# Economic Bottom of the Barrel Processing To Minimize Fuel Oil Production

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The recent years have been marked by global uncertainties ranging from economic to geopolitical. These uncertainties have resulted in a steep rise in crude prices affecting worldwide refinery operations. Faced with the burden of skyrocketing feedstock prices and uncertainty of supplies, refiners are much more conscious of these issues than in years past. As feedstock prices play a crucial part to the profitability of refiners the natural thought is to find ways to process less expensive crude oils. As crude prices increase so does the cost for refiners to bring in feed to process at the refinery. There are around 160 types of crude oils being produced worldwide and the price differentials between crude oils can be $15 /barrel or higher. Refiners find themselves faced with the difficult question of searching for crude blends to maximize the use of their existing assets or to choose crude blends, which will require additional capital investment but will offer opportunity to increase return on investment.

In parallel to this phenomenon, there is another challenge, which has developed through the years. As the world recognizes the benefits of using natural gas as fuel, demand for fuel oil has seen a drop, adversely affecting fuel oil prices. This in turn has weakened the economics of those refiners with limited fuel oil outlets, and has reached a level where changes are needed.

These are the major factors driving refiners to look at ways to process alternative lower costs crude oils, and the primary cause of the wave of interest in bottom of the barrel solutions. Most refineries will need to install new units using either carbon rejection or / and hydrogen addition technologies to convert fuel oil into more valuable products. Many of the traditional solutions will result in capital intensive projects. With coke disposal being a problem for certain refiners and the high cost of hydrogen consumption becoming an increasing burden, refiners often wonder what other alternatives they may have.

## TWO CRITICAL ISSUES: CRUDE OILS & FUEL OIL

As security of supply and rising crude prices are becoming greater concerns, refiners' attention turn to less traditional crude oils. As crude price differentials also continue to widen due to the direct link of supply shortage & demand increase, refiners see in less traditional crude oils another venue to maximize margins; but how to get there is the key question. These crude oils could be high in Sulfur, low in API, containing high Total Acid Number (TAN). Production of less traditional crude oils is also on the rise.

The net result of processing a higher volume of heavy or extra heavy crudes in the refinery diet is an increase in Vacuum Residue (VR) volume and a decrease in feed supply to the existing conversion units.

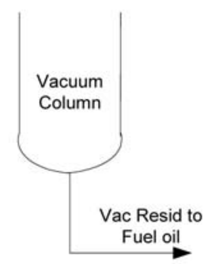
The disposition of this high sulfur fuel oil will become difficult due to new environmental requirements. Moreover, with the decline in fuel oil demand and the natural gas switch, fuel oil pricing could continue to drop in the long run.

The best projects of the future should not only allow processing of less expensive, opportunistic crude oils but should be able to reduce fuel oil make without compromising refinery reliability. In order to meet the above objectives the new projects may include some or all of the following elements:

- Allow shift to less expensive heavier, sour crude oils and other opportunity crude oils.
- Convert all or a high percentage of fuel oils, particularly high sulfur fuel oil, into more valuable products.
- Reduce processing cost by using more optimized processing scheme.
- Reduce utility costs and keep emissions low.

## TYPICAL RESIDUE PROCESSING CONFIGURATIONS

**Simple Refinery**




Representative of many Indian refineries, these do not include any conversion or upgrading facilities for the bottom of barrel streams. The entire vacuum residue (VR) is typically disposed off by blending into high sulfur fuel oil product. When available, decant and cycle oils from fluid cracking units, unconverted oil from hydrocrackers, heavy gas oils, etc. can be used as cutter stocks to produce a high sulfur fuel oil. Sometimes even higher value distillates have to be blended into fuel oil to meet viscosity specifications.

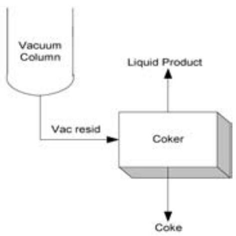
Fuel oil producers will also find it difficult to sell large volumes of high sulfur fuel oil as new regulations have already been introduced which limit sulfur in fuel oil. These refineries typically look for the addition of cost effective residue upgrading options.

Some of the potential technologies that are available to the refiner for achieving the above goals are as follows.

- Technologies that reject carbon:
  - Solvent deasphalting (ROSETM) and Pelletizer (AQUAFORMTM)
  - Thermal cracking processes (coking, thermal cracking, & visbreaking)
- Technologies that add hydrogen:
  - Fixed bed hydrotreating / hydrocracking
  - Ebullated bed hydrotreating / hydrocracking
  - Fluidized bed hydrocracking

All of the above technologies except the fluidized bed hydrocracking are well established and are in use today. This paper will focus on the ROSE and AQUAFORM technology option, the effects of the DAO on FCC and the options for the disposition of Asphaltenes.

