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Carbon Utilization & Petrochemical Integration: Capturing Value via Residue to Chemicals Projects

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Abstract:

Consensus forecasts envision a global petroleum market impacted by the following macro-scale trends in the medium and long term:

1. Stagnant or declining petroleum-derived motor fuels demand in developed countries as a result of improvements in vehicle fuel efficiency and alternative fuels developments
2. Sustained global demand growth for petrochemicals trending with population and global GDP growth

When coupled with regulatory environment causing the power industry to shift feedstocks away from carbon-intensive, high-sulfur fuel oils and petroleum coke to natural gas and renewable sources, these market forces may incentivize the refiner to increase petrochemical production while simultaneously reducing fuel oil and coke output. In short, the refiner who can best maximize the conversion of its residual carbon feed molecules to aromatics and light olefins will be positioned to capture additional margin in the petrochemical value chain.

This paper will specifically focus on commercially proven technology solutions for producing petrochemicals from bunker fuels, atmospheric, and vacuum residues: (1) H-Oil® residue hydrocracking coupled with distillate

hydrocracking and aromatics production and (2) H-Oil® unit integrated with Petrochemical Complex by upgrading the heavy by-products of Steam Cracker units. Technology highlights, commercial applications, case studies, and comparisons to proven thermal cracking technologies will be presented.

H-Oil® has a cumulative licensed capacity of over 1,200,000 BPSD over its more than 55 years of history. The Hengli Petrochemical complex currently starting up utilize H-Oil® to maximize para-xylene production from sour crude feedstocks.

Key word: Petrochemicals, Naphtha production, HSFCC, H-Oil®, high conversion,

Market Trend

Whereas Natural Gas Demand and Fuels demand will increase by 1% to 1.5% per year, Petrochemicals demand increase is estimated at 4% per year. This demand will blow-up while residue fuel will decrease.[1]

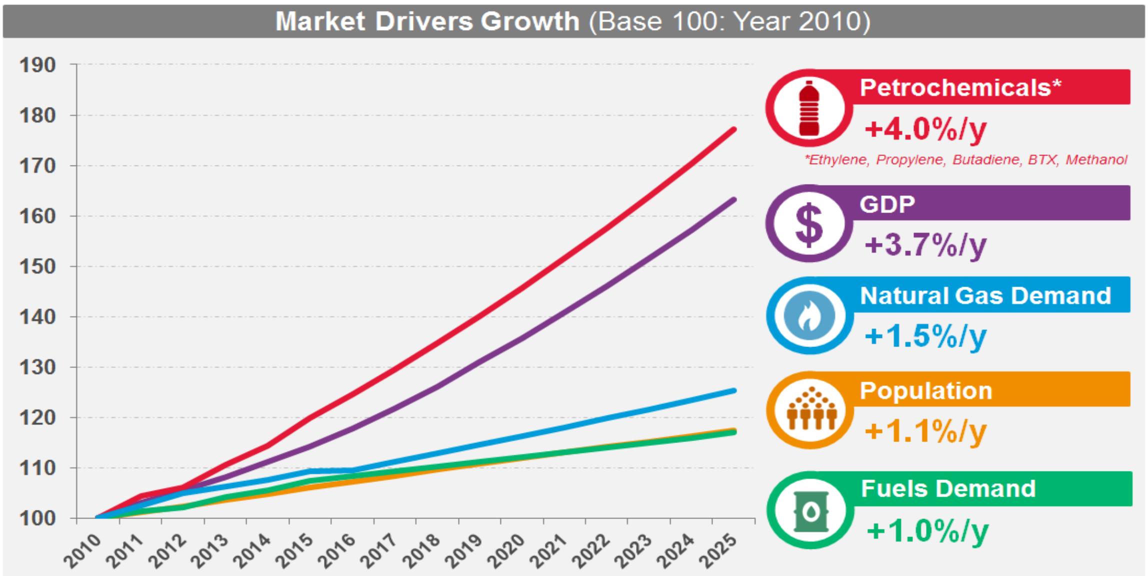

Exhibit 1: Market Drivers Growth

Demand for plastics – the most familiar group of petrochemical products – has outpaced that of all other bulk materials (such as steel, aluminum or cement), and has nearly doubled since 2000, [2]. Moreover, with the recent introduction of regulations concerning marine fuel oil by the International Maritime Organization, the demand for high sulfur residual fuel oil will continue to decline in the near future because of the difficulty in meeting the new low sulfur standard for residual fuel oil. Consequently, refiners will now have an incentive for complete residual oil destruction for heavy high sulfur crudes. The PIRA energy consulting firm forecast the net supply of high sulfur fuel oil could decline by 1.4 million barrels per day “BPD” from 2020 and low sulfur (0.5 wt % or less) fuel oil will grow by 900,000 BPD.

