

Crude Oil Quality Group Meeting in Chicago on June 7, 2007

Latest Refining Advances to Process HACs and BOB

Presented by
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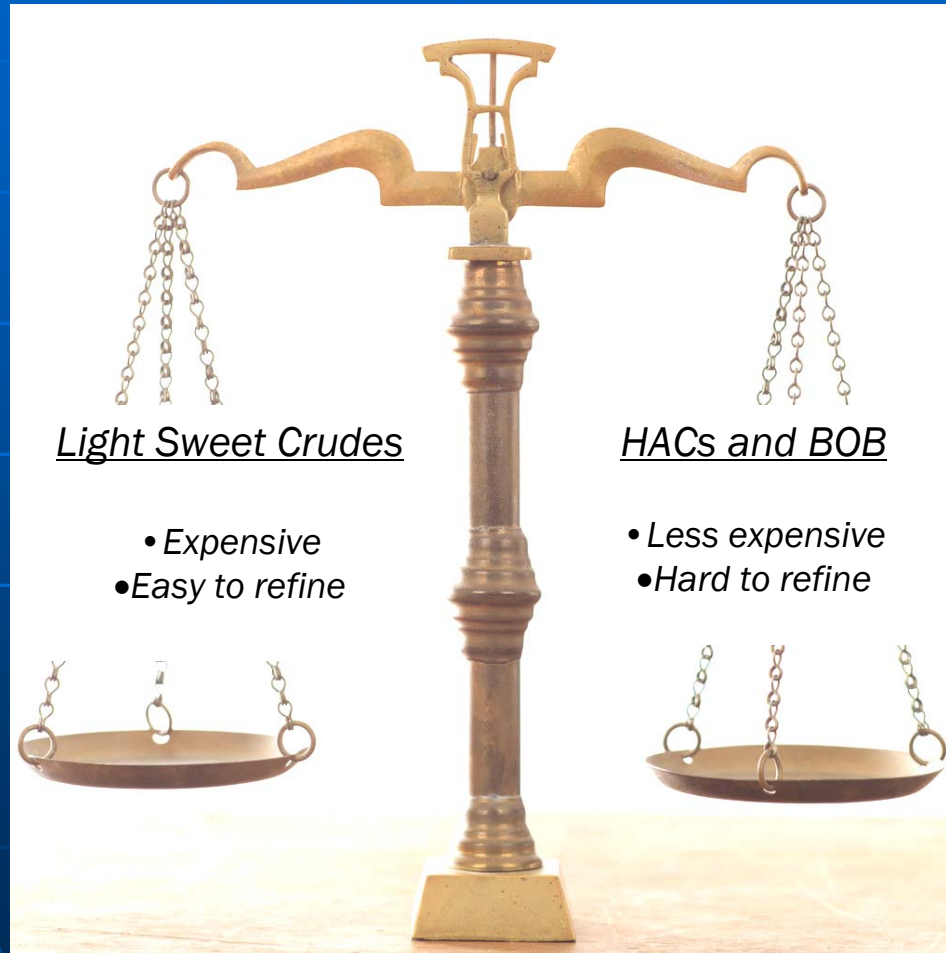
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The purpose of this presentation is to give an overview of the latest technologies in processing opportunity crudes, such as high-acid crudes (HACs), and heavy and extra-heavy oils containing disproportionate amounts of bottom-the-barrel (BOB) fractions.

The presentation covers the following.

- General concerns over HACs
- HACs' impacts on individual processing units and the solutions
- General concerns over heavy oils and extra-heavy oils
- BOB upgrading technology advances:
 - Crude Distillation
 - Solvent Deasphalting
 - Coking
 - Visbreaking
 - Resid FCC
 - Resid Hydroprocessing
 - Unconventional Treating and Upgrading Technologies
- Conclusions

The primary driving force for processing HACs and BOB is to achieve consistently high refining margins in light of many uncontrollable factors, i.e. oil prices, economic conditions, and governmental regulations.



Basically, five types of crudes available to refiners around the world:

Crude Type	°API	S, wt%	Bottoms, vol%
Light Sweet	>30	≤0.5	<50-60
Light Sour	>30	>0.5	<50-60
Heavy Sweet	≤30	≤0.5	>50-60
Heavy Sour	≤30	>0.5	>50-60
Extra Heavy (from oilsands and bitumen)	<15	>0.5	>60

