In favour of HYDROGEN ADDITION

MITRA MOTAGHI, BIANCA ULRICH AND ANAND SUBRAMANIAN, KBR, USA, DISCUSS THE RELEVANCE OF SLURRY PHASE RESIDUE HYDROCRACKING TO TODAY'S MARKET.

While Veba Combi Cracker and slurry phase hydrocracking have been developed and practised for many decades, it is only now that the inherent features of this technology have gained relevance. These features are expected to add significant value to the refining market today. In this article, the authors outline the changing market conditions, economics and product qualities, and correlate their alignment with the strengths of this technology.

Market trends

In the face of soaring crude oil prices, depressed natural gas prices and impending new regulations, refiners are presented with an unprecedented situation of addressing low margins by reevaluating their resid processing options. The ability to reliably eliminate fuel oil production, maximise high quality distillate yields from every barrel of crude, and achieve a truly bottomless status, is critical for sustaining the value of the installed assets in the years to come.

In its simplest form, refining is a process of changing the carbon to hydrogen ratio of naturally occurring crude oils. At a molecular level, the operation of all 650 refineries in the world is essentially targeted at converting high carbon to hydrogen ratio feedstocks into high hydrogen to carbon ratio transportation fuels. This change in ratio between the crudes and products can only be accomplished through the rejection of carbon molecules or the addition of hydrogen molecules.

Carbon rejection is favoured by low crude prices and high hydrogen prices, when it is economical to reject the residuum as petroleum coke, while producing the required transport fuel volumes by incremental crude oil processing. Hydrogen addition is favoured by high crude prices and low hydrogen prices, when it is more economical to upgrade the residuum to transport fuels, while maximising the transport fuels production from the base crude capacity.

Crude price fluctuations are subject to a number of factors including global economics, supply and demand relationships, geopolitical issues, natural and manmade disasters. The hydrogen price in most territories is determined by the price of natural gas, the principle feedstock for hydrogen production. In essence, the residuum upgrading technology choices for a refiner are invariably linked to these two factors, and all economic analysis clearly point to a transition from carbon rejection to hydrogen addition at US$ 50 - 60/bbl benchmark crude price even when considering a relatively high US$ 10/million Btu natural gas price. Abundant alternative sources of gas are predicted to inhibit growth in domestic and international natural gas pricing for years to come. Projections indicate that both crude and natural gas price are expected to sustain at levels substantially favouring investment in hydrogen addition technologies.

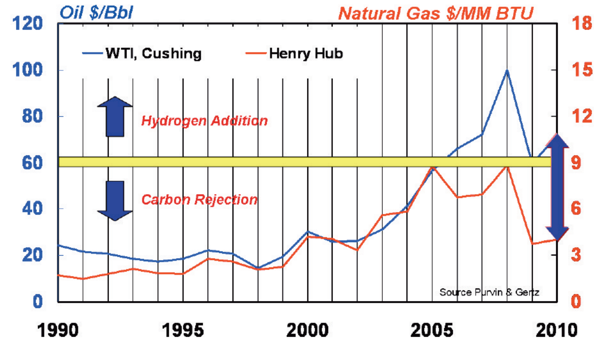

Figure 1. Crude/natural gas price differentials.

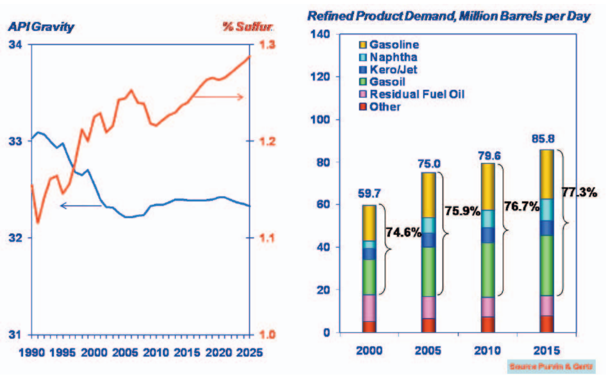

Figure 2. Demand for lighter products increases as crude API drops.

