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THERMAL CRACKING
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Delayed coking's ability to convert heavy vacuum residues into lighter distillates and petroleum coke not only is an economical method for upgrading residual oils but also permits refiners to process a wide variety of crude oils including opportunity crudes that contain heavy, high sulfur residues. Although delayed coker design can be distinguished by feedstock, operating conditions, equipment configuration and processing goals, probably the most differentiating category is coke product - specialty grades or fuel grade. Specialty coke grades include anode and needle cokes for specific markets. Fuel grade coke, an unwanted byproduct, is produced to maximize clean distillate liquid yields.

ANODE GRADE COKE: Anode coke, having a distinctive sponge appearance, less than 250 ppmw to 350 ppmw metals content and less than 3.0 wt% sulfur, is used to produce carbon anodes that are consumed in aluminum production. While low-metal, low-sulfur crudes are favored for anode coke production, these feed types are commonly paraffinic and result in low density cokes. Green low-metal, low-sulfur coke destined to be calcined anode coke typically will have the following characteristics: (1) 8 - 10 wt% volatile combustible matter (VCM), (2) less than 3.0 wt.% sulfur, (3) less than 0.3 wt% ash, (4) less than 200 ppmw nickel, (5) less than 200 ppmw vanadium and (6) 80 Hargrove Grindability Index (HGI). VCM and HGI have strong correlatable influences on various proprietary vibrated bulk density (VBD) tests for calcined anode coke. Consequently, VBD can be controlled by operations of both the delayed coker and the calciner. Calcined low-metal, low-sulfur coke qualifying as anode grade typically will have the following characteristics: (1) 0.3 wt% VCM, (2) less than 3.0 wt.% sulfur, (3) less than 0.3 wt% ash, (4) less than 200 ppmw nickel, (5) less than 200 ppmw vanadium, (6) more than 0.78 grams/cubic centimeter (g/cc) VBD, (7) more than 2.06 g/cc real density, (8) 40% greater than 4 mesh and (9) 10% less than 28 mesh. Because delayed cokers producing anode coke must be operated to produce specification coke, liquid product quality and quantity sometimes is accepted as produced.

FEEDSTOCKS FOR ANODE COKER: Atmospheric or vacuum residues from paraffinic through asphaltic crudes containing satisfactory metals and sulfur contents are used to produce anode grade coke. Typical crudes producing anode coke include North Sea, North African, West African, Louisiana Sweet, Taching and Minas. Because of an unusual sulfur distribution, several California crudes can produce anode grade coke despite high overall sulfur contents. Blending decant oil into delayed coker feed may enhance anode coke properties, if coking operations can be adjusted to compensate for decant oil's distillation, aromaticity and coke property modification tendencies. Also, unusual feedstocks, such as unfiltered coal tar, are being used to produce anode quality coke. Anode coke production has been demonstrated from a 50/50 blend of aromatic distillates and decant oil. Limited success from deep residue desulfurization of coker feed reinforces previous evidence that feed pretreatment is usually not economical. Economics are severely challenged, when coke yields need to be limited. However, anode coke production may possibly be produced from deasphalted oil (DAO) produced by deasphalting a high metals, medium sulfur residue. DAO would be expected to have low metals and, depending on residue characteristics, relatively low sulfur.

ANODE COKER DESIGN FACTORS: While a few delayed cokers are operated primarily to produce anode grade coke, most delayed cokers producing anode coke are operated to provide residue conversion capability, while incidentally producing anode grade coke. However, light paraffinic residues, with Watson K factors greater than 11.8, frequently produce unacceptable coke density, when coker operation is maximizing liquid yields. To produce acceptable anode coke density from light, sweet waxy feeds operating severity will almost always increase pressures to above 35 psig at the top of the coke drum and recycle ratios to above 35 %, thus, yielding more coke and less liquid products than at typical fuel coke production operating conditions. When processing marginal sulfur content feedstocks, the incrementally higher coke yields will be lower in sulfur, contributing to the difference between meeting and not meeting anode coke sulfur specifications. To maintain coke quality, when producing more coke, cokers on short cycles must adjust operating conditions to compensate for short residence times. Increasing coking temperatures, which may increase coke drum overhead temperatures by about 20 to 50 F higher than on typical fuel grade cokers, will lower HGI and VCM, thereby, increasing calcined coke's VBD.