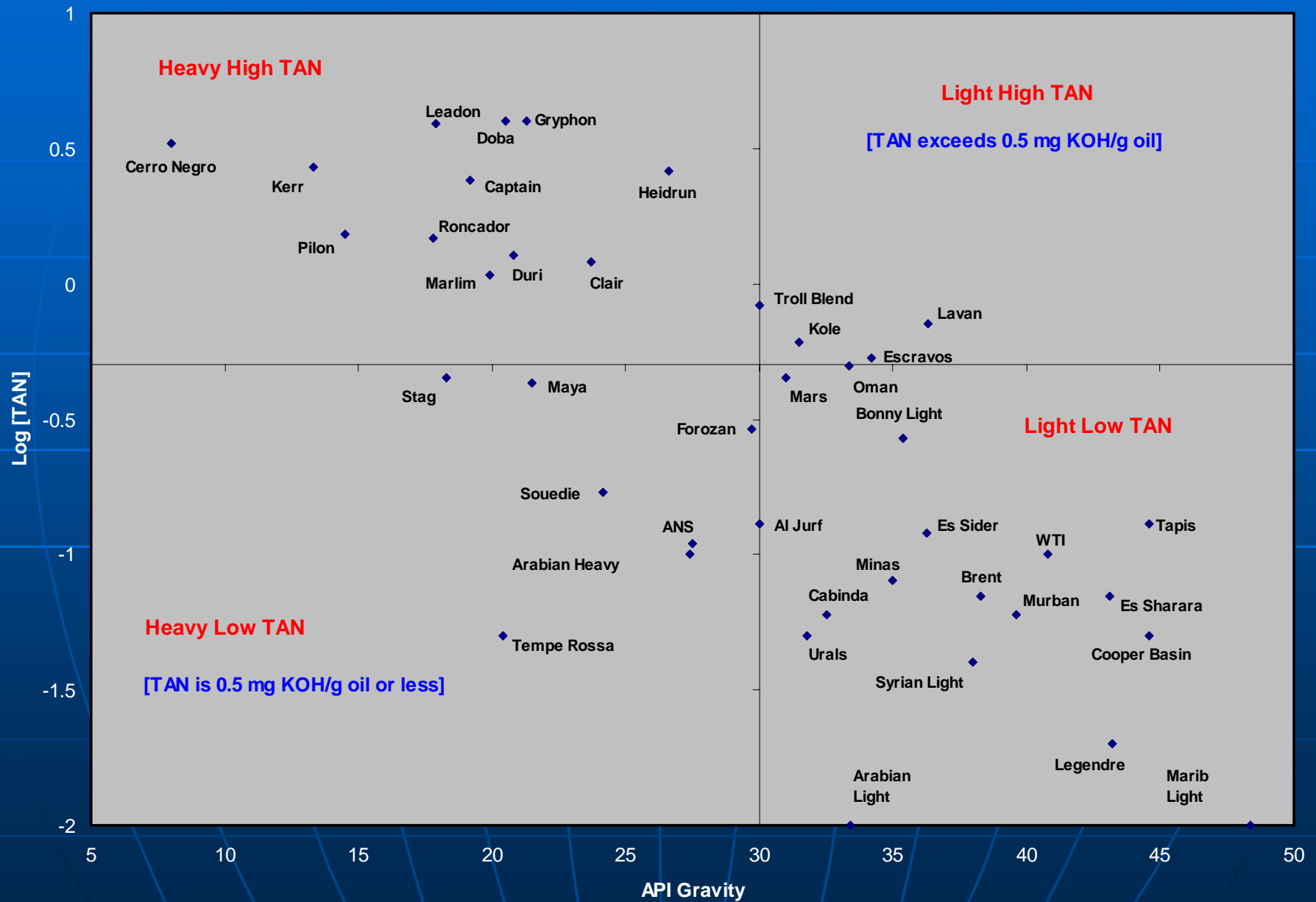
High-acid crudes: neutralization number or Total Acid Number (TAN) exceeding 0.5-1.0 mg KOH per gram of oil.

Qualities of crudes commonly processed in refineries around the world.