### Carbon Rejection



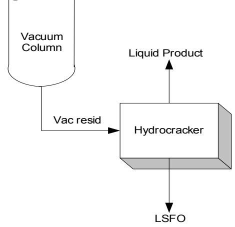

Delayed coking is the most commonly used carbon rejection process. Roughly half of the US refineries have cokers. Visbreaking and thermal cracking are less severe thermal processes than delayed coking and more popular in Europe. Thermal cracking is normally used for cracking distillates. Visbreaking is used for reducing viscosity of residue by thermal cracking. These refineries include visbreaking/thermal cracking operations to reduce requirements for cutter stock for blending into fuel oil.

In delayed coking, VR feed can be typically cracked up to 65-80% with 20-35% of the feed being rejected as low value petroleum coke. The liquid products are further converted into transportation fuels while gas products are used as fuel.

The cokers are capital intensive, require large real estate, and will produce hydrogen deficient product streams that would require hydrogen addition prior to being blended in to the product streams or processed in the existing reformers and FCC units.

In refineries with no FCC pretreatment, a significant debit in FCC performance will occur. In general, a negative impact on existing secondary processing units — hydroprocessing, FCC, reformer, sulfur plant and amine system will occur.

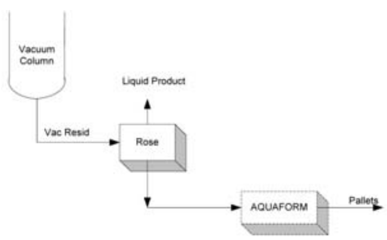
### Hydrogen Addition




Vacuum residues can be hydrotreated or even hydrocracked using either fixed bed or more typically in an ebullated bed reactor. The high metal content of the VR require use of guard beds or one of the online catalyst removal / addition systems to achieve long runs. Unfortunately both options significantly increase capital and operating costs.

The ebullated bed reactor designs include provision for online catalyst addition and removal. Resid hydroprocessing units are generally very expensive and require significant plot space. The products from the ebullated bed units normally require further treating in fixed bed reactors. In most of the cases upgrading the heaviest portion of the residue through hydrogen addition will consume large amounts of hydrogen and catalysts, and the incremental benefits derived will not justify the incremental investment requirements.

## SOLVENT DEASPHALTING WITH PELLETIZATION




The option to use Solvent Deasphalting in combination with the generation of solid fuels is a very cost effective means of dealing with atmospheric or vacuum residues and reducing the fuel oil production. Typically 40 -70% of the VR can be economically extracted at a quality suitable for processing in an FCC unit. The pitch can be pelletized for sale as solid fuel in the cement, steel or power industry.

The sulfur or metals content in the feed is attractive to the cement industry, which currently thrives on low BTU coal and petroleum coke fuel sources. Specifically for the Indian market, where the fuel needs for the cement industry are enormous, the partial switch to high BTU asphaltenes represents an attractive synergistic opportunity for both industries.

This paper will focus on the technologies involved highlighting the performance, benefits and limitations for the specific applications under consideration.

### Supercritical Solvent Deasphalting Unit - ROSETM

Solvent extraction was first introduced in the 1930's as a means of extracting paraffinic lube oil blending stocks from mixed base and naphthenic crude oils. After widespread implementation of fluid catalytic cracking, refiners soon recognized the negative impact on FCC yield performance from processing aromatic feed stocks. Recognizing an opportunity soon thereafter, refiners turned to solvent extraction as a means of producing viable high Watson K FCC feedstock from residue that was otherwise too contaminated for economic FCC processing (*see Table 1*).

It was discovered that residual oils could be «decarbonized» with paraffin solvents to produce FCC feeds with sufficiently low concentrations of carbon residue and metals to allow economic processing in the FCC units. In the 1970's, Kerr McKee developed a solvent deasphalting process, the ROSE Process, that separates most of the solvent from the deasphalted oil (DAO) in the supercritical phase regime rather than utilizing energy intensive boil-off and condensation for solvent recovery. The supercritical solvent recovery breakthrough greatly reduced the utilities expense associated with operation of the units, and the ROSE process quickly became the dominant residue deasphalting process. ROSE technology was acquired by The M.W. Kellogg Company in 1995 and now it is part of the refining technology portfolio offered by Kellogg Brown & Root LLC (KBR).