ANODE COKER DESIGN VERSUS FUEL COKER DESIGN: Anode coker temperature and pressure design conditions are generally more severe than fuel coker design conditions. Even though anode coker feedstocks contain less sulfur, indicating lower corrosion rates, metallurgy selection should consider processing high sulfur feeds so that the refiner's options are not limited. Anode coke which is dense and hard with strong mechanical integrity requires higher energy jet pump and coke cutting system specifications than are normally required for fuel coke cutting. Depending on coke quality, large diameter coke drums now common in fuel cokers may not be suitable when producing dense, hard anode coke. To reduce the need for additional fractionator pumparound and overhead reflux and to provide direct heat transfer to the feed for anode over fuel coker designs, a portion of the feed can be directed over the shed wash section in the bottom of the fractionator tower.

NEEDLE GRADE COKE: High quality needle coke produces graphite electrodes used in electric arc steel furnaces. For needle coke to be turned into graphite electrodes the coke must be: (1) calcined to drive off volatiles and increase density, (2) combined with binders and formed into prebaked bars, (3) baked with the binders and (4) graphitized and machined into the final electrode dimensions. Needle coke is classified as regular, premium and super premium depending on desirable crystalline structure in which carbon threads or needles are oriented in the same direction, strength and chemical impurities. Green low-ash, low-sulfur coke destined to be calcined needle coke and machined into electrodes, typically will have the following characteristics: (1) 5 - 7 wt% VCM on a dry basis, (2) less than 0.1 wt% ash and (3) less than 0.5 wt% sulfur. Calcined low-ash, low-sulfur, needle grade coke typically will have the following characteristics: (1) less than 0.1 wt% ash, (2) less than 0.5 wt% sulfur, (3) 2.10 - 2.14 g/cc real density and (4) less than 25% less than 1.0 mm mesh. Low-ash, low-sulfur needle grade coke electrodes typically will have the following characteristics: (1) 0.00000025/C coefficient of thermal expansion (CTE) between 30 C and 125 C, (2) 0.00032 ohm-in electrical resistivity and (3) 2,500 psi flexural strength. Crystallinity affects graphite electrode properties, such as CTE and electrical resistivity. The electrode fabrication process is enhanced by high density and low fines granulometry of calcined coke. Sulfur in electrodes can cause puffing. Ash in electrodes can increase electrical resistivity and decrease electrode strength.

FEEDSTOCKS FOR NEEDLE COKE: Aromatic tars, such as decant oil and thermal tar, removed from distillates are feedstocks that produce the better grades of commercial needle coke in needle grade delayed cokers. Use of other feedstocks, such as ethylene cracker tar and filtered coal tar has resulted in some success but generally needle coke quality is inferior. Because tar feedstocks are usually produced from petroleum distillates, ash content can be achieved mainly by filtration. Optimal amounts of aromaticity in feedstocks improve needle coke product grade, because aromatic species reaction through an intermediate mesophase is required to produce needle coke. Therefore, feedstock blending has been synergistic with increasing needle coke quality. Current design trends include feedstock pretreatment using desulfurization, solvent extraction and or thermal treatment.

NEEDLE COKER DESIGN FACTORS: Optimum operating conditions for maximizing coke quality varies with feedstocks but are typically between 50 psig and 90 psig drum pressure and

60% to 100 % recycle. Needle cokers are generally operated at high temperatures to reduce VCM, which decreases HGI and friability, thus producing few coke fines. However, short cycles may adversely affect coke quality.

NEEDLE COKER DESIGN VERSUS ANODE AND FUEL COKER DESIGNS: Higher design pressures and temperatures require thicker needle coke drum walls. Needle coker heaters must be thermally and mechanically capable of operating under more severe conditions. Hard, dense needle coke, being hardest to cut, requires significantly higher jet pump discharge pressures for given drum capacities and may require designers to limit drum sizes to up to 24 feet in diameter, which is currently the largest needle coke drum diameter in operation. Properly sized jet pump systems limit coke fines production and enhance product granulometry. Using optimized chute systems, stationary screen devices and minimum mechanical contact minimizes coke fines production. New needle coker designs include post treatment operation that conditions and strengthens coke by extending mesophase reactions.

ADDITIONAL NEEDLE COKER CONSIDERATIONS: Extensive pilot plant operation is necessary to (1) confirm coke quality, (2) optimize operating conditions and feed blend and (3) define pretreatment and post treatment requirements. CTE is highly dependent on proprietary test formulations and temperature ranges. Results from different labs must be compared cautiously.