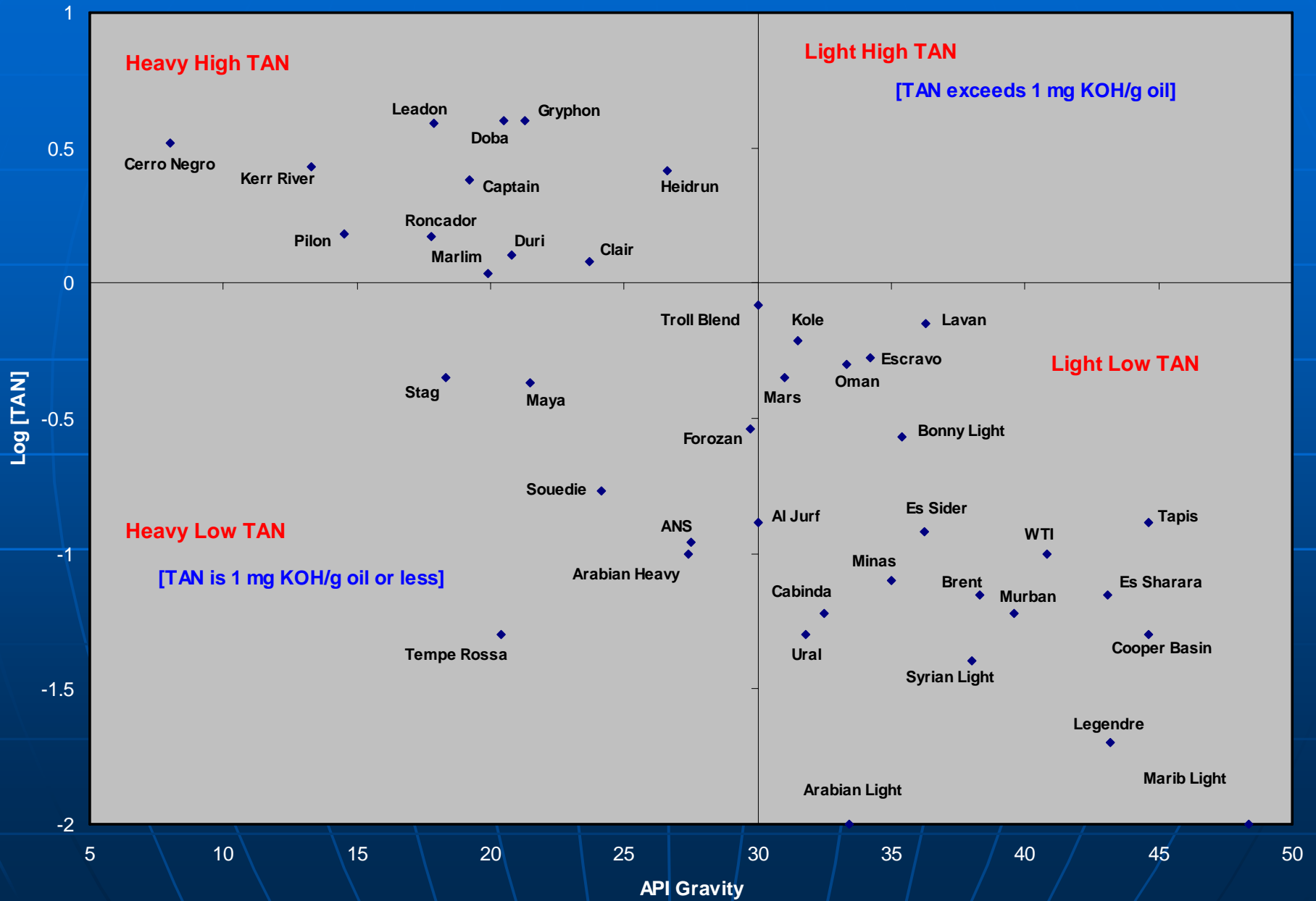
Sulfur vs. API Gravity



TAN (0.5 mg KOH/g) vs. API Gravity



TAN (1.0 mg KOH/g) vs. API Gravity



General Concerns over HACs

- High concentrations of naphthenic acid (NA) can adversely impact the reliability and operations of the refinery.
- Commonly reported problems are corrosion, desalter glitches, fouling, catalyst poisoning, product degradation, and environmental discharge.
- Diesel produced from HACs has a low cetane number.

Common Practices to Handle HACs

- Use methods to predict the corrosion behavior of crudes and their relative risk levels.
- Inspect and monitor equipment to identify specific areas that are at risk for NA corrosion and to verify that control methods are being used effectively.
- Apply corrosion control methods, including crude blending, corrosion inhibitors, suitable metallurgy, process changes and modification or removal of naphthenic acids.
- Alloys like 316 SS and 317 SS are often used as upgrading metal, but there are others that are even more resistant to NA corrosion.
- Modifying or removing naphthenic acids through neutralization, decarboxylation, hydrotreating, and extraction are means that are in use and/or being developed further.

Solutions to Mitigate HACs' Impacts on Individual Processing Units and products

At the refinery, NAs are implicated in increased fouling in desalters, corrosion of the distillation units, operational problems in downstream units like hydrotreaters, FCCUs, and lube plants, as well as hindrance to compliance with environmental regulations via undesirable impacts on waste water treatment facilities.

Desalter

Impacts	Solutions
Poor salt removal and separation of oil and water.	<ul style="list-style-type: none"><li data-bbox="905 659 1570 797">• Remove NAs and calcium salts prior to desalter. Focus on ARN acids.<li data-bbox="905 813 1633 1000">• Use a multi-component additive package to break the emulsion, solubilize calcium, and inhibit scale and corrosion.<li data-bbox="905 1016 1570 1105">• Blend HAC with a lower-density crude.

Crude Preheat Train Heat Exchanger

Impacts	Solutions
<ul style="list-style-type: none">• Fouling reduces plant capacity.• Reduced heat transfer increases operating costs.	<ul style="list-style-type: none">• Improve desalter performance.• Analyze crude blends for potential destabilization of asphaltenes.

Crude Distillation

Equipment	Impacts	Solutions
Distillation unit furnace	Naphthenic acid corrosion of furnace tubes and transfer lines.	<ul style="list-style-type: none"> • Upgrade metallurgy. • Use corrosion inhibiting additives. • Monitor susceptible areas (e.g. elbows) for corrosion.
	Fouling of furnace tubes.	<ul style="list-style-type: none"> • Use asphaltene dispersant. • Improve desalter performance
	Increased coking.	Improve desalter performance.
Distillation columns	Naphthenic acid corrosion of structured packing in vacuum column.	<ul style="list-style-type: none"> • Use metallurgy with at least 2.5% Mo. • Inject corrosion inhibitor into the HVGO return and into the spray oil return below the HVGO draw tray.
Distillation unit side cut piping	Naphthenic acid corrosion.	<ul style="list-style-type: none"> • Upgrade metallurgy. • Use corrosion inhibiting additives. • Monitor susceptible areas (e.g. elbows) for corrosion.

Crude Distillation (Continued)

Equipment	Impacts	Solutions
Lines for feeding vacuum column bottoms to other units	Naphthenic acid corrosion.	<ul style="list-style-type: none"> • Upgrade metallurgy. • Use corrosion-inhibiting additives. • Monitor susceptible areas (e.g. elbows) for corrosion.
Distillation column overheads	Corrosion by light carboxylic acids and CO ₂ in condensate water.	<ul style="list-style-type: none"> • Imidazoline inhibitors for low concentrations of acid. • Modify tower trays to prevent accumulation of water.
	Increased HCl corrosion due to NA-enhanced hydrolysis of chlorides.	Adequate desalting and water removal.
Offgas lines in atmospheric units, vacuum unit gas compression systems, and coker gas recovery systems	Decomposition of naphthenic acids can lead to plugging by deposits of ammonium carbonate and/or bicarbonate.	Remove naphthenic acids upstream of the distillation units.
Storage tanks for distillation tower bottoms	Fouling.	Use dispersant.

