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What are the ecological and profitable uses of refinery residues?

With prices always under pressure and stricter environmental legislation being implemented, refineries are increasingly forced to look for new ways of processing heavy residues. Rising price differences between light low-sulfur and heavy high-sulfur crude oils produce greater amounts of residues at refineries. Stricter environmental laws will further restrict the incineration of heavy residues at power plants due to the emissions, and limit the sulfur content of marine fuel oils (MFOs) to 0.1% from 2015 onward. The current sulfur content is 1.5%. The sale via MFO is presently the last possible outlet for many refineries to get rid of heavy residues. Alternatively, other conversion systems, such as visbreakers and cokers provide for a deeper processing of heavy residues and lead to substantial investments. These technologies also produce smaller amounts of residues that are in need of disposal in an environmentally sound manner.

The enrichment of highly condensed aromatic hydrocarbons in the form of aromatics, resins and asphaltenes, not to mention sulfur and nitrogen compounds and metal contaminants—such as vanadium (V), nickel (Ni) and iron (Fe)—takes place in the heavy residues. From an ecological point of view, the heavy residues constitute a significant problem. Thus, refineries are increasingly interested in highly efficient residue technologies, allowing heavy residues to be processed up to 100%.

Sustainable combination. Though solvent deasphalting (SDA) and bitumen production are well-known and widely used technologies, combining these two processes makes it possible to approach the residues issue in a sustainable way. Adjusting the SDA process to bitumen-capable feed production provides an opportunity to convert heavy refinery residues (particularly vacuum residues) into products for the marketplace.

In SDA, heavy residues are split by extraction, using solvents (such as propane, butane or pentane) at under-critical or overcritical conditions, into deasphalted oil (DAO) and a pitch (asphalt). At the fuel refinery, the DAO can be further processed in a fluid catalytic cracking (FCC) plant or a hydrocracker to become valuable gasoline, diesel and fuel oil components. At the lube oil refinery, it can be used as bright stock for lube oil production.

The bitumen-capable pitch is mixed with flux components—like vacuum gasoil (VGO), slop wax and extracts—and processed at a bitumen processing plant, where it undergoes a specific blowing process to become high-quality bitumen products (FIG. 1). The weatherproof inclusion of accompanying components taking place in the bitumen production leads to an environmentally friendly solution for the heavy residue pollutants.

The DAO quality depends on the feed specification for the downstream process. In the catalytic processes, the requirements are particularly determined by the catalysts employed. TABLE 1 lists the typical feed specifications for certain follow-up processes.

The SDA process can be tailored to the necessary specifications by adjusting certain process variables. It can be conducted both under-critically and overcritically. By increasing the pressure, especially in an overcritical mode, substantial yields in the 60% to 70% range can be obtained in relation to the feedstock. However, there is a disadvantage: the DAO quality deteriorates substantially and the required quality criteria for the follow-up process can often no longer be maintained. The overcritical

TABLE 1. Typical DAO feed specifications for follow-up processes

Designation	Unit	FCC plant	MHC plant	Lube oil plant
Metals (V, Ni)	ppm	< 30	< 12	< 2
Conradson carbon residue (CCR)	%	< 9	< 5	< 0.4
Nitrogen (N content)	ppm	< 5,000	< 4,000	-

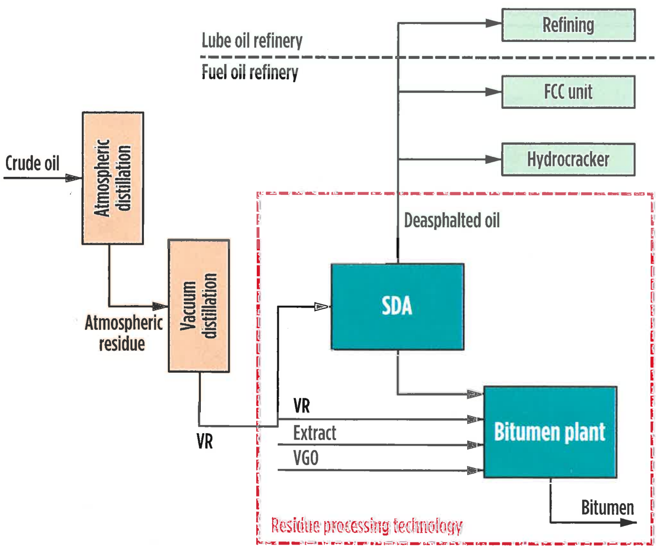

FIG. 1. The necessary process to create high-quality bitumen products.

SDA mode is often used to separate resins, and that is no solution when it comes to bitumen production.

The DAO yields may also be increased by selecting specific solvents and mixtures for different components. For the SDA process and the lube oil production propane is usually used as a solvent. Propane ensures the quality criteria as listed in TABLE 1 for the lube oil plants. Meanwhile, adding a small amount of n-butane to propane gives a considerably higher DAO yield. The higher the yield, the more the quality decreases.

The DAO yield may also be increased up to a certain extent by increasing the solvent amount. Looking at the necessary downstream solvent separation from the extract and the raffinate, the solvent amount used should be minimal.