The solvent deasphalting (SDA) process removes asphaltenes from atmospheric and vacuum residues using solvent extraction. Most of metal, sulfur and carbon (Conradson carbon -CCR) is concentrated in

***Table 1 — Watson K for typical FCC feedstocks***

| Feedstock Source | Atm Resid | Vacuum Gas Oil | Propane DAO | Butane DAO | Coker Gas Oil |
|---|---|---|---|---|---|
| Arabian Light | 11.60 | 11.68 | 11.81 | 11.74 | 11.4 |
| Arabian Heavy | 11.44 | 11.62 | 11.86 | 11.78 | 11.4 |

65

the asphaltenes. The deasphalted oil (DAO), which contains very low quantities of metals, low sulfur, and CCR, is an excellent feedstock for processing in conventional refinery units, such as, fixed bed VGO hydrotreaters and the FCC. They can also be processed in high pressure hydrocrackers and thermal cracker units. Typical yield and quality are shown in *Table 2*.

Several SDA units (mostly ROSE units offered by KBR of Houston, Texas) are operating successfully in combination with hydrocrackers, hydrotreaters, and FCC units. This is an important aspect of ROSE units as refiners move towards heavier crude oils. The contaminants, if left in the processing chain, will become the limiting factors of downstream units.

**FCC Feedstock Considerations**

Feed properties that are most important to consider when processing residue in an FCC unit are (1) asphaltenes (C7 insolubles) which cause deactivation of downstream catalyst systems (2) vanadium, which is the controlling parameter setting FCC catalyst make-up rates, (3) carbon residue which is the major factor affecting coke burning and catalyst cooling requirements, and (4) hydrogen content which impacts FCC conversion and yield selectivity.

Atmospheric or Vacuum Residues with lower concentrations of carbon residue and metals, particularly paraffinic, low vanadium crude oils, are naturally better suited to upgrading in FCC units, and often significant volumes of such residues or even 100 percent atmospheric residue can be charged to FCC units with little or no changes to the FCC hardware. However, the availability of these high quality crude oils is diminishing and more contaminated, heavier crude oils are making up an increasing proportion of the worlds crude oil supply.

Even if blended in small concentrations into FCC feedstocks, atmospheric or vacuum residues from lower quality crude oils often contain higher concentrations of metals and carbon residue than would be economic for FCC processing because of the contaminant's impact on required catalyst make-up rate and FCC yields; therefore before processing in the FCC unit, the residues from such crude oils must first be upgraded with such processes as vacuum distillation, coking, residue hydrotreating or solvent deasphalting to reduce carbon residue and metals content.

- While directly processing residue from some high quality crude oils in the FCC unit can be economic, this option is not very flexible with respect to refinery crude oil supply.
- Vacuum distillation can separate vacuum gas oil from atmospheric residue, but vacuum distillation leaves potential FCC feed behind in the vacuum residue.
- Coking eliminates vanadium and carbon residue from its gas oil products but the coker gas oils are hydrogen deficient, resulting in poor yield selectivity when processed in an FCC unit.
- Residue hydrotreating can reduce contaminants to economic levels while increasing FCC feed hydrogen content but the capital and operating costs of residue hydrotreating are high.

ROSE solvent deasphalting separates a less contaminated, hydrogen rich material (DAO) from atmospheric or vacuum residue that can be economically cracked in an FCC unit, mitigating issues associated with the processing schemes described above. The increased hydrogen content and lower contaminants of the DAO relative to the residue together with low investment and operating costs often makes ROSE an economical option for producing good quality FCC feed from residue.

It is interesting to note that the contaminants that are most detrimental to the FCC unit operation are also the ones that show the sharpest partitioning in the ROSE unit. e.g. metals > carbon residue > nitrogen > sulfur, resulting in a natural synergy between these processes.

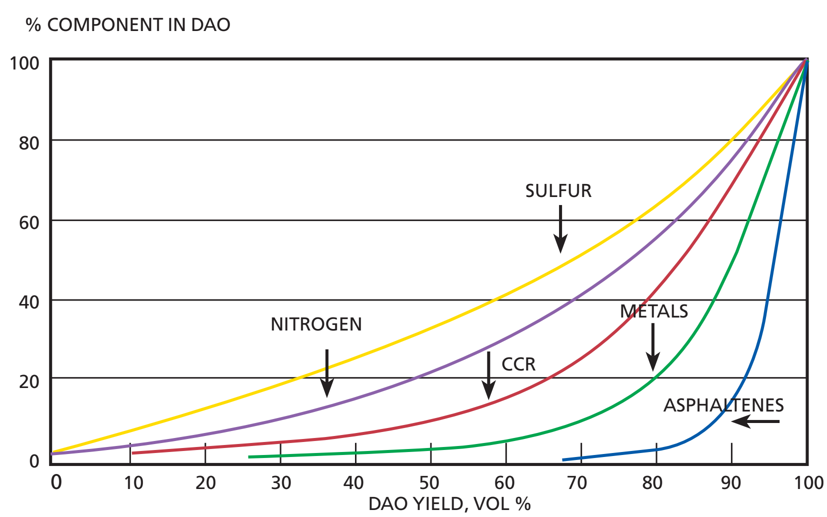
The contribution of DAO and CGO added to VGOs is shown in Table 3. For the same operating

