Anode-grade coke from traditional crudes

A combination of solvent deasphalting and delayed coking is an option to minimise fuel oil production and produce anode-grade coke

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In an era of economic and political uncertainties, refinery margins will continue to be dictated by processing heavier, sourer crudes. The dramatic increase in residuum content from 10% in light sweet crudes to 50% in extra-heavy crudes poses interesting challenges, while presenting some unique opportunities. This is especially true when it comes to producing high-value products from low-value, bottom-of-the-barrel streams.

According to conventional wisdom, the residuum is either removed as fuel oil or asphalt, or subjected to thermal conversion processes for upgrading. Traditional resid upgrading methods include resid fluidised catalytic cracking (RFCC), visbreaking (VB) and delayed coking (DC).

RFCC is a widely used carbon rejection technology to convert high-boiling, high-molecular-weight hydrocarbon fractions to more valuable gasoline, olefinic gases and other products. However, due to the nature of the process, it is limited to processing lighter, low-metals, low-sulphur residues.

Visbreakers are essentially a means of improving the viscosity of the residuum so as to minimise the addition of valuable distillate boiling-range cutter stock to meet fuel oil specifications. As world economics seems to be influenced by the use of natural gas, the production of fuel oil has a negative effect on refinery product slate and economics. This situation is expected only to worsen as refiners face regulatory pressures ranging from new maritime bunker fuel specifications to carbon dioxide cap and trade and carbon footprint limitations. This leaves refineries with the challenge to minimise fuel oil production.

Carbon rejection choice

Residues from heavy crude oils contain high concentrations of sulphur, complex hydrocarbons and heavy metals such as nickel and vanadium. Due to the nature of these residues, delayed coking technology is the most commonly used carbon rejection technology. In addition, it enables the refiner to significantly reduce production of low-value fuel oil. Coking is a thermal cracking process in which, typically, a low-value residual oil, such as atmospheric or vacuum residue (VR), is converted into valuable distillate products and off-gas, leaving behind low-value fuel-grade coke. High-sulphur petroleum coke prices are distressed and, as is evident in Canada, coke is just being piled up in large quantities with no real economic outlet.

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On the other hand, anode-grade coke is in high demand in the electrode industry. The world market for anode-grade coke is projected to be approximately 17–20 million tpa. The high price differential between the two grades, coupled with increasing demand for anode-grade coke, creates an unprecedented need to find an alternate path to improve the economics of coke production while maintaining higher refinery margins.

Production of anode-grade coke is greatly influenced by the sulphur and metal content of the feed or, for all practical purposes, the VR. The volume and quality of the residue is essentially determined by the quality of the vacuum gas oil fraction and the ability to process this fraction through conventional hydroprocessing or catalytic cracking conversion units. In most cases, the limiting factor is the metals content or the Conradson carbon residue (CCR) in the gas oil.

The residue volume and quality is by balance a reject defined by gas oil quality. Furthermore, not much attention has been paid to improving the quality of the residue prior to coking, primarily because of issues associated with the methods used to improve the residue quality.

One approach to reduce the metals and sulphur content of the residuum is hydrotreating. While hydrotreating addresses the sulphur and metals content of the feed, it is an expensive proposition incurring high capital investment due to high operating pressures and high hydrogen consumption with poor catalyst cycle length. In addition, hydrotreating increases the level of saturates in the residuum, which may make it unsuitable for anode coke production because other physical requirements, such as volatile carbonaceous material content, bulk density and grindability, may no longer be met. So, in reality, hydrotreating is not an economic option for residuum upgrading for anode coke production, and is therefore not widely practised.

solvent preferentially extracts paraffinic and resinic molecules, leaving behind asphaltenic products. While solvent deasphalting is primarily an aromatics rejection process, it is also a metals and CCR rejection process. The aromatic molecules that are rejected contain

