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Understand differences between thermal and hydrocracking

Successful operation and product yields are controlled by reactions at the molecular level

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Optimizing performance from existing residual upgrading equipment is achieved through maximum asset utilization. During the upgrade of residual facilities, economic goals of the project required operating at the upper end of the design envelope due to equipment limitations. The solution may involved new equipment to remove the identified bottlenecks. But, budget and investment constraints can limit funding, and careful prioritization is needed to justify capital expenditures. Understanding the conversion, yields and product qualities between competing conversion processes allows better investment selection. This case history discusses in detail thermal cracking kinetics—a common link between coking—and residual hydrocracking.[1]

Generic coker kinetics and simulation models. For many years, the coking chemical reaction has been studied by the refining industry, and the kinetics are fairly well understood. A simplified coker cracking mechanism consists of cracking and polymerization reactions, as shown in Fig. 1. Thermal cracking reactions form lighter liquid products than the feedstock and solid coke. The formation mechanism of the lighter products is achieved by rejecting hydrogen from the larger feed molecules, thus producing a hydrogen-deficient reactant—coke.

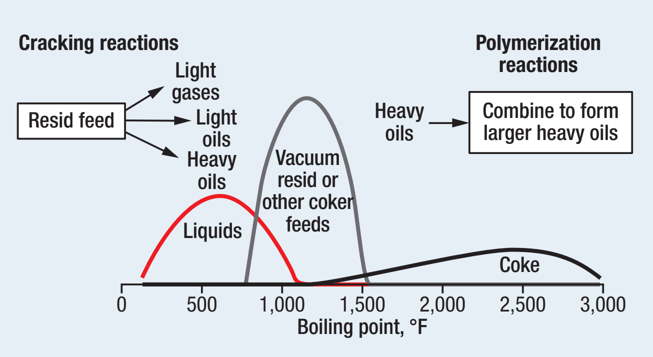

FIG. 1 Coker cracking mechanism.

To demonstrate this mechanism, a delayed coker will be used to evaluate the process mechanics. The same evaluation can be used for any thermal cracking processes, for example visbreaking, fluidized cokers or flexicokers. A simulation model can provide the fundamental kinetic representations of the delayed coker operation. This discussion used a simplified version of the simulation model thermal cracking kinetics to explore the reaction yield effects for a single feedstock to allow comparison to hydrocracker yields and products.

Resid hydrocracker kinetics and simulation model. The simple hydrocracker kinetics have also undergone extensive investigation, and they are believed to be fairly well understood. The hydrocracker kinetics are complicated by the ability to vary

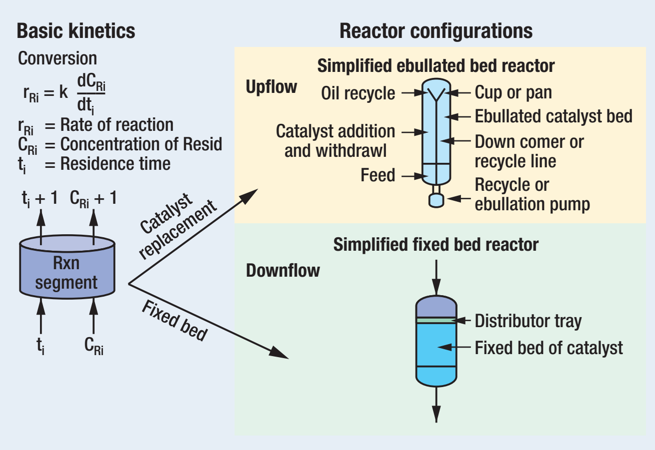

FIG. 2 Simple kinetics for hydrocracking reactions.

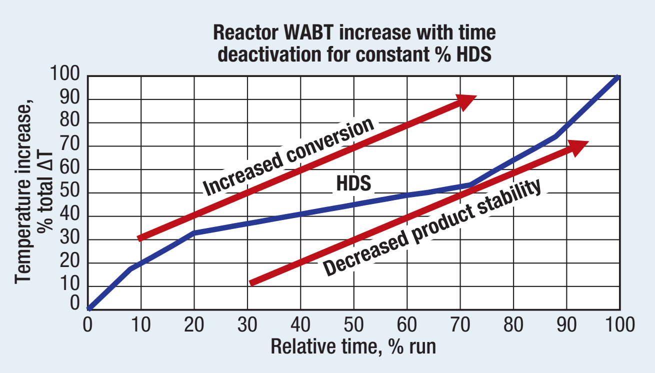

FIG. 3 Catalyst activity over run length.