Coker

Equipment	Impacts	Solutions
Coker furnace	Increased coking.	
Coker unit	Naphthenic acid corrosion due to NAs in the vacuum resid.	Modify or remove the naphthenic acids from the resid.

Fluid Catalytic Cracking

Impacts	Solutions
Degradation of catalyst activity by calcium.	Improve desalter performance.
Naphthenic acid corrosion in distillation unit increases metal content of FCCU feed, reducing both throughput and catalyst life.	Control naphthenic acid corrosion in the distillation unit.

Hydroprocessing

Impacts	Solutions
Naphthenic acid corrosion in feed line upstream of hydrogen injection.	<ul style="list-style-type: none">• Upgrade metallurgy to Mo alloy.• Use recycle hydrogen with H₂S.
Iron sulfide deposits can plug catalyst beds and promote dehydrogenation reactions.	<ul style="list-style-type: none">• Use corrosion inhibitor upstream to reduce iron content in feed.• Eliminate fouling by injecting an organic polysulfide.• Use an upstream reactor vessel filled with catalyst as a filter.
Fouling and deactivation of hydrotreater catalyst by phosphorus-containing corrosion inhibitors.	Reduce or eliminate use of such inhibitors.

Fixed-Bed Sweetening Unit for Distillates and Gas Oils

Impacts	Solutions
Plugging.	Neutralize and remove the naphthenic acids upstream.

Lube Extraction

Impacts	Solutions
Naphthenic acid corrosion.	Upgrade metallurgy.

Waste Water Treatment

Impacts	Solutions
Crude oil carryover into desalter water effluent.	Improve desalter performance.

Refined Products

Product	Impacts	Solutions
Distillate fractions	•High acid content leads to color problems and haze.	Apply hydrotreating, caustic extraction, or a solid extractant like silica gel.
	•Diesel fractions have low cetane.	Use a cetane improver or blend in some gas oil with higher cetane.
Diesel fuel	•Increased iron content.	Control naphthenic acid corrosion in the distillation and hydroprocessing units.
	•Low cetane index.	Use cetane improver or blend in a higher-cetane gas oil.
Kerosene and jet fuels	•High acid content leads to color problems and haze.	Apply hydrotreating, caustic extraction, or a solid extractant like silica gel.
Fuel oils	•High levels of calcium lower the product's value.	Improve desalter performance.
Coke	•High levels of calcium lower the product's value.	Improve desalter performance.

General Concerns with Heavy Oils and Extra-Heavy Oils

Major concerns are blending and mixing

Many US refineries are short on crude tankage. It is common for crudes (e.g. LLS, WTI, and ANS) from multiple fields to be mixed in pipeline systems. These crudes have different compositions, and there are economic penalties for that variance.

Asian refiners that often process waxy crudes may have problems accepting heavy crudes from Canada and Venezuela, because there are incompatibilities between the high-asphaltene crudes and the high-paraffinic crudes. Heavy, aromatic crudes are often separated from light, paraffinic crudes to avoid asphaltene precipitation.

General Concerns with Heavy Oils and Extra-Heavy Oils (Continued)

Reported unit problems and common practices to handle incompatibility

- Catastrophic fouling and coking in the preheat train, caused by crude oil incompatibility and the precipitation of asphaltenes on the blending of crudes, can result in net economic loss.
- Common problems are stable water emulsions in the desalter, fouled preheat exchangers, and/or coking in the pipestill furnace tubes. Use the oil compatibility model and tests to predict the proportions and order of the blending of oils. It helps prevent incompatibility prior to the purchase and scheduling of crudes.

BOB Processing Technology Advances

BOB upgrading can be undertaken using combinations of separations (distillation or deasphalting), thermal processing (coking or visbreaking), fluid catalytic cracking, or hydroprocessing.

Crude Distillation

- When crude blends get heavier, atmospheric and vacuum tower distillate cut points tend to suffer due to the increasing difficulty of vaporization.
- Changes can be made such as increasing the temperature and residue stripping efficiency, lowering the pressure and flash zone oil partial pressure, and modifying the pumparounds.
- For the atmospheric unit, other key areas include the oil preheat train and charge furnace, column internals, and metallurgy of the unit exposed to higher sulfur and high TAN.
- For the vacuum towers, evaluations should be made regarding furnace sizing and outlet temperature, decoking capability, wash-zone capacity, and steam requirement (if it is a wet column).
- One of the first and most attractive options is deep-cut vacuum distillation via a revamp of the unit to cut deeper into the resid to make additional FCC or hydrocracker feed.

Solvent Deasphalting

- Solvent deasphalting (SDA) units separate the high-quality, lighter paraffinic fraction from vacuum resid to be used as a feed for traditional FCC and hydrocracking units.
- HACs can be processed directly from atmospheric tower bottoms.
- The latest SDA unit designs include application-specific extraction devices, the optimal design of heat-exchange systems, the lowest solvent-to-oil ratios, supercritical solvent recovery, and multiple product recovery.
- Large-volume throughput to save both capital and operating costs is critical to achieve maximum efficiency. Therefore, the towers tend to have low length/diameter ratios and trays instead of packings.