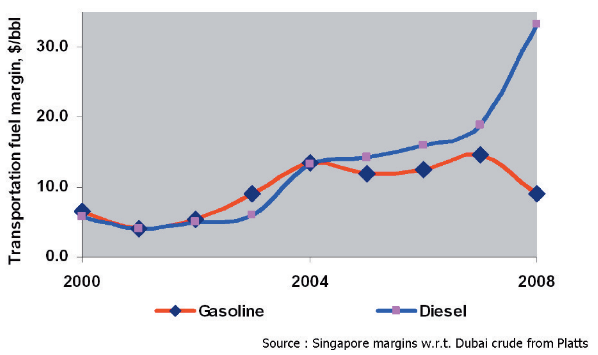

Figure 3. Widening price gap between diesel and gasoline.

Refinery margins are sustained by a combination of three basic factors: the cost of crude, the type of products produced, and the ability to upgrade stranded streams to higher value products.

The cost of crude is the predominant factor in the overall operational economics and accounts for the substantial surge in refinery upgrades targeted at processing cheaper, heavier or more challenging crudes. In most cases, the surge in refinery upgrades is determined by the light heavy differential, which has trended over the past years in favour of heavier crudes, forcing refiners to make modifications to their bottoms processing technologies while taking on a higher percentage of heavy oils in their crude diet.

The combined capacity of all the operating refineries in the world totals to approximately 85 million bpd of crude, with a projected annual 1.0 - 1.5 million bpd growth in crude processing capacity. As is evident from the decreasing API of the composite worldwide crude blend, almost all new crudes entering the market place are substantially heavier than the current crude basket and involve the addition of extra heavy crudes such as Canadian and Latin American bitumens.

As the world's supply of crude oil becomes heavier and contains higher sulfur over time, refiners must invest to meet the growing demand for light, high quality, ultra low sulfur transportation fuels. The overwhelming majority of this investment will be targeted at residuum upgrading. While refiners pay less for heavier crudes, and as the residuum content of these crudes increases dramatically from 10% in light sweet crudes to 50% in extra heavy crudes, the future trends show a substantial increase in residue production enhancing the market space for hydrogen addition based upgrading technologies.

The second determining factor in refinery economics is the quality of the product slate. In a market dominated by FCC units, a predominant trend in most parts of the world, including the US, shows a clear shift toward lower density, higher cetane index, ultra low sulfur diesel production. New investments in refineries already indicate this shift with emphasis on converting existing assets to make diesel. The price differential between diesel and gasoline is likely to be sustained by supply and demand over the long haul and is validated by the billions of dollars of investment announcements by all the major international and national oil companies towards dieselisation.

This is an important consideration for refiners, when making long term, high dollar investment decisions, and the economics clearly point to hydrogen addition as opposed to carbon rejection. The dieselisation benefit is telling, and with the quality requirements favouring higher hydrogen content, hydrogen addition clearly stands out as the technology of choice for the future.

The third major determining factor is the upgrading of stranded streams. Refineries are littered with low value streams that are blended off, often downgrading higher value products for the sole purpose of finding positive outlets for less saleable streams. The bulk of the operating refineries around the world have little or no residuum processing capability and produce large volumes of high sulfur fuel oil

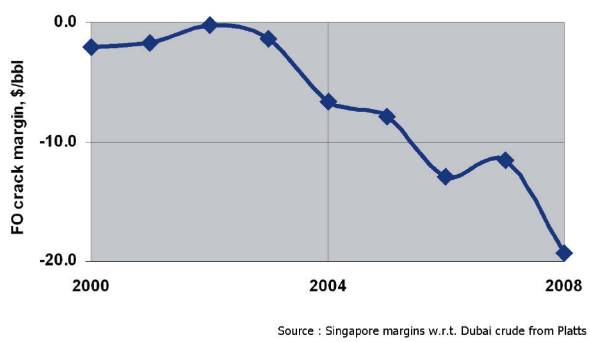

Figure 4. Fuel oil margins are dropping as crude prices increase.

and bunker fuel. As is evident from price trends, producing fuel oil will result in negative refinery economics. It is only expected to worsen as refiners face regulatory pressures ranging from new maritime bunker fuel specifications to carbon dioxide cap and trade and carbon footprint limitations.

As the world's governments move towards cleaner bunker fuels, refiners will be forced to find new ways to deal with the large residuum pool. It is a task that is becoming more pressing as oil producers bring to market increasing amounts of heavy crudes, which cost less, but feature substantial increase in resid content.