For the residue technology within an SDA and a bitumen unit, not only must the DAO have the required quality, but the pitch should be a bitumen-capable feed. Whether a pitch is bitumen-capable or not can be estimated based on a feed screening. Except for the main bitumen parameters, chemical composition (like paraffin and asphaltene content) and thermal stability need to be investigated. Final evaluation of bitumen quality is possible after the complete test program is completed. This includes all process steps required for bitumen production. The basic pitch tests, like penetration, softening point, penetration index and aging resistance will reveal the feed's bitumen capability.

TABLE 2 lists the required pitch criteria from the SDA for the production of bitumen type 50/70. In addition, the pitch of two refinery residues—a vacuum residue (VR) and a visbreaker tar (VT) from the SDA—are compared with the required criteria.

TABLE 2. Pitch for production of bitumen 50/70

Designation	Unit	Bitumen 50/70	VR	VT
Penetration	0.1 mm	50–70	57	50
Softening point	°C	46–54	46	47.2
Penetration index	–	-1.5–0.7	-1.96	-1.91
Paraffin content	Ma.-%	< 2.2	1.86	2.04
Kin. viscosity (135°C)	mm^2/s	≥ 295	335	283
Change in mass	Ma.-%	+/- 0.5	-0.01	-1.67
Remaining penetration to org.	%	≥ 50	49	24
Change of softening point (R&B)	°C	≤ 9	6.8	15.4

Analysis. The VR pitch shows that the penetration index (–1.96) is far below the –1.5 value. Further, the remaining penetration after testing at 163°C is not reached. This means that the VR pitch is not a bitumen-capable feed and can not be used.

The criteria comparison for VT pitch reveals substantial deviations in four major points. The penetration index (–1.91) is far too low, as is that of the VR, and the thermal stability is too low. In addition, the kinematic viscosity, at 135°C, is too low. Especially problematic and typical for a visbreaker residue is the extremely high negative change in mass (–1.67) and the insufficient remaining penetration (24) of the VT pitch. The last two criteria show that the VT pitch is not bitumen-capable.

The VR pitch can be further optimized in the SDA plant, meaning the pitch stability can be further improved by yield increase. It is confirmed that the heavy residues from visbreakers provide no bitumen-capable feed, even if an SDA is incorporated.

The lowering of the viscosity and the instability of the visbreaker products due to thermal cracking usually preclude the production of high-quality bitumen products.

At the pilot plant for this concept, blowing tests will always be necessary for a final assessment of the feedstock's bitumen capability. The tests also contribute to decision-making as to whether a bitumen plant makes sense. The SDA process is also optimized so that both a high-quality DAO and a bitumen-ca-

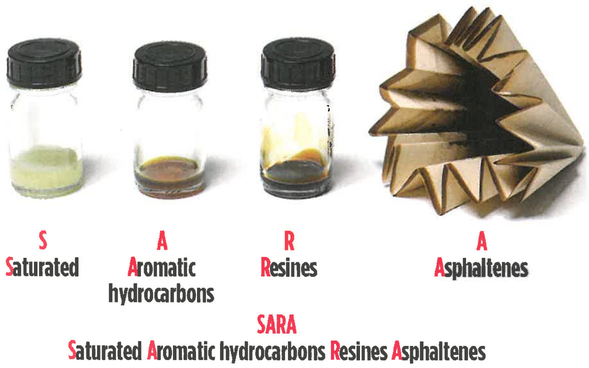

FIG. 3. SARA analysis is deconstructed.

FIG. 2. Pilot plant in Leipzig, Germany, with autoclaves for under-critical and overcritical conditions.

FIG. 4. A propane deasphalting plant at H&R Ölwerke Schindler in Hamburg, Germany.

pable pitch can be produced. Finally, the decision to incorporate this combined residue technology depends on the compliance with required criteria both for the DAO and the pitch.

FIG. 5. Bitumen pilot plant in Vienna, Austria.

Pilot plants do exist for SDA tests in which the quality parameters for various heavy residues (FIG. 2) are assessed. Tests can be carried out for under-critical or overcritical conditions where a range of solvents and solvent mixtures are used at different temperatures and solvent quantities. Special analyzers for saturated aromatics, resins and asphaltenes (SARA) feed analysis (FIG. 3) and end products have been set up. In connection with the entire process parameter determination and other analytical data, the process can be simulated and result in the design of an SDA plant. The SARA analysis permits an optimal structure analysis of the mixtures for the theoretical calculation of the thermodynamic process. The data and analysis for a scale-up are supported by the results from, and experience with, a fully equipped reference plant (FIG. 4) for propane deasphalting (PDA). The plant supplies a high-quality DAO as bright stock for the base oil production.

The pitch from the SDA plant can be tested in a pilot plant like the one in FIG. 5.

Moving forward. The close coordination of the tests is the basis for building a complete residue technology for a refinery. The combination of these two technologies is also the most cost-effective method of residue processing and gives the customer a maximum economic advantage. The use of this technology requires, however, that both the DAO quality for the follow-up process and the pitch's bitumen capability are guaranteed to produce high-quality bitumen. HP