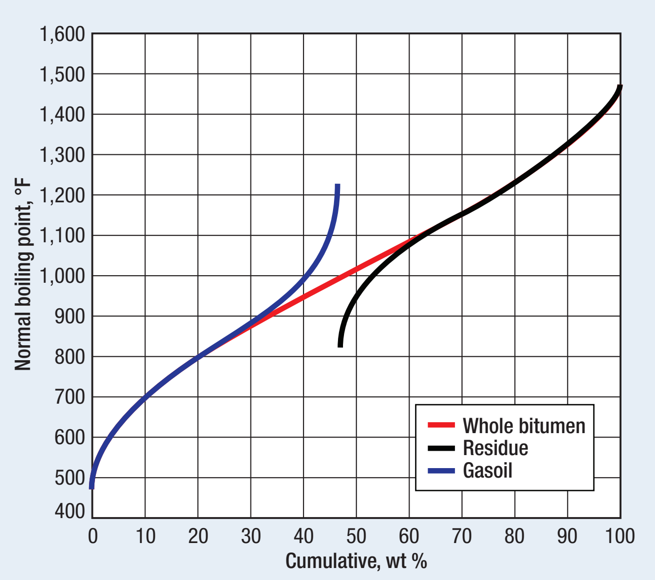

FIG. 4 Product cuts of SAGD Athabasca Bitumen.

TABLE 1. Feedstock qualities

Description	Bitumen
Production method	SAGD
% Diluent in blend, vol%	0
API	9
Elemental Analysis, Dry, w%	
C	84.1
H	10
S	4.6
N	0.4
Metals, wppm	
Ni	60
V	170
Others	300
Oxygen, w%	0.8
Total, w%	100

the operating temperature, pressure, reaction time and catalyst type. Residual hydrocracking is typically done at high pressure, temperature and reaction times. Hydrocracking catalyst are limited to cobalt/molybdenum (Co/Mo) or nickel/Mo (Ni/Mo) types with a selection of pore distribution to control sedimentation or hetro atom removal. Ebullated-bed or moving-bed reactors can maintain the hetro atom removal by catalyst addition, and product stability is improved by catalyst activity.[4]

Fig. 2 shows a simple representation of the hydrocracking kinetics. The comparison to coker conversion was made by using an ebullated bed reactor. The same comparison can be made using moving-bed or fixed-bed residual hydrocrackers.

New model. A new simulation model was developed for a residual hydrocracker. This model utilizes fundamental reaction and reactor kinetics to predict residual hydrocracker performance. The following discussion uses a simplified version of the model kinetics to explore the reaction yield effects for the same feedstock as used for the delayed coker yield projection.

Conversion. Coking and hydrocracking kinetic models use a thermal-cracking mechanism to simulate conversion of residual feed into lighter products. The individual coking and hydrocracking thermal cracking kinetics were developed independently using data from each process. No comparison or usage of one mechanism by the other was conducted until this study that has demonstrated the two are nearly identical and was confirmed by recent pilot unit testing.[1,2] Catalytic cracking of residual does not occur in the hydrocracking process.

Kinetic studies and recent pilot data indicate that the thermal conversion with or without catalyst is within the experimental error once adjustments are made for residence time effects. The extent of conversion is controlled by either lack of hydrogen (coking) or hydrogen addition (hydrocracking). Hydrocracking allows hydrogen to fill the split chain that short circuits the polymerization or condensation reactions; such reactions prevent coke formation.

The "hydrogen addition" process has a product slate higher in hydrogen content than the feed, and it is all liquid, with only a small amount of sediment formation. Hydrogen addition lowers the product's liquid density, which realizes a higher than 100% volume liquid yield.

Coking allows polymerization or condensation to continue until coke is formed, thus increasing the liquid-product hydrogen content by removing carbon. This is referred to as "carbon rejection." The coke removal results in a volume liquid yield less than about 75%.

While catalytic cracking does contribute to conversion, without catalyst, conversion is limited to a relatively low level due to the lack of hydrogen replacement. Vacuum reside (VR) conversion without catalyst is limited to about 25 wt%–30 wt% at 1,000°F$^+$ conversions. At higher conversion, the unconverted reaction products, in the same boiling range as the feed, are unstable causing sedimentation downstream of the reactors and equipment plugging. The unconverted reaction products' instability is possibly a function of the lower asphaltenes content of the feed and removal of the asphlatene solubilizing resin fraction.