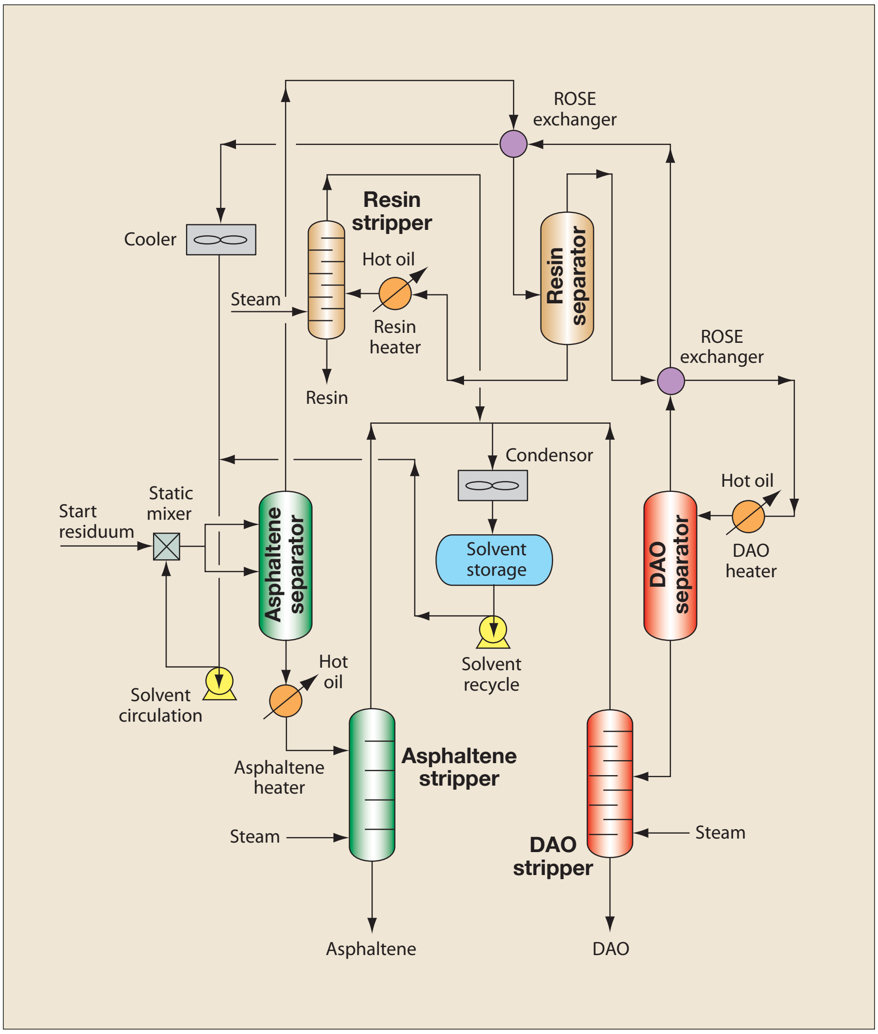

Figure 1 Three-product ROSE

Three-product ROSE

The solution to obtaining anode-grade coke from traditional crudes, therefore, lies in alternative low-sulphur, low-metals content feed options to the coker unit. The options become obvious when analysing the residuum at the molecular level, where it is clear that the undesirable impurities in the coke are essentially asphaltenic in nature and can be separated by solubility-driven processes.

The solution involves the use of a proven solubility-based physical separation process — solvent deasphalting — in which a paraffinic the majority of the metals and CCR, thereby producing a deasphalted oil (DAO) that can be processed in downstream units directly or after the removal of resins.

While DAO has been traditionally hydrotreated and/or catalytically cracked owing to its higher value molecules, the resin that is produced has so far been used only for production of fuel oil or road asphalt. The resin product is a relatively low-metal, low-sulphur residuum that is high in asphaltene-free CCR. Due to these characteristics, resin is very good for producing higher quality coke, and an excellent feedstock for the production of anode-grade coke.

Inherent in the solvent deasphalting process is the ability to draw out the resinic molecules and to adjust the volume and quality of the resin. The operating conditions of the asphaltene separator can be adjusted to lift the resinic molecules in the DAO. The resinic molecules are then recovered from the DAO by partially expanding the solvent under supercritical conditions. This arrangement provides the flexibility to balance the streams to downstream processing needs, while consistently meeting the required DAO quality and exercising other disposition options for the intermediate resin streams.

While this addresses the issue of providing low-sulphur, low-metals feed to the coker, the issue of dealing with streams used to make fuel oil remains. While the higher value distillate products used for cutter stock can be used as saleable products, streams of much poorer quality, such as the clarified slurry oil (CSO) from the FCCU, now require an alternative outlet. The slurry oil is a highly aromatic reject from the FCCU. Being denser than water, transporting the CSO by sea is not easy either. However, the CSO, despite being a reject from the FCCU, has low sulphur primarily because of the hydrotreated feed to the FCCU.