Solvent Deasphalting (Continued)

- The deasphalted oil yield is increased if butane or pentane is used instead of propane, though more metals and Conradson carbon are found in the product.
- It is advantageous to integrate deasphalting with visbreaking, coking, or hydroconversion due to a molecular limitation to heavy oils separation undertaken by deasphalting. The result is a very heavy pitch, which is basically asphaltenes and contains most of the metals, nitrogen, and coke precursors.
- Potential new outlets for the asphaltenes are feedstock for gasification units and pelletization for shipment as a solid fuel.

Delayed Coking

- This carbon rejection technology is the most popular way to upgrade residual oils.
- The pitfall of delayed coking is that only 70-80% of the total heavy oil barrels are converted into valuable transportation fuels, while the remaining portion is downgraded to less valuable coke.
- There are three limitations to achieving higher liquid yields: (1) secondary cracking of valuable volatile liquid products, (2) a combination of smaller-ring aromatics to form polynuclear aromatics, and (3) the formation of PNAs via aromaticization of hydroaromatics.

Delayed Coking (Continued)

- To minimize the secondary cracking of volatile liquid products, a coker reactor with a very short vapor residence time but a lengthy resid residence time to achieve complete conversion to coke of 100% CCR is preferred. The latter two limitations can be minimized by separating the higher-quality fraction of the resid prior to coking.
- The latest developments in conventional delayed coking technology emphasize design and operation of major equipment (e.g. coke drums, heaters, and fractionators), coke quality and yield flexibility, and operability and safety.
- Research work and patent activity focus on the effect of feedstock quality on coker product yields.

Visbreaking

- Originally used to reduce the resid viscosity for meeting heavy oil specs.
- Nowadays, it cracks straight-run fuel oil into valuable gasoline and gas oil and produces residual fuel oil to be sold as marine fuel.
- As the operating severity is raised to maximize conversion, coking and fouling also increase and the stability of the visbroken resid and, consequently, the stability of the heavy fuel oil decrease. Research established that coke formation is a function of the production of condensed PNA hydrocarbons.
- Two of the patented approaches for dealing with this problem include the use of a catalyst to activate existing hydrogen in resid feeds and the addition of hydrogen-donor streams to the feed.

Resid Fluid Catalytic Cracking

- RFCC offers better selectivity to higher gasoline and lower gas yields than coking or hydroprocessing, though it needs higher-quality feeds (e.g. mixtures of VGO and atmospheric resids and CCR limited to 3-8 wt%) than the other two processes.
- Nowadays, as many as 75% of FCCUs worldwide process feedstock consisting of some resid. From the standpoint of refinery profitability, the benefit of resid upgrading is that it offers a way to reduce fuel oil output and produce greater volumes of valuable products without processing larger amounts of crude.
- Important operating parameters for resid operations are feed temperature, reactor temperature, dispersion steam, stripping steam, rate of heat removal, recycle rates, CO production, and catalyst selection.

RFCC Catalyst Advancements

- Catalyst matrices are being designed to provide coke-selective bottoms cracking and reduction of the dehydrogenation activity of contaminant nickel and vanadium.
- Certain pore structures do not limit access of large hydrocarbon molecules to active cracking sites, but do permit rapid exit of product molecules so as to prevent secondary cracking to less valuable materials.
- Catalyst suppliers have developed more sophisticated and controlled ways of putting their products together, even to the extent of being able to tailor catalysts for more specific applications.
- The latest catalyst research shows interest in fluoride salts, crystalline aluminosilicate zeolite in an inorganic oxide matrix, an outboard vessel containing a vanadium trap, and so on.

Recent RFCC Process and Hardware Developments

- RFCC design includes two-stage regeneration, mix temperature control, and/or catalyst coolers in order to control unit heat balance and to recover some of the heat for steam production.
- Other areas of focus include feed injection nozzles and catalyst strippers, along with the riser (to minimize slip) and the termination device (to reduce the secondary reactions in the dilute phase).
- Improved injection and stripping are needed to meet the challenge of getting a high conversion of heavier feeds to valuable products.

Recent RFCC Process and Hardware Developments (Continued)

- High dispersion of feed maximizes cracking on the catalyst's active sites.
- More effective stripping reduces the hydrocarbon load on the spent catalyst, keeps the regeneration temperature down, and increases conversion.
- A vendor is working on a compact novel design that combines the reactor and regenerator in a single pressure vessel.

Resid Hydroprocessing

- Hydroprocessing (or hydroconversion) offers better liquid yields (as high as 85%) than commercial coking's 50-60%.
- It makes up about 20% of global BOB upgrading capacity, and can take several forms depending on the purpose.
- Resid hydrotreating (RHT) improves quality for product blending or additional processing, whereas resid hydrocracking (RHC) is the most rigorous form of hydroconversion.

Resid Hydrotreating

- Hydrotreating of atmospheric resid ahead of an RFCCU has gained popularity as a way to reduce fuel oil production.
- RHT and coking in combination may be a preferred route based on metals and concarbon contents of the resid.
- High-conversion facilities with upgraded hydrotreating capabilities using higher-activity catalysts are the most effective plant configurations.
- RHT has several issues: high pressure (200 bar), high hydrogen requirement, metal contamination, a short catalyst life due to fast poisoning rate, diffusion of asphaltenes through small catalyst pores, and deposition of coke and sediment downstream of the reactor in hot and cold separators. Process designers are currently focusing on innovative, new technology to eliminate these drawbacks.