Reactors. The reactor type plays an important part in the total hydroconversion levels. The conversion is limited to about 35%–45% for fixed-bed reactor systems due to product sedimentation and catalyst deactivation. Ebullated-bed or moving-bed VR hydrocrackers allow catalyst replacement online, and higher conversions are possible before the sedimentation limit occurs. Catalyst type plays an important part in mitigating sedimentation. Pore size distribution and catalytic metals are important factors to maximize conversion for a given VR feed. Correlations between feedstock quality and conversion focus on the saturates, aromatics, resins and asphaltene (SARA) feed contents. Different ratios of SARA components have been related to higher conversion potential of the feed. Using low-activity slurry catalysts indicate that some surface area is required to allow conversion and product stabilization.[3] One of the exciting opportunities in residual hydrocracking is developing a catalyst that is active for cracking. This is an high interest research area by the catalyst manufactures.

Cokers. For coking units, conversion is a function of the Conradson Carbon Residue (CCR) in the feedstock. The liquid product is a function of: 100-CCR × feedfactor. The feedfactor varies from 1.5 to 2 and depends on feedstock quality. The CCR is typically less than 30 wt% resulting in a conversion to liquid of about 70 wt% along with a net feed liquid loss of about 30 wt%. In contrast, hydrocracking conversion is limited to about 70 wt% with the unconverted product remaining a liquid. Some refining operations are running at conversion exceeding 70 wt% with special circumstances for handling the liquid product. For this study, the conversion was kept at 70 wt% to allow the comparison to coking.

Hetro atom. The downflow reactor has a fixed-catalyst volume, and catalyst activity decreases with time. Catalyst deactivation increases due to feed contaminants. To maintain a constant HDS activity, the reactor temperature is increased, thus decreasing product stability as shown in Fig. 3. Ebullated-bed reactors and other catalyst replacement technologies allow adding fresh catalyst while maintaining the catalyst activity, reactor temperatures and conversion at constant levels. The corresponding product stability is achieved at higher conversion levels.

Feedstock. For this example, the feedstock is a typical Athabasca bitumen as produced by the steam assisted gravity drainage (SAGD) method. Table 1 lists the qualities of the SAGD produced bitumen.[1] The diluent distillates were removed, and the VR product meets feed quality. The new model was used to fractionate the SAGD Athabasca bitumen to a 1,020°F-residue cut point, as shown in Table 2 and Fig. 4.

General assumptions. The operation was assumed to process 100,000 bpd of VR from SAGD bitumen (see Tables 1 and 2). The delayed coker and associated equipment were assumed to make equivalent final liquid product with a sulfur contents similar to the ebullated-bed hydrocracker. This requires hydrotreating all liquid products in fixed-bed units plus the associated hydrogen production. The 100,000-bpd ebullated-bed hydrocracker and hydrogen plant were assumed to provide a unit capable of 70% conversion and allow comparison directly to the coker yields. Perfect fractionation of the products was used to facilitate this comparison. Other considerations such as offsites, location, utilities or relative economics were not considered.

Coking. Severe thermal conversion occurs in the delayed coker. The coker drum requirements for processing the 100,000 bpd of VR was assume to be 6 drums or 3-2 drum modules. The current practice is to target a four to five year run length with slowdowns for heater cleaning. Online spalling is assumed to extend the heater run.

Technology. The latest drum technology would be used with automatic unheading for the drum associated with automated coke cutting. The blowdown system recovers all produced vapor and has an onsite sour-water stripper (SWS). The pad coke is loaded to a grisly then to a conveyor belt system that loads the coke into rail cars for shipment. Fines suppression and containment are an integral part of the design.