So while the CSO may not have the superior quality required for producing high-value distillate products, it can still be blended with the resin from the three-product ROSE (residuum oil supercritical extraction) process to be used as feedstock for production of anode-grade coke. In fact, an optimum feed to the delayed coker to produce anode-grade coke would be a blend of the resin from the ROSE process, the CSO from the FCCU and the required amount of VR to compensate for any quality giveaway. In effect, what this gives the refiner is the ability to insulate the coke grade from fluctuations in the quality of the crude and hence always produce anode coke, irrespective of the quality of the crude. Furthermore, the use of ROSE resin along with the available CSO will substantially moderate the variations in VR quality that the refinery may see with changing crude slates, thereby enhancing the flexibility and reliability of the anode-grade coker.

Although ROSE offers an excellent feedstock for anode coke production, it introduces the issue of disposal of the asphaltenes produced. While the resin cut can be utilised for making anode-grade coke, the asphaltenic molecules remain. These asphaltenes can be subjected to coking too but, owing to their high impurity levels, will only produce low-quality high-sulphur fuel-grade cokes. However, delayed coking can only tolerate a CCR of 34–38%. Therefore, the amount of resin extracted depends on the quality of the remaining pitch or, in other words, only so much resin is drawn out so that the CCR of the pitch remains within the limits of the delayed coking unit. As a result, the refinery will produce a fixed amount of anode-grade coke and the balance will be a lower amount of poorer quality fuel-grade coke.

If the CCR of the asphaltenes is too high for delayed coking, another alternate would be to divert these molecules away from the refinery to industries or end users outside the refining business who have an incentive to process these streams. The major challenge here is in the handling and transportation of these molecules. The asphaltene product is a high-viscosity liquid that solidifies at ambient temperature. A low-cost, high-capacity solid pelletisation technology such as KBR's Aquaform is an obvious solution. This will help refiners to economically store and move these rejects to a more desirable end use, such as solid fuel for cement kilns, the steel industry or the utility industries.

Delayed coking

In its simplest form, delayed coking is a semi-continuous process, irrespective of the type of coke produced. Although the coking process is continuous, coke removal, handling and disposal are carried out in a batch manner. The feed is heated to the reaction temperature in a direct-fired heater and subsequently transferred to the coke drums. The coking reaction is delayed until the heated feed is transferred into the coke drums, where the residence time is long enough for the coking reactions to go to completion. Coke is deposited in the drum and the cracked vapour product exits the drum from the top, then enters the downstream fractionator. Coke is removed from the drum by taking the drum off-line. In order to achieve near steady-state unit operation, the coke drums operate in pairs, so that one drum is in filling mode, while the other is off-line for decoking. The chemistry of coking is similar to a severe thermal cracking process, wherein the larger molecules such as paraffins and paraffinic side chains are cracked into smaller molecules, which then polymerise and condense to form coke.

Depending on feed quality and the operating conditions of the coker, the quality of coke produced may vary from fuel-grade and anode-grade to needle-grade coke. Fuel-grade coke is used primarily in power and cement plants as fuel; anode-grade coke is widely used in the aluminium industry for the manufacture of electrodes; and high-grade needle coke is a premium coke used to manufacture electrodes for the steel industry. Table 1 shows typical specifications for three grades of coke.

The operating conditions of the coker unit are selected according to the quality of the feedstock and the process objectives. The three primary operating variables that affect product yield and coke quality are coke drum pressure, recycle ratio and coke drum temperature. Table 2 shows commercial data published by a US refiner to illustrate the typical range of coker operating conditions for producing different grades of coke.

Most modern coker units are designed and operated at low pressure, low temperature and low recycle ratios to maximise the yield of distillate products and hence produce fuel-grade coke as a byproduct. Cokers producing anode-grade and needle-grade coke need to be subjected to more severe conditions of temperature and pressure, along with a high recycle ratio. Increasing the recycle ratio means increasing the hydraulic capacity of the coker. This means that the fresh feed to the coker needs to be reduced to stay within the limitations of the hydraulic