While delayed coking has been the technology of choice in the past, its economics are likely to be severely hindered by low yields, poor quality of hydrogen deficient distillate products, low grade coke production, and its impact on and substantial disruption to the existing refinery operations. Although mature with low implementation risks, in a carbon footprint future, this technology will likely face stiff environmental and regulatory resistance even in the face of lower crude prices. In addition, high sulfur petroleum coke prices are expected to remain distressed, and as is evident in the Canadian inland environment, will require piling up in large quantities with no real economic outlets. This trend cannot be sustained in the long run.

Today, the market imposed challenge to refiners is to find a hydrogen addition based resid conversion option whose best case economics are sustained by near complete conversion, high diesel selectivity, Euro V grade products, high reliability, ease of implementation that is achievable at a relatively moderate capital investment.

While refiners have picked at this problem for years, it was not until recently that hydrogen addition technologies capable of transforming all contents of a barrel of heavy crude into clean fuels have been seriously considered as economically viable solutions. This is a consequence of the realisation that this time around, unlike the past, the high crude prices and low gas prices are set by free market supply/demand considerations and are therefore likely to be sustained in the years to come. As is evident by the flurry of new announcements and activities, slurry bed hydrocracking appears to emerge as the technology of choice as a response to this development. While some refiners have resorted to new research and development efforts, others have secured technology positions by leveraging much of the prior research efforts through acquisitions.

The residuum landscape

Residuum oils can be broadly classified by the metals and Conradsons Carbon Residue (CCR) content in these heavy boiling range liquids. This essentially defines the suitability and type of applicable conversion technologies.

Fixed bed hydroprocessing is practised for essentially atmospheric or vacuum residue desulfurisation, and its operating envelope is severely constrained. These units achieve low residue conversions (typically 15 - 20%) and are limited to processing very low metals and CCR containing feedstocks. The high operating pressures and the consequent high investment costs, high catalyst costs and low cycle length, and the relatively low net benefits impose a significant dampening effect on its widespread implementation.

Ebullated bed hydrocrackers can handle higher level metals and CCR, but they are limited in overall conversion (less than 80%). The inability to convert asphaltenes without encountering severe fouling problems, and the necessity to introduce aromatic solvents and high recycle rates to sustain reasonable overall conversion, contribute significantly to the high capital and operating costs. The project economics is further impaired by the need to reprocess the distillate products and to handle the large volume of unconverted residue. In effect, this represents a partial solution, leaving the refiner with several of the same issues, but on a smaller scale that existed prior to undertaking the investment.

Slurry phase hydrocracking, on the other hand, is a robust option that can transcend the entire residue landscape, remain immune to the CCR or metals content in the feed, and result in near complete conversion of the residuum to higher value, lighter distillates. One such slurry phase technology is the Veba Combi Cracker (VCC™), a commercially proven residue upgrading technology suitable for converting 95 wt% of the residues into high quality distillates and is suitable for the refinery, field upgrading, and coal to liquids applications.

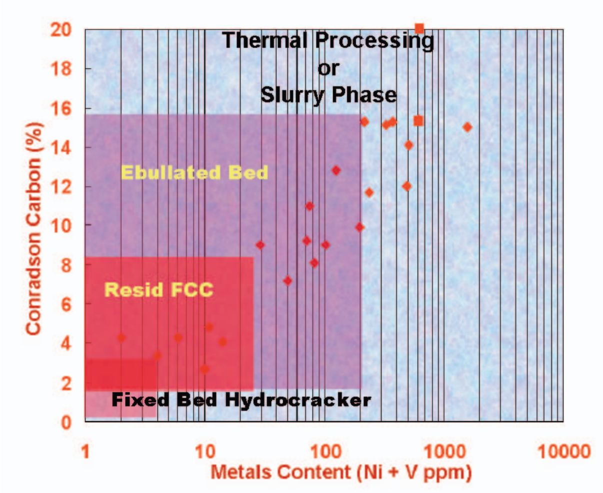

Figure 5. Slurry phase hydrocracking transcends the entire resid landscape.