Resid Hydrotreating (Continued)

- Several catalyst companies have introduced new resid HDM, transition, and HDS catalysts in the past few years.
- Because of the importance of protecting downstream cracking catalysts, particular focus has been given to the development of HDM catalysts with optimized alumina pore systems that provide high metals capacity and activity.
- Meanwhile, a research institute said its "Butterfly" extrudate RHT catalyst offers good HDM and HDS activities as well as a long life in treating RFCC feedstocks.

Resid Hydrocracking

- Resid hydrocracking catalysts used in ebullated-bed processes need to be multifunctional, i.e. performing the simultaneous removal of metals, sulfur, and carbon residue as well as the hydrocracking of vacuum bottoms.
- Recent work in RHC catalysis has focused on pore size distribution to maximize conversion and minimize sediment formation.
- Dispersed catalyst compositions have been patented for use in suspension-bed reactors to prevent coke formation. The key to higher conversion is to design a reactor to maximize the solubility of the converted asphaltenes, and the economics depend on how the unconverted carbonaceous, high-PNA byproducts are used.

Resid Hydrocracking (Continued)

- Efforts are continuing to tackle a tendency for sediment to form when vacuum resid conversion exceeds 50-60%.
- A recent development in processing technology combines slurry hydrotreatment conducted at mild conditions in the presence of a molybdenum-based dispersed catalyst with solvent deasphalting. This slurry process is said to yield higher-quality products than delayed coking or visbreaking, offer greater feedstock flexibility than fixed-bed hydroconversion, and achieve higher conversion than ebullated-bed hydroconversion.
- Integration of hydrotreating and resid hydrocracking offers significant investment benefits to produce ULSD.

Unconventional Treating and Upgrading Technologies

- New process concepts for converting resids and other heavy feeds are at various stages of development ranging from patent coverage only to commercial application.
- These innovations have arisen in response to the criteria of economics, flexibility, and selectivity, where the need for improvement over older processes is seen.
- The new methods also suggest what to expect from future commercial processes in terms of benefits.
- Some processes use an adsorbent to remove coke precursors and metals from resids, and until recently, they have required the use of an added solvent or solvents along with the sorbent. ExxonMobil Research & Engineering Company (EMRE) has developed a sorption process that it claims needs no additional solvent for the sorption itself.

Unconventional Treating and Upgrading Technologies (Continued)

- Given the growing global importance of diesel as a transportation fuel, cracking processes that can produce additional amounts of this fraction from heavy petroleum materials must be of special interest. Patent activity continues to appear for newer developments.
- A process has been patented for converting heavy fuel oils and vacuum resid into stabilized oil-in-water emulsions to mitigate problems with handling and emissions.

Unconventional Treating and Upgrading Technologies (Continued)

- New hydroconversion processes have appeared, including EMRE's Once-Through Mild Slurry Hydroprocessing (O-T MSHP), Genoil's Hydroconversion Upgrader (GHU) and Kobe Steel/Syncrude Canada's extension of a slurry-phase hydrocracking technology formerly used for processing brown coal.
- The heaviest development activity is in the area of thermal cracking. These processes fall into four groups -- one where H donors are involved (IOC acid-enhanced separation of cracked products), a second where the cracking is assisted by the use of a heat transfer medium (EMRE SCT Thermal Cracking), a third using supercritical conditions (KBR Supercritical Cracking), and a fourth where mechanical activation is employed (CPJ process).