Specifications for three grades of coke

Property	Fuel coke	Calcined anode coke	Calcined needle coke
Bulk density, kg/m^3	880	720–800	670–720
Sulphur, wt%	3.5–7.5	1.0–3.5	0.2–0.5
Nitrogen, ppmw	6000	–	50
Nickel, ppmw	489	200	5–7
Vanadium, ppmw	141	350	–
Volatile combustible material, wt%	12	0.5	0.5
Ash content, wt%	0.35	0.4	0.1
Moisture content, wt%	8–12	0.3	0.1
HGI	35–70+	60–100	–
Coefficient of thermal expansion, x 10-7°C	–	–	1–5

Table 1

Typical range of coker operating conditions for producing different grades of coke

	Fuel grade	Anode coke	Needle coke
Drum pressure, bar	1.0–1.5	1.5–3.0	4.0–7.0
Recycle ratio, vol%	5–10	25–30	50–80
Drum temperature, °C	435–440	440–445	450–455

Table 2

Three potential feed streams			
	Vacuum residue	Slurry oil	Resin
SG @60F	1.0279	1.0926	1.017
API gravity	6.2	-2.0	7.6
Sulphur, wt%	3.9	0.9	3.5
CCR, wt%	20.3	9.9	17.6
Nickel, wppm	47	1	20
Vanadium, wppm	163	1	65

Table 3

capacity of the original coker unit. Hence, three-product solvent deasphalting becomes the obvious choice to cut down the amount of original feed to the unit, wherein the extracted resinic molecules, along with the stranded streams from the refinery such as CSO and balance VR, become a reduced fresh feed to the coker unit. The balance capacity can be met by increasing the recycle ratio, which, in fact, favours anode coke production.

Refinery case study

In this example, an FCC-based refinery is processing heavy crudes and has no bottoms processing capability. Under the current operating scenario, the VR is cut with distillates and sold as high-sulphur fuel oil.

The quality of VR is too high in sulphur and metals content, such that the addition of a delayed coker processing the entire VR stream would result in the production of low-grade petroleum coke. When processing the entire VR stream, the large size of the coker and the lack of an economic outlet for the high-sulphur petroleum coke made this solution economically unattractive.

In an attempt to improve the coke quality, several combinations of VR and CSO from the FCCU were tested, confirming that the production of anode-grade coke from the existing crude slate was not viable. Changing the crude slate was not an option, and an economic analysis indicated that the production of anode-grade coke would have a significant and positive impact on refinery margins.

In an effort to reduce overall fuel oil production, the refinery is also considering the implementation of a traditional two-product solvent deasphalting unit as a low-capital option to separate sufficient volumes of high-quality DAO to be sent to the FCCU, while rejecting the pitch to fuel oil.

The option to use a three-product solvent deasphalting unit to produce a DAO stream for feed to the FCCU, a pitch stream for fuel and an intermediate resin stream for use as a coker blend stock was evaluated. The three potential feed streams — VR, ROSE resin and CSO for testing in a delayed coker — are shown in Table 3.

Several combinations of VR, CSO and ROSE resin were tested for coke quality. The results (see Table 4) indicate that a combination of resin and CSO will produce high-grade anode coke. This is primarily because of the ability of the ROSE unit to sufficiently improve the sulphur, metals and C_7 insolubles content in the resin stream to allow for the production of anode-grade coke.

The use of ROSE resin along with the available CSO will also substantially moderate the variations in VR quality that a refinery may see with changing crude slates, thereby enhancing the flexibility and reliability of the anode-grade coker.

Conclusion

Anode coke production can be realised from traditional crudes by adopting a technology solution that involves the integration of a commercially proven niche version of the ROSE process and FCC slurry oil to custom blend feed for anode coke production.

The combination of solvent deasphalting and niche-delayed coking represents an economic solution to minimise fuel oil production and produce anode-grade coke, which can be implemented at a fraction of the cost of other resid processing options.

Combinations of VR, CSO and ROSE resin tested for coke quality				
	Coke specs	20/80 CSO/VR	40/60 CSO/VR	CSO+ resin
Dry gas, wt%	–	4.2	4.2	4.2
C_3+ liquid, lv%	–	61.8	59.9	60.7
Coke, wt%	–	33.0	35.3	34.4
Coke quality				
Capacity, bpsd	–	20 000	20 000	20 000
Coke, MT/D	–	1090	1177	1144
Sulphur, wt%	<3.0	4.2	3.2	2.9
Nickel, ppmw	<200	113	79	36
Vanadium	<200	391	272	115
Coke type	–	Fuel grade	Fuel grade	Anode coke

Table 4

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