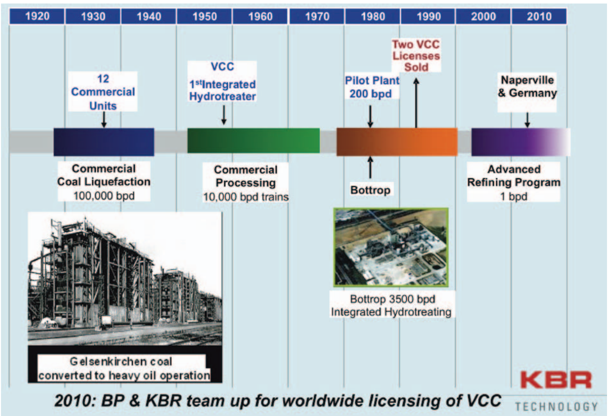

Figure 6. History of the VCC technology.

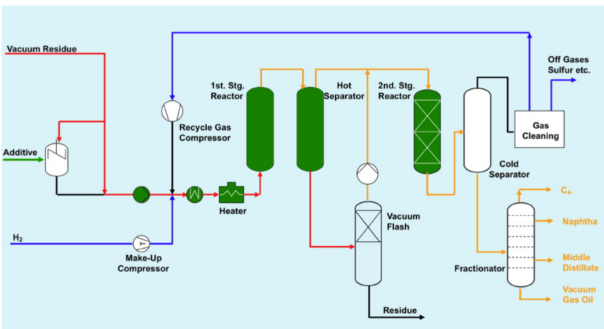

Figure 7. Schematic of the VCC process.

In the rest of this article the authors will use the history and experience of the VCC to address the process chemistry, commercial experience, unit reliability, and consequently, the relevance of this technology today.

Veba Combi Cracker

The origin of slurry phase hydrocracking and the VCC date back to 1913, when Freidrich Berguis was awarded his first patents for the process of liquefying coal. The 1931 Nobel Laureate had demonstrated that liquid products can be realised by simply subjecting coal to a high enough temperature and pressure in the presence of hydrogen.

In Germany, 12 commercial units were built and operated between 1927 and 1945 producing approximately 100 000 bpd of transportation fuels from coal, coal tar and coal pitch based feedstocks to meet the need of that time. Well documented evidence shows that these units operated consistently above design capacities and at over 90% unit availability under very difficult conditions. This remarkable reliability can be easily explained once the basic chemistry of slurry phase hydrocracking and the operating features of this technology are clearly understood.

In 1945, several of these units were dismantled and sent to the eastern block countries, while the remaining units including the six operating trains at Gelsenkirchen were converted to 10 000 bpd trains for processing refinery vacuum residues. In the mid 1950s, the integrated second stage fixed bed reactor was added to the process when it was realised that mild hydrofinishing of the slurry phase products could result in higher quality distillate products. In essence this integrally coupled combination of the slurry phase hydrocracker and the trickle bed hydrofinisher was the origin of the VCC process as it is known today.

The units operated in the integrated mode on residues until 1967, when the low crude oil price (US$ 2/bbl) and the end of government subsidies forced the units to be shutdown and subsequently dismantled. The crude oil price was too low to justify adding hydrogen to the residue when other fuel oil outlets existed and the high distillate product quality was viewed negatively for its high hydrogen content, and the economics of the technology could not be sustained.

The VCC process was resurrected in response to the hike in crude oil prices following the oil embargo of the 1970s and a new 3500 bpd unit was built in Bottrop and started up in 1981. In addition, a 200 bpd large pilot plant and two small pilot units for testing purposes were built with the intent to test multiple feedstocks, residues, bitumens and coal. The oil embargo ended and the world saw a substantial crash in crude price.

These units operated until 2001 when the sustained low oil prices (<US$ 10/bbl) and the huge increase in natural gas prices essentially lead to the decommissioning and shutdown of the Bottrop unit. The economic incentives for the technology were once again lost.

The renewed crude price surge in recent years is spurred by genuine market supply and demand conditions attributable to the 8% growth in the high population economies of India and China, and unlike other manmade events such as war or embargoes in the past this trend is likely to be sustained in the long run.