FUEL GRADE COKE: Fuel grade coker is the predominant design for today's new coker designs, which involve (1) maximizing liquid product yields, (2) providing high degrees of flexibility for feedstock variations, (3) improving run lengths of increasingly heavier feeds, (4) operating economically and safely and (5) meeting environmental requirements. Green high-ash, high-sulfur, high-metals coke destined to be fuel, typically will range from sponge to shotcoke and have the following characteristics: (1) greater than 0.35 wt% ash, (2) 3.5 wt% to 7.0 wt% sulfur, (3) more than 300 ppmw nickel plus vanadium, (4) less than 12 wt% VCM, (5) 8 wt% to 12 wt% moisture and (7) 35 to 70 HGI. Shot coke consists of small spheres or "beebees" of up to 3/16 inch diameter, depending on the crude source, held together in a matrix of amorphous coke. When shot coke is broken up, beebees are freed and can become like ball bearings underfoot. If graded as 'high sulfur", shot coke will bring low sales prices in traditional fuel petroleum coke markets, such as export, cement kiln firing and some utility station firing. An alternative opportunity to lower sales prices is coke fired cogeneration producing steam and electricity for refinery or export.

FUEL COKER DESIGN FACTORS: Designs maximizing liquid product yields include low operating pressures in coke drums of 15 psig and ultra-low recycles of 5 % or less. Generally refiners are operating old and new cokers at the lowest recycle ratios that coker gas oil quality and unit operations will permit. At constant coke drum pressure, a typical yield variation from reducing recycle ratio from 10% to 5% is: (1) dry gas decreasing from 5.59 LV% FOE to 5.24 LV% FOE, (2) mixed LPG decreasing from 8.79 LV% to 8.32 LV%, (3) total liquids increasing from 72.2 LV% to 73.79 LV% and (4) coke decreasing from 30.06 wt% to 28.69 wt%. However, as heavy coker gas oil yields increase, distillation end point, carbon residue, metals content and specific gravity also increase. A comparison of typical old, 25 psig drum, 15% recycle, fuel coker gas oil with typical new 15 psig drum, 5% recycle fuel coker gas oil results in (1) increased yield from 25.7 wt% to 35.2 wt%, (2) increased endpoint from 920 F to 1,060 F, (3) decreased gravity from 19.6 API to 16.3 API, (4) increased CCR from 0.35 wt% to 0.8 - 1.0 wt% and (5) increased nickel plus vanadium content from 0.5 wt% to 1.0 wt%.

LOW PRESSURE FUEL COKER: Low pressure coker designs involve (1) increased compressor size and horsepower, (2) minimally increased fractionator and vapor line size and (3) use of low pressure drop components in vapor paths. A recent coke economics evaluations at various pressures considered coking pressures between 15 psig and 30 psig without having to change compressor frame size, testifying that compressor loads required for low pressure design do not have as large an impact on costs as once thought. Fractionator sizing follows load calculations, such that in a medium sized coker fractionator diameter increase was only one foot for changing from 25 psig drum operation to 15 psig operation. Fractionator overhead condenser pressure drop design requires larger tube sizes in air fan condensers but does not adversely affect plot arrangement and is lower than was considered necessary on older cokers. Effectively injecting gas oil quench into coke drum overhead lines reduces coke deposits that had caused high coking pressures. New coker designs use spray nozzles. Economic evaluation of coking 35,000 BPSD heavy high sulfur vacuum residue at constant low recycle ratio of less than 5% and coking pressures from 15 psig to 30 psig results in significant benefit at 15 psig. Factors considered in the economic evaluation were (1) product revenue, (2) compressor, coke drum, fractionator and other capital costs and (3) power, 150 psi steam and 600 psig steam utility costs.

COKE DRUM DESIGN: Coke drum design factors include safety, mechanical integrity and drum size. New, large cokers have incorporated reduced cycle operations from conventional 24 hours to as low as 18 hours. Larger drum diameters than heretofore standard 27 foot diameter drums are combined in coker design with reduced cycle operations sometimes to avoid including an additional pair of drums that might have been required under previous standard design guidelines. Performing the cycle safely and consistently is ensured through various decoking operations designs. Improved mechanical integrity design factors include (1) metallurgy, (2) welding details and (3) fabrication and mechanical detailing. Larger coke drums, such as 29 foot diameter, having greater coke capacity require thoroughly reviewing designs of (1) coke cutting, (2) quench water, (3) blowdown, (4) coke handling systems and (5) adjacent hydraulic systems.

ADDITIONAL DELAYED COKER INFORMATION: In a future Thermal Cracking Notebook, delayed coking topics, such as (1) coke drum structure systems, including switch deck, overhead valve operating platforms and coke cutting deck, (2) coker heaters, (3) coker fractionator, (4) coke handling systems, including coke pit or pad considerations and sizing and coke dewatering, (5) blowdown systems, (6) coke drum life considerations, including skirt to shell junction, shell and cladding cracking and drum bulging ,and (7) piping will be discussed.

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