Hydrocracking. The residual hydrocracker operating targets used a moderate conversion to stay within the operating constraints of sedimentation and reactor stability. The 100,000-bpd unit would have two trains with one to three reactors per train. The gas-recovery system would allow recovering the majority of the unconverted hydrogen for recycling to the reactors. To maintain conversion levels (70% conversion,) an ebullated-bed or slurry-type reactor would be required due to catalyst the replacement. Operating conditions vary depending on the number of reactors in the train, reactor type (ebullated bed or slurry) and the feedstock type. Table lists the typical operating conditions for an ebullated bed unit.[5]

Catalyst addition. VR conversion at 70% requires a reactor design with catalyst replacement. The ebullated-bed reactor design is currently the only commercially demonstrated design that meets the conversion and catalyst replacement criteria. In the ebullated-bed process, batch replacement of catalyst is used to maintain catalytic activity. Emerging technologies may also achieve this or higher conversions and offer a new perspective on residual upgrading. The ebullated-bed reactor catalyst replacement rate is proportional to the metals level in the feed.[6] This study uses a catalyst addition rate sufficient to provide a reasonable product sulfur level for producing synthetic crude.

TABLE 2. Product characteristics of SAGD Athabasca bitumen

	Whole bitumen	Gasoil	Residue
Vol%	100.00	47.72	52.28
API	9.00	16.37	2.88
UOP K	11.33	11.40	11.27
MW	527	384	763
C/H, wt	8.70	8.02	9.26
Sulfur, Wt%	4.60	3.45	5.55
Nitrogen, ppm	4,000	2,299	4,756
MCC, wt%	14.5	1.1	25.7
Metals, ppm	530	207.75	776

Operational run targets. The operational target would be a two year run length between shutdowns for equipment cleaning and a four to five year turnaround cycle. During the run, VR conversion, hydrodesulfurization (HDS), hydrodenitrification (HDN), hydrodemetalization (HDM) and CCR reduction would all be maintained due to the ability to replace catalyst.

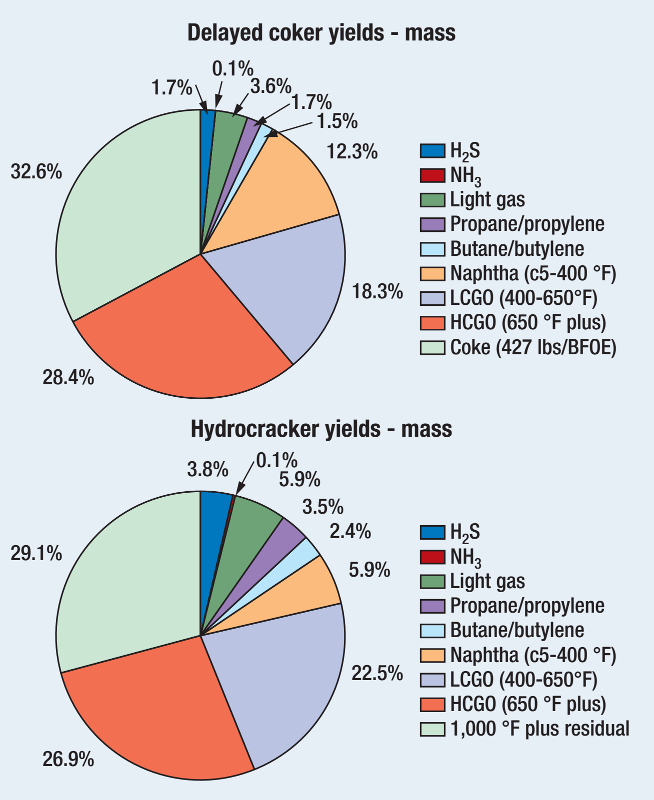

FIG. 5 Delayed coker and hydrocracker yields.

Delayed coker and hydrocracker yields

	Delayed coker	Hydrocracker
H_2S, %	1.7	3.8
NH_3, %	0.0	0.1
Light gas, %	3.6	5.9
Propane/propylene, %	1.7	3.5
Butane/butylene, %	1.5	2.4
Naphtha (C_5–400°F), %	12.3	5.9
LCGO (400°F–650°F), %	18.3	22.5
HCGO (650°F plus), %	28.4	26.9
Coke or residual, %	32.6	29.1

Other catalyst replacement technologies. Catalyst replacement is not limited to ebullated-bed units, and several technologies offer replacement in a bunker-type operation for a trickle-bed design.[12–14] These processes typically have lower conversion targets since catalyst replacement is at a lower rate. The VR conversion is also expected to be thermal and is a function of the space velocity and temperature.