***Table 2 – ROSE Yields and Qualities***
***Feed: Middle East Vacuum Residue***

| | VR Feed | Asphaltene | DAO |
|---|---|---|---|
| Yield, wt% | 100 | 51 | 49 |
| SG, at 15.5oC | 1.043 | 1.118 | 0.974 |
| Sulfur, wt% | 5.7 | 7.3 | 4.0 |
| Conradson carbon, wt% | 23.8 | 40.0 | 6.6 |
| Nickel+Vanadium, ppmw | 222 | 425 | 11 |
| C7 Insolubles | | | <100 ppmw |
| Watson K | | | 11.71 |

***Table 3 – FCC Yields from VGO, DAO and CGO***

| | 100% DAO | 100% VGO | 100% CGO |
|---|---|---|---|
| API<br>Sulfur, WT% | 19.2<br>0.79 | 24.7<br>0.75 | 19.0 |
| CCR, wt% | 3.9 | 0.39 | Less than 1 |
| NI + V, PPM | 16 | 1 | Less than 1 |
| FCC Yields, WT% | | | |
| Conversion | 80.3 | 81.05 | 63.2 |
| C2- | 4.86 | 3.65 | 1.49 |
| Total C3's | 6.37 | 6.80 | 4.60 |
| Total C4's | 10.30 | 11.76 | 8.87 |
| Total Gasoline | 48.98 | 52.12 | 40.16 |
| Total Cycle Oil | 19.70 | 18.95 | 35.78 |
| Coke | 9.79 | 6.72 | 6.0 |



severity, the conversion, yields, and product quality from processing VGO and DAO are about the same. A very interesting observation is the CCR content of the DAO; an equivalent CCR in the VGO would have made this an unacceptable FCC feed; but not so for DAO. This obviously confirms that coke precursors in the FCC feed are obviously better correlated by asphaltene concentration as opposed to the coarser determination of carbon residue by Conradson Carbon measurement method.

## ASPHALTENE UTILIZATION

Economic utilization of the asphaltene product from a ROSE unit is the key to ROSE process economics. Listed below are some of the options refineries are utilizing to maximize the value of ROSE asphaltene product followed by a discussion of each option, with special emphasis on solid fuels which we believe will be very attractive for the Indian market.

- Fuel oil blend component
- Specialty commercial asphaltenes
- Conversion (coker) feedstock
- Partial oxidation feedstock
- Solid fuel

### Asphaltene Product to Fuel Oil

It is sometimes possible to burn the asphaltene product directly as fuel oil, but in most cases, it is first blended with other low-value streams to produce a lower viscosity product that meets fuel oil specifications. The fuel oil production can often be cut to less than half by installing a ROSE unit and blending asphaltenes instead of vacuum residuum into fuel oil.

Some refiners blend the asphaltenes with distillate materials to produce No. 6 fuel oil. Light cycle oil and slurry oil from the FCCU makes excellent blending stocks because of their high aromatic content. A visbreaker can be used to reduce the viscosity of the asphaltene and thus reduce the required amount of blending stock. However, the high sulfur content of the asphaltene may limit its use in No. 6 fuel oil production.

Asphaltene quality depends on crude slate, and as the crude slate becomes heavier and more sour, the asphaltene produced from these crude oils will also contain a higher quantity of sulfur. Environmental regulations will therefore dictate how much flue gas cleanup is required and, hence, the viability of direct firing burning of asphaltenes.

### Commercial Asphaltenes

Specialty products, such as paving asphalt or roofing asphalt, can be made by blending the ROSE asphaltenes with suitable aromatic oils.

### Asphaltene Coking

Asphaltenes may be successfully coked in refineries with existing cokers. Many refiners are now successfully cracking asphaltenes in their cokers. Normally asphaltene is blended with vacuum residuum to achieve good flow properties. The blend is then cracked in cokers. Asphaltene cracking is being carried out by both delayed and fluid coker operators. Cracking ROSE asphaltene instead of vacuum residuum reduces total coke make by 10-20%. The liquid yield also improves. At the 2003 NPRA, some refiners have reported the use of more than 50 percent asphaltenes in their coker feedstocks.KBR has processed asphaltene in the coker pilot plant. Typical pilot plant yields from coking the asphaltenes are provided in *Table 4*.

