1 in regards to why there is an ongoing large increase in shale oil production followed by it gradual decline.

Peter LoGiudice
07.10.2013

Excellent well thoughtout overview-Thanks

Joseph
07.03.2013

What will be the typical Calorific Value of Shale oil in Kcal/ Kg? C/H2 Ratio
Any estimation of Metal Contents like Vanadium, Na, Si etc