Emerging technologies. Although we are focusing on ebullated-bed processes for VR destruction, several new processes are being brought to market. These processes use a fine catalyst in a slurry instead of the ebullated-bed extrudates.[8–11] The process claims are improved conversion, along with lower investment and operating costs. The slurry catalyst having a smaller particle size is believed to reduce the transport effects between the large residual molecule and the catalyst pore. Incorporated into the new technologies are improved catalysis that increases activity, reduce sedimentation and allow lower operating temperatures or pressures for initial conversion of residual. These technologies are still believed to achieve the conversion via thermal cracking, and the catalyst improvements are in hydrogenation activity.

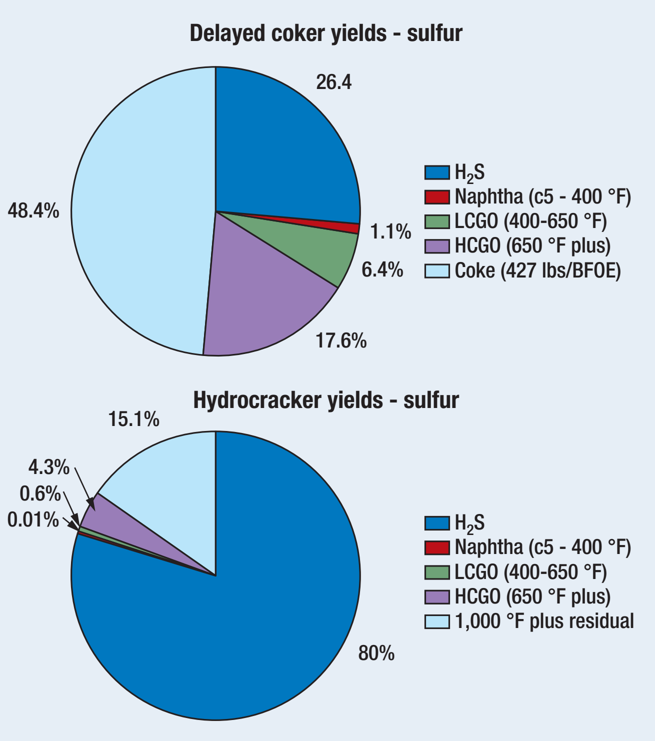

FIG. 6 Coker and hydrocracker sulfur balance.

Yield comparison. The mass yields were developed using the protocols discussed in the preceding sections. A comparison shows the mass yield distributions are similar between the delayed coker and the residual hydrocracker units, as shown in Fig. 5. The comparison shows that the yield distribution is nearly identical for the two processes. The major difference is the hydrogen addition to the lighter fractions instead of hydrogen removal.

Sulfur balance. In the hydrocracker, most sulfur is hydrogen sulfide (H_2S) due to the catalytic activity of the process. Products do not meet the clean fuels specifications for sulfur but the liquid products (C_5 to 1,000°F) have about 5 wt% of the total sulfur. The remaining sulfur content is in the gas phase as H_2S. Additional hydrotreating is needed to meet clean fuels specifications. In the delayed coker, sulfur mostly reports to the coke and H_2S. Liquid products have about 25 wt% of the total sulfur and require additional hydrotreating to meet clean fuels specifications, as shown in Fig. 6.

Nitrogen balance. In hydrocracking, the nitrogen mostly concentrates in the residual bottoms product. Nitrogen is concentrated in the asphaltenes and are difficult to remove via hydrotreating. Nitrogen removal achieved in the form of ammonia (NH_3).

In coking, the nitrogen mostly reports to the coke because nitrogen is concentrated in the asphaltenes. Relatively small amounts of NH_3 remain, because there is no hydrotreating or free hydrogen reactions. Nitrogen content is higher in the liquid products (approximately twice the hydrocracker), as shown in Fig. 7.

Carbon and hydrogen balance. Hydrocracking is a hydrogen-addition process, but the carbon is still rejected to the heavy residual stream. Carbon rejection (1,000°F plus stream) is a function of conversion and catalyst life. The delayed coker is a carbon rejection process with a high concentration of carbon leaving with the coke. As shown in Figs. 8 and 9, the liquid products are carbon rich and are generally aromatic. The hydrocracker injects hydrogen into the balance and both saturates the residual bottoms and removes sulfur and nitrogen from the liquid products (Fig. 10).

Liquid product quality. The hydrocracker yields are much less aromatic and have been hydrotreated. As summarized in Table 4, coker products have lower sulfur and nitrogen levels with the coke receiving a greater portion of the contaminates—despite the lack of hydrogen and active removal of sulfur and nitrogen.