Note that the coke yield is much less than would be expected from a traditional feed with high CCR. The ratio of feed CCR to coke yield is about 1.2 for this feedstock. Lower CCR feedstocks can be expected to have a feed CCR to coke yield ratio of 1.5 to 1.6 under similar conditions.

### Asphaltene to Partial Oxidation Unit

The asphaltene can be fed to a partial oxidation unit to produce synthesis gas. Hydrogen in the synthesis gas can be used for hydroprocessing units. The remaining synthesis gas is fired to produce steam and power. There are presently two ROSE units in operation feeding partial oxidation units and three more planned as the prime outlet for their asphaltene product.

### Solid fuel

*This represents the most simple and cost effective option for asphaltene disposition for the Indian market, where a large demand for high BTU solid fuel exists.*

The heating value, organic carbon and chemical properties such as sulfur, nickel and vanadium are governed by the feed properties. The asphaltene pellets can be used



*Table 4 - Data from KBR Delayed Coker Pilot Plant*

| Feed | |
|---|---|
| Source | Pentane asphaltene |
| Conradson carbon, wt% | 38 |
| Yields, wt% | |
| Gas | 6.9 |
| C3-C3 | 3.8 |
| C5-205°C | 12.1 |
| 205-343°C | 16.4 |
| 343°C+ | 15.0 |
| Coke | 45.8 |

as solid fuel in the cement kilns, the steel industry, and in the utility industries. The pellets can be added to fuel grade coke or coal as additive to enhance combustion characteristics. The asphaltene pellets have 20%-50% higher heating value than petroleum coke.

The high HGI value of the pellets indicates easy grindability. Unlike coal, the asphaltene pellets have low ash content and high organic carbon content (high boiling hydrocarbons, typically >1000 F) that provide improved combustion characteristics.

In view of the superior heating value, combustion characteristics, ease of grinding, the asphaltene pellets should demand a higher value per ton when compared to fuel grade coke and coal.

## AQUAFORM™

There are existing older commercial technologies to produce solid fuel from the solvent asphaltene. However, these processes are generally high in maintenance, low in reliability and are manpower intensive.

KBR's AQUAFORM technology is an ideal solution to solidify asphaltenes and other heavy hydrocarbons. AQUAFORM is a low cost process, easy to operate, and has a high expected on-stream factor. This unit can process a variety of feedstocks and is self cleaning during shutdown.

The pellets produced by the AQUAFORM process are resistant to dusting and can be easily handled, stored, and transported. The asphaltene pellets have a higher heating value and better fuel properties compared to petroleum coke and thus represent improved fuel value.

A simplified flow diagram for the AQUAFORM process is presented below. Hot liquid asphaltenes are pumped to a pelletizer vessel at the optimal temperature required for successful pelletization. Liquid asphaltenes are converted to droplets in the vapor space of the pelletizer vessel using a proprietary high capacity feed distributor.

The surface hardened pellets fall in to a water bath and on to a vibrating screen where the pellets are dewatered. The pellets may be transported to a silo or pit or other loading facilities by a conveyor.

KBR's proprietary feed distributor is the heart of the system, giving substantial capacity, flexibility, and reliability improvements versus other solidification process technologies. The feed distributor can be adjusted to vary the size of the pellets as well as unit capacity.

The pellets are near spherical with an expected size distribution between 1 and 3 mm and have good grindability, storage and transportation characteristics as indicated by the high Hargrove Grindability Index (HGI), storage test temperature and low friability. The high angle of repose provides high capacity on conveyors. The small amount of residual moisture on the pellets helps to minimize dust formation during transport.

## CONCLUSION

The combination of solvent deasphalting and asphaltene pelletizer technologies represents an economic solution to upgrade vacuum residues and reduce or eliminate fuel oil production that can be implemented at a fraction of the cost of all other resid processing options.

The deasphalted oil is an excellent feedstock and can be easily processed in the existing refinery FCC or other conversion units, and the solid asphaltene pellets can be sold to the cement, steel and power industries.

Since the contaminants (metals, sulfur etc.) are rejected in the solid fuel to the cement industry, there is very minimal impact to the auxiliary units (sulfur plant, amine regeneration etc.) within the refinery.

The Indian refiner and cement producer can benefit enormously from the synergies that exist between the two industries. ■