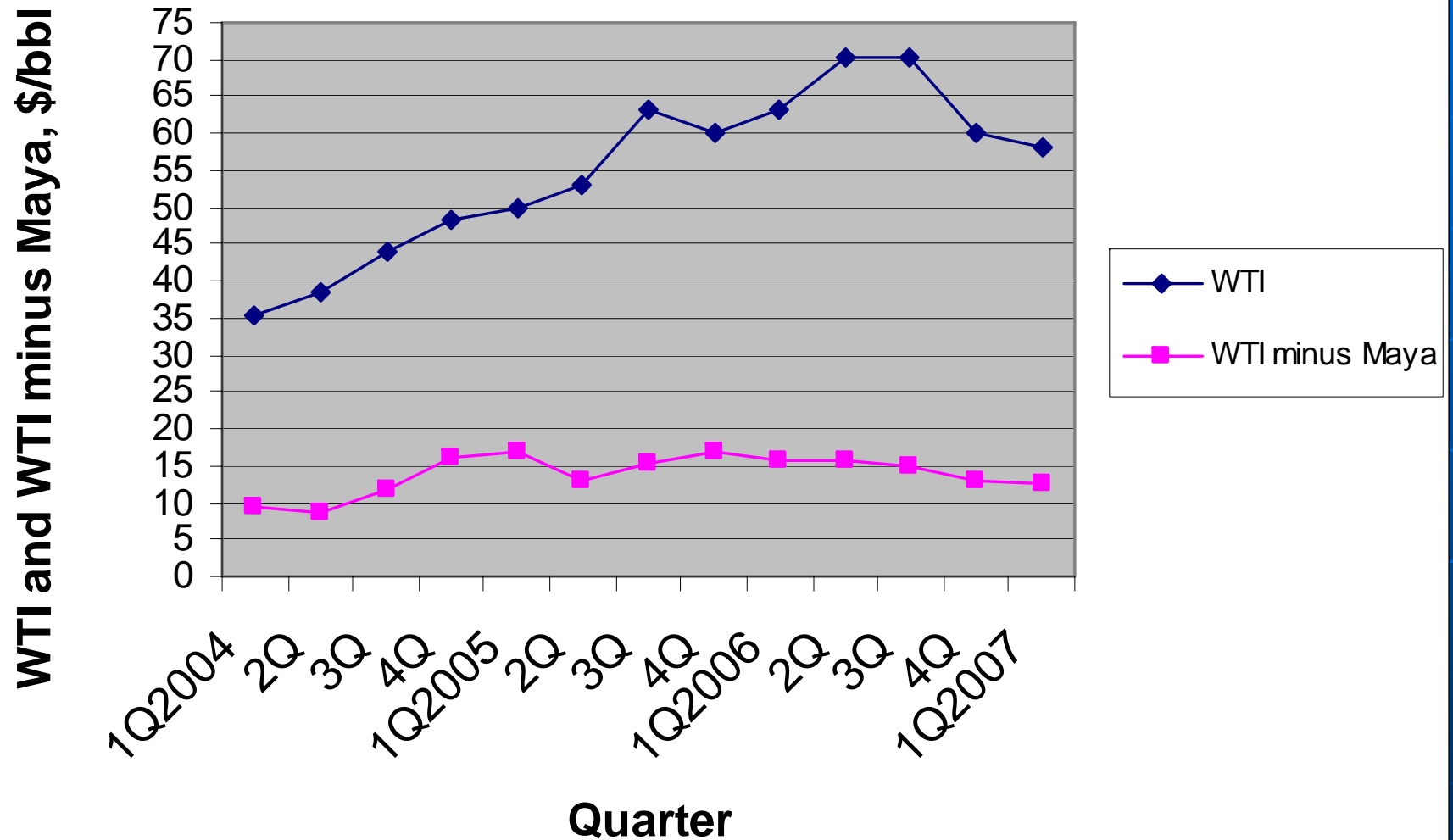
Conclusions

Crude selection is the most important decision refiners must make on a daily basis.

The criteria to determine which crudes to acquire include

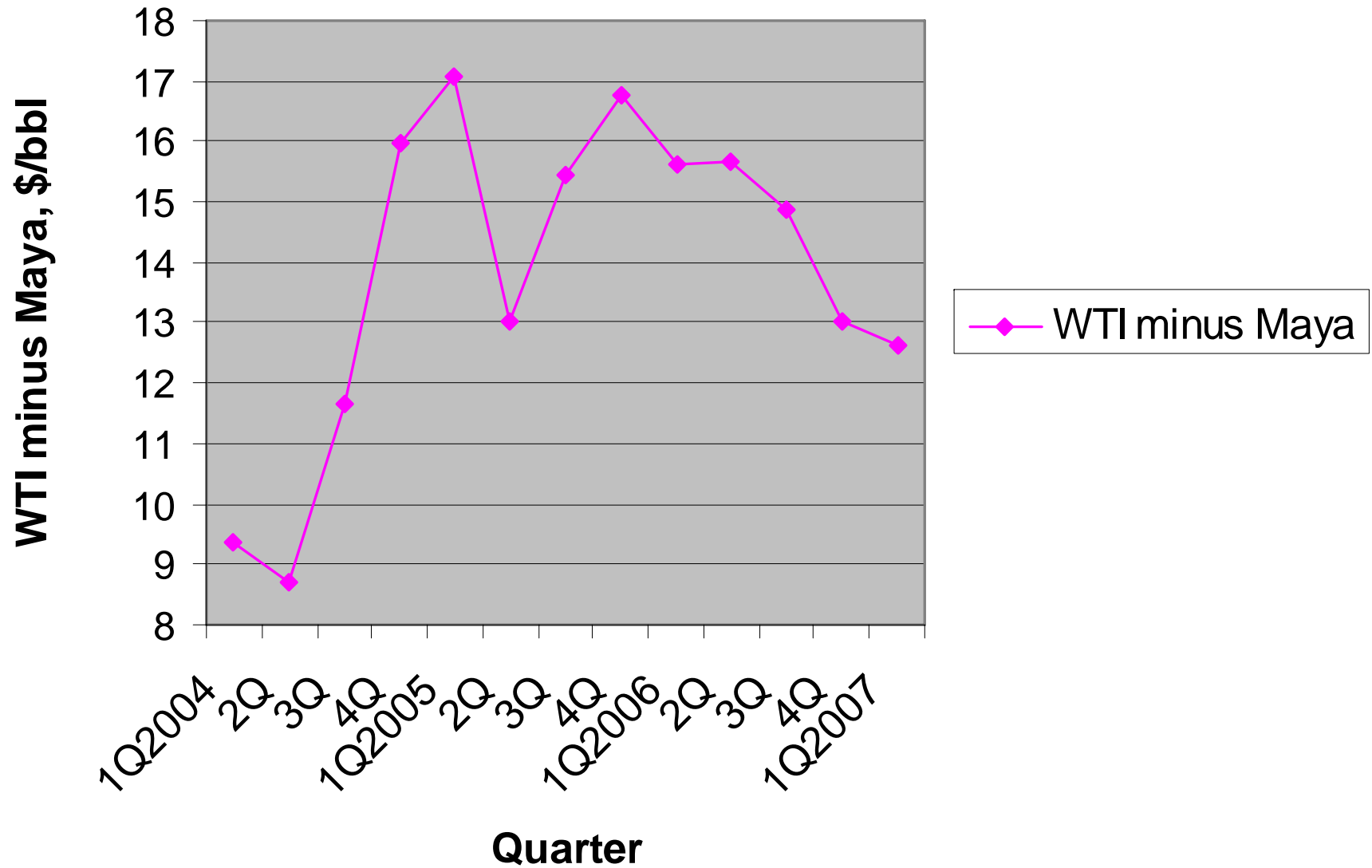
- oil source reliability and term deals,
- delivery advantages,
- discount versus other crudes,
- plant operational flexibility,
- potential processing problems and risks,
- mitigation options and costs,
- environmental concerns, and
- product demand mix.