Configurations. Conversion in delayed coking and hydrocracking are both via thermal-cracking kinetics. Most heavy-oil streams must undergo multiple refining steps to produce finished products. The economics favor a multi-step process and capitalize on the strengths of both processes. Other issues that can play in the analysis and economics are:

- Conversion in the hydrotreater
- Hydrogen availability
- Coke disposal—market value
- Product margins (diesel vs. gasoline market).

Options. The conversion in hydrocracking and coking are both thermal kinetically driven. The yield difference is primarily in the production of liquid fuel oil (hydrocracking) or coke (delayed coking). The future opportunity for hydrocracking catalyst development may allow a yield shift due to the catalyst cracking activity. At this time, in residual hydrocracking, the yield shift has not been observed. **HP**

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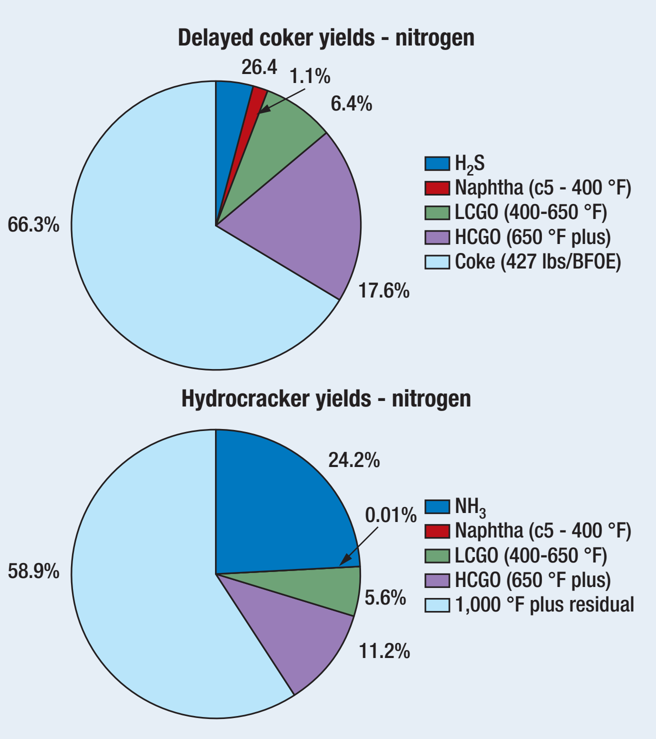

FIG. 7 Coker and hydrocracker nitrogen balance.

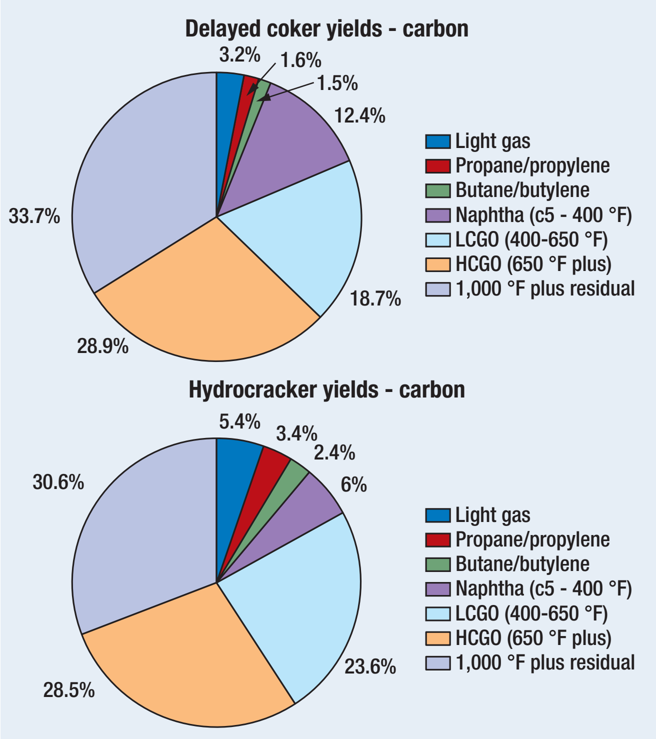

FIG. 8 Coker and hydrocracker hydrogen balance.