Following BP's acquisition of Veba, VCC has become an integral part of the BP advanced refining programme. A new 1 bpd VCC pilot plant designed, built and commissioned in 2008 is now in place at BP's research facilities in Naperville, USA.

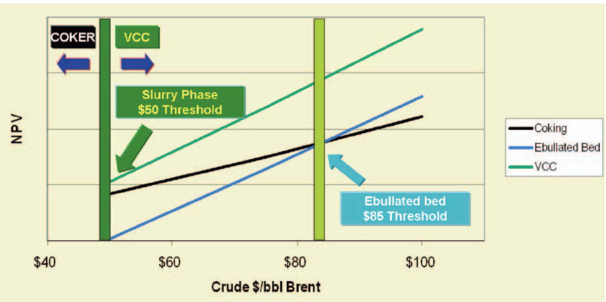

Figure 8. Net present value of available technologies versus crude price.

Table 1. VCC technology yield and products qualities

Conversion	Overall		>95%
Conversion	Asphaltene		>90%
Product	Yields wt%		Quality
H_2S	4.6		
Ammonia	1.0		
C1 - C4	7.6		
Naphtha C5 - 350˚F	12.0	Sulfur	<1 ppmw
		Nitrogen	<1 ppmw
Diesel 350 - 650 ˚F	47.0	Sulfur	<10 ppmw
		Cetane index	>46
		Cloud point	<-15˚C
VGO 650 - 975 ˚F	26.0	Sulfur	<100 ppmw
		CCR	<0.15 wt%
		Metals	<1 ppmw
Residue >975 ˚F	<5.0		

Note: assumes Arabian VR 4.3% sulfur content.

Slurry phase hydrocracking

While slurry phase hydrocracking has been reliably practised for several decades, it has historically enjoyed very little widespread acceptance as the technology of choice for resid upgrading. The strength of this technology is characterised by near complete (>95 wt%) resid conversion, high (>90 wt%) asphaltenes conversion, and high quality distillate products, but it involves high hydrogen consumption.

The appropriateness of any technology choice must be weighed against the prevalent market conditions, and its relevance is deeply rooted in the principles of molecule management. Embedded in this approach is the core belief that refining margins are maximised by selectively maximising the value of every molecule in naturally occurring crude oils in every stage of processing.

In its simplest form, vacuum residues can be broadly classified by saturates, aromatics, resins and asphaltenes (SARA) analysis. The degree of difficulty, the severity of operation (pressure and temperature), hydrogen uptake, and the capital investment required rise with the increase in carbon number. A close examination of the resid at a molecular level will reveal that the asphaltenes form the heaviest, most hydrogen deficient part of the resid and contain virtually all the impurities. The obvious inference leads to these simple questions that must be answered prior to undertaking large investments:

- Is it worth converting the heaviest molecules?
- Is the hydrogen addition to the heaviest molecule economically justifiable?
- Are there alternative outlets such as pet coke or fuel oil?
- Is there a need to make boutique, ultra low sulfur distillate products?

The economics of not upgrading, partially upgrading or fully upgrading these molecules is substantially influenced by the essential controlling factors of crude price, natural gas price and capital investment. Historical low crude oil prices, high natural gas prices, a robust fuel oil market and a low valuation for boutique product qualities, have had an inhibiting effect on the value of upgrading the most difficult asphaltene molecules in the refinery resid. In the past, it was both economical and convenient to discard these molecules as coke, or as is the case in ebullated bed hydrogen addition applications, as unconverted residual fuel oil. It is not surprising that while the essential elements of slurry phase hydrocracking were sound, the market landscape and the regulatory landscape were not ready for the value that this technology could deliver.

Posing the same questions today, the answer is an obvious yes. The change in the crude and natural gas price structure, the new regulatory environment, the diminishing fuel oil and petroleum coke market, the increase in distillate demand and the new transportation fuel qualities now make these asphaltenes molecules worthy of upgrading, and call for high conversion, high hydrogen uptake and the production of finished distillate products. In general, this market and regulatory landscape aligns well with the slurry phase hydrocracking process. Specifically, the VCC features that have been developed through decades of innovation are now highly relevant and readily available to the market.

A comparison of the net present value (NPV) of three technology routes derived from upgrading a refinery residue as a function of benchmark crude price shows a remarkable trend in favour of slurry phase hydrocracking. Both the economic and regulatory trends are heavily weighted in favour of VCC, and the current and future market conditions are aligned with the inherent features of this technology.