WTI and WTI minus Maya in 1Q 2004 through 1Q 2007



Source: Valero Energy Quarterly Earning Reports

WTI minus Maya in 1Q 2004 through 1Q 2007



Source: Valero Energy Quarterly Earning Reports

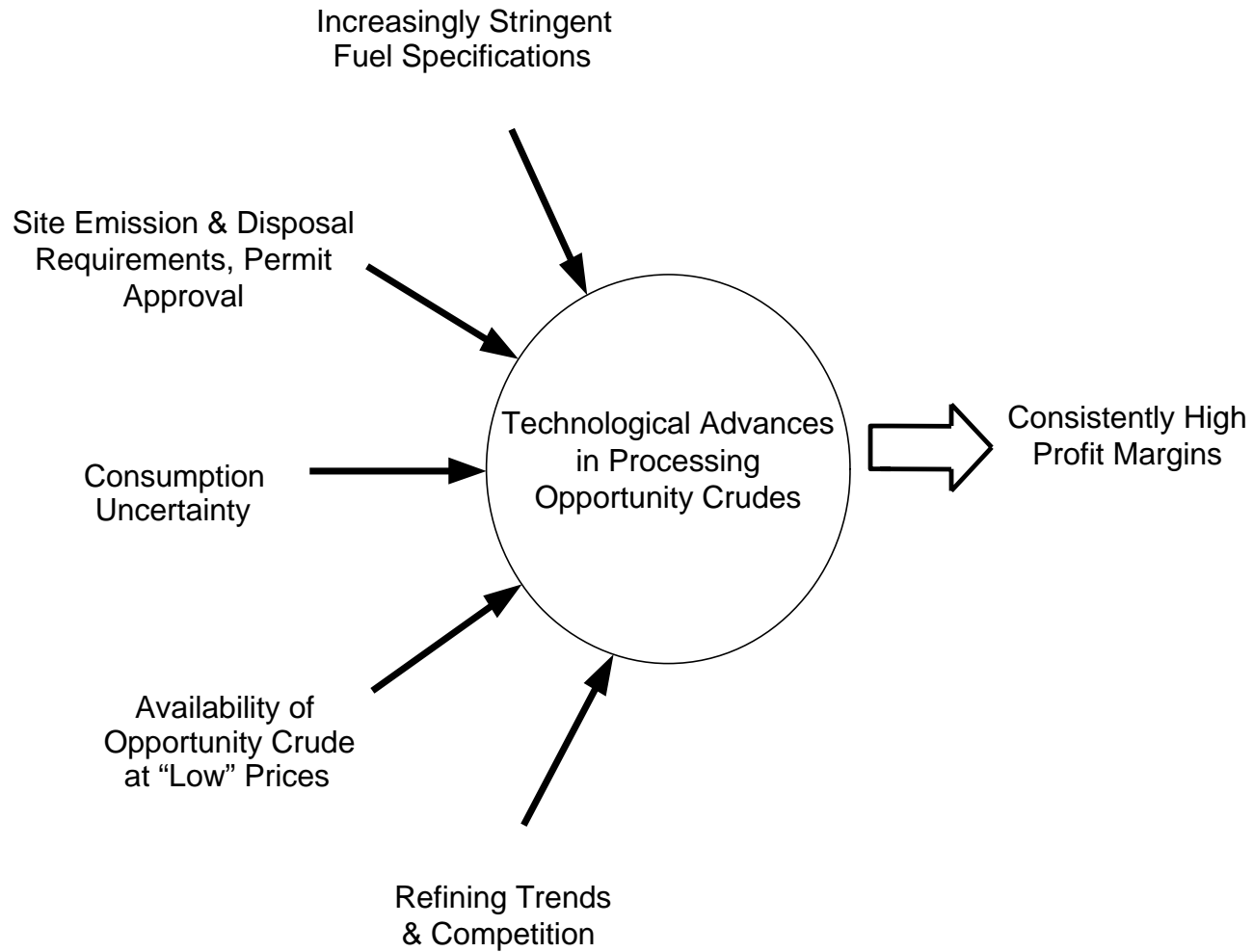
High TAN Crudes Discount to Brent

World Bank's model to calculate the crude discount to Brent based on quality differentials indicates

- API gravity: $0.69¢ \times (\text{Brent Price}) \times (\text{Subject Crude API} - \text{Brent API})$
- Sulfur: $-5.6¢ \times (\text{Brent Price}) \times (\text{Subject Crude Sulfur} - \text{Brent Sulfur})$
- TAN: $-5.1¢ \times (\text{Brent Price}) \times (\text{Subject Crude TAN} - \text{Brent TAN})$.

If one assumes that a crude has 21.1 °API, 1.77 wt% sulfur, and TAN of 1.80 mg KOH/gram of oil, the discount of this crude to Brent (at \$60/bbl) should be \$17.11/bbl.

FACTORS INFLUENCING OPPORTUNITY CRUDE PROCESSING



This presentation is an excerpt from a multi-client strategic report entitled

Opportunity Crudes: Technical Challenges and Economic Benefits

- *Strategies of processing high acid crudes and the bottom-of-the-barrel using advanced technologies.*

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