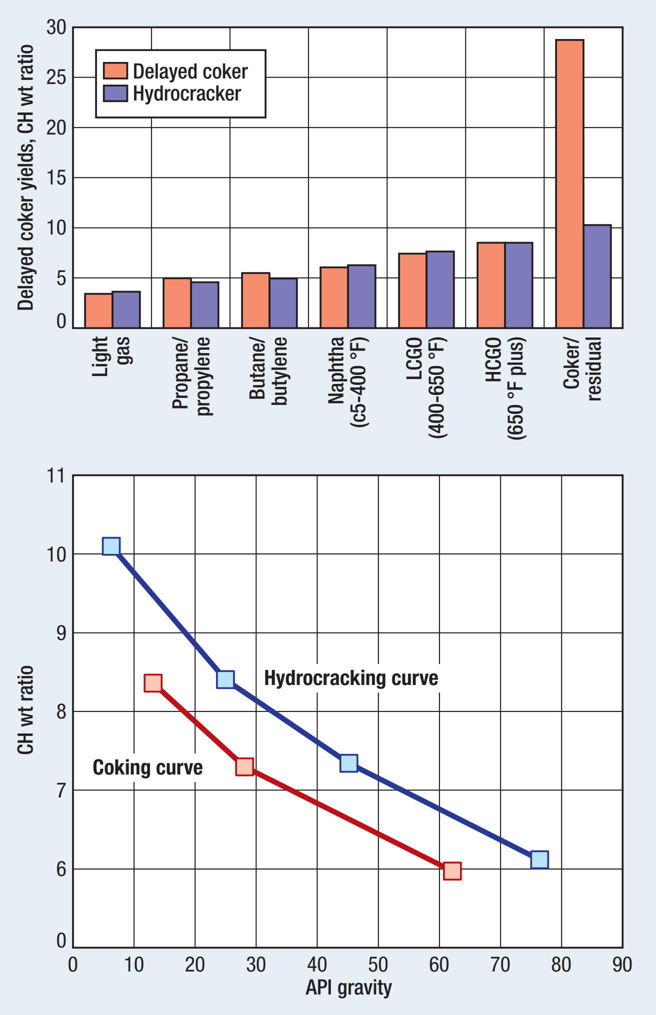

FIG. 9 Carbon to hydrogen ration for delayed coker and hydrocracker.

TABLE 3. Ebullated-bed operating conditions

Condition	Range
Reactor temperatures, °F	770–825
Reactor outlet pressure, psig	1,620–2,650
Reactor hydrogen outlet pressure, psia	1,100–1,850
Conversion range, % @ 975°F	55–80
Hydrogen consumption, SCFB	760–1,700
HDS, wt%	60–85
HDCCR, wt%	40–70
HDM, wt%	65–88

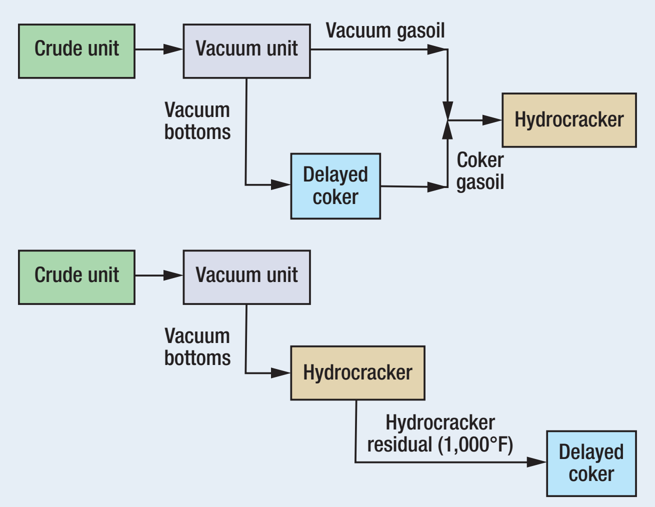

FIG. 10 Configurations

TABLE 4. Liquid product quality comparison

	Delayed coker			Hydrocracker		
Liquid products	API gravity	Sulfur, Wt%	Nitrogen, ppm	API gravity	Sulfur, Wt%	Nitrogen, ppm
Naphtha (C_5–400°F)	62.5	0.5	630	76.6	0.0	6
LCGO (400°F–650°F)	28.3	2.1	2,358	45.4	0.1	976
HCGO (650°F$^+$)	13.5	3.7	3,712	25.7	0.7	1,628
1,000°F plus residual	N/A	8.8	10,813	7.2	2.3	7,919

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