To meet this incremental petrochemicals demand, feedstock from petrochemical complex will not be anymore ethane but more and more naphtha. The proportion of naphtha as feed to petrochemical complex will increase to 64% whereas ethane will represent only 1% of the feed in 2030.[3]

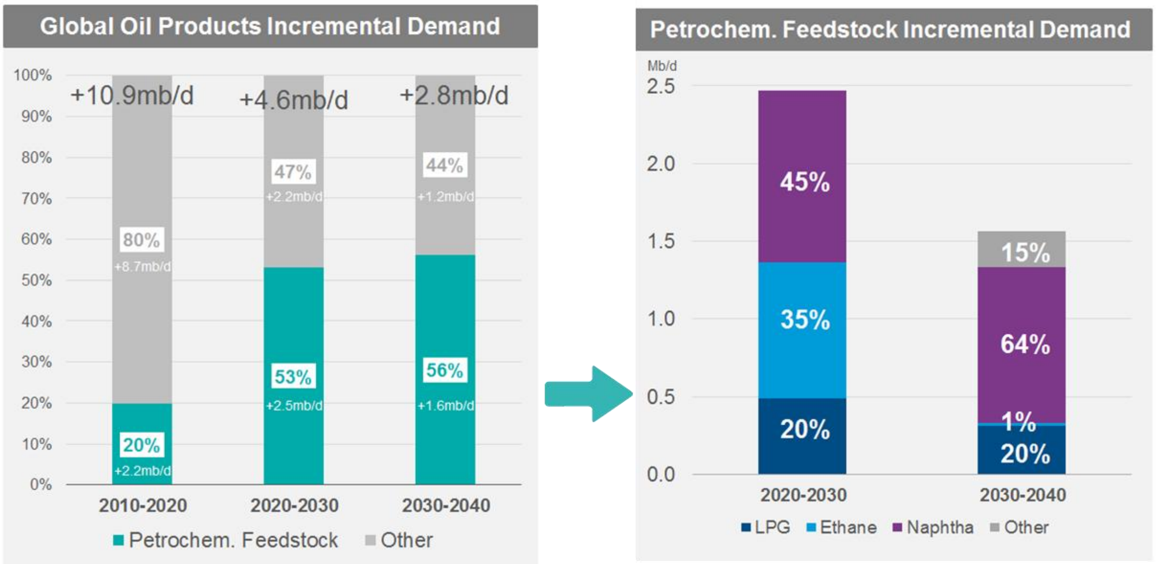

Exhibit 2: Global Oil Products and Petrochemical Feedstock Incremental Demands

Therefore refiners today have no chance than upgrade in maximum their residue into naphtha and integrate with downstream petrochemicals to increase the margin over the entire upgrading chain from crude oil to finished products.

Integrating Refining and Petrochemicals offers several advantages to the oil companies by:

- Expanding into higher growth markets with a portfolio diversification and conducting business in the coming years with flexibility and agility,
- Mitigating risks related to raw material and product price variations,

- Reaching the final step in chemistry by developing fine and specialty chemistry from oil along with high value chemicals business,
- Optimizing the overall scheme with material and heat integration and getting the most from intermediates.

Refiners are gradually assessing options to further upgrade their products into petrochemicals and more valuable chemicals by increasing conversion and implementing technologies.

Crude to Chemical Complexes: What are the Options?

To get the most from the crude feedstock and especially from the residue part, the challenge lies in conversion to push toward naphtha.

Why naphtha cut is key in a crude to chemicals project?

Naphtha represents the gearing effect in a refining and petrochemical site as the light naphtha can be processed in a steam cracker whereas the heavy part can be processed in the aromatic complex.

In a refinery, the straight-run naphtha is directly available after the crude distillation unit combined with a hydroprocessing treatment. To improve the balance towards naphtha, the stakes are so on the conversion naphtha that comes either naphtha from thermal cracking such as coker unit and even FCC unit or from different upgrading units such as Diesel or VGO hydrocracker unit combined with Vacuum residue upgrading technology.

Resid Conversion to Olefins

The Fluid Catalytic Cracking units are converting residue fractions to light components, olefins as well as gasoline. Direct propylene production from FCC technologies is covering a third of the total worldwide propylene production.

With the basis of strong contributor to the global production of olefins, FCC technologies have evolved to tighten their operating conditions, adjust their catalyst formulation and thus go further in the production of chemicals.

HS-FCC Technology Focus

Reaching unrivalled propylene yield by converting heavy hydrocarbon feedstock, the HS-FCC technology is an innovative down-flow reactor under severe FCC conditions.

This process has been co-developed with Saudi Aramco, King Fahd University of Petroleum & Minerals (KFUPM) and JXTG Nippon Oil & Energy and is licensed by Axens and TechnipFMC.