The economic evaluation for one operating North American refinery vacuum resid clearly shows that the net present value of the ebullated bed process only exceeds that of the delayed coker at a high benchmark crude price of US$ 85/bbl. This is primarily because of the lower conversion, the stranded large volume of lower value unconverted residuum, and the production of aromatic distillate products that need retreatment.

On the other hand the net present value of the VCC exceeds that of the delayed coker at a benchmark crude price of US$ 50/bbl, making this the technology of the future.

Reliability

The value of slurry phase hydrocracking in general and VCC in particular can only be derived if reliable long term operations can be sustained. This reliability can only be achieved if high asphaltenes conversion can be accomplished without fouling the unit. A molecular evaluation of the residuum will reveal that the asphaltenes are held in solution by the saturates and aromatic compounds.

The initial conversion chemistry for the slurry phase hydrocracker is essentially thermal in nature and somewhat similar to that seen in other carbon rejection processes. The potential condensation reactions associated with these cracked molecules (seen in carbon rejection processes that lead to heavier residuum molecules and eventually coke) are arrested by the high hydrogen partial pressure. Therefore, unlike other thermal processes, this reaction system produces lighter than feed products, with little to no condensation or coke type products.

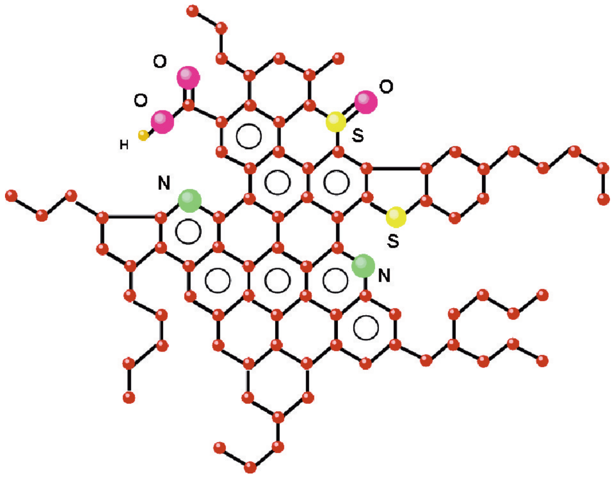

Figure 9. Typical asphaltene molecular structure.

As the conversion progresses, and as the saturates that hold the asphaltenes in solution are easily cracked, the residuum loses its solvency, and the asphaltenes precipitate. For better understanding, an analogy can be drawn to the operation of the solvent deasphalting process. In that case when the saturates are dissolved in a light paraffinic solvent, phase separation occurs, precipitating the asphaltenes as pitch.

These unconverted asphaltene precipitates containing the heavy metals will tend to find surfaces to adhere to (in this case the walls of the reactor, piping, and heat exchange equipment) leading to severe fouling. This limitation has led several ebullated and resid hydrocracking technologies to reduce their overall per pass conversion, or to resort to recycle and/or the addition of external large volumes of aromatic solvents, all in an attempt to dissolve these unconverted asphaltenes molecules.

The VCC technology operates with stability and high conversion in a mode that is devoid of fouling. This issue has been researched over several decades dating back to the origins of the VCC technology. Over 1000 patents and over 2000 filings exist, which cover the entire landscape of catalytic and additive possibilities. These efforts led to the discovery and use of a low cost additive, which enables high conversion and low fouling.

This combination of high hydrogen partial pressure and additive system is unique to VCC and is a major contributor to the decades of reliable operation at high (>95%), once though conversion, with no signs of fouling. The hydrogen addition needed to meet final product quality is met by adjusting the trickle bed hydrofinisher conditions, essentially isolating the residue from the catalytic part of the process. The reliability of the process has been proven by operating factors that have consistently exceeded 90% over several decades of operation.

Conclusion

The authors believe that the current market conditions and regulatory developments substantially favour investment in hydrogen addition technologies and are well aligned with the strengths of the slurry phase hydrocracking technologies, and specifically VCC. The near complete, once through, distillate selective conversion to high quality finished products can be reliably achieved with high onstream factors.