The main features of the HS-FCC process are:

- a down-flow reactor to minimize back mixing and obtain a narrower distribution of residence times;
- higher reaction temperatures (550°C to 650°C) than conventional FCC units;
- high catalyst to oil ratio (C/O) enhancing contribution of catalytic cracking over thermal cracking;
- short contact time for light olefins selectivity and highly selective catalyst.

The first industrial scale HS-FCC unit has been licensed by Axens and successfully started-up at the S-Oil Onsan refinery.

S-Oil Project Example

Located in South Korea, S-Oil performed a major expansion project to enhance the existing complex competitiveness. The objectives were multiple:

- Maximize propylene production
- Minimize remaining HSFO (3.5%S) production
- Maxime the economics

Therefore, S-Oil decided to revamp their RHDS into a 100% VRDS unit, add an ARDS unit followed by a HS-FCC. LSFO and HSFO drop, LPG and propylene are multiple respectively by 2.2 and 3.6 whereas middle distillates and gasoline production stays constant.

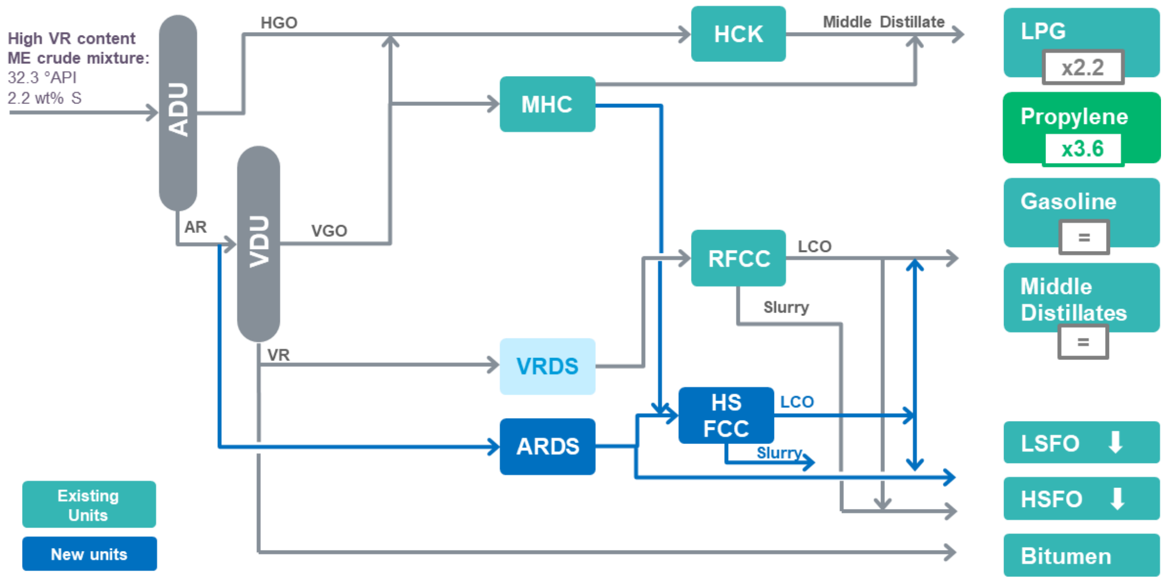

Exhibit 3: S-Oil Simplified Refinery Scheme

Resid Conversion to Naphtha

To improve the balance towards naphtha, the stakes are on the conversion naphtha that comes from different upgrading units such as:

- Diesel and Vacuum Gasoil (VGO) Hydrocracker (HyK™) units, especially in maximum selectivity towards naphtha production
- Resid hydrocracker units with high conversion ebullated-bed units

A great number of the latest Oil-to-Chemicals projects worldwide are based on the ebullated bed hydrocracker H-Oil® coupled with diesel and VGO HyK™ technologies licensed by Axens which stands for the heart of the conversion in these schemes, converting the most refractory and the lowest value cut, the vacuum residue, towards naphtha and Distillate. The full conversion of the middle distillate and VGO in the hydrocracker section sustains the strategic naphtha intermediate cut for olefins / aromatics production.

H-Oil® Focus

The H-Oil® Process is based on the ebullated-bed reactor system that was invented in the 1950's and the first patent was issued in 1961. A demonstration plant started up in 1963 at the Cities Service refinery in Louisiana and its successful operation led to the first large scale commercial plant which started up in 1968 at the KNPC Shuaiba refinery in Kuwait. The process has been described in many publications. Over 90% of the world's vacuum residues that are hydrocracked use the ebullated-bed reactor. The ebullated-bed reactor operates at a constant temperature and catalyst activity. The exotherm generated inside the reactor is quenched by the cold feed and the catalyst activity is controlled by varying the amount and type of catalyst that is added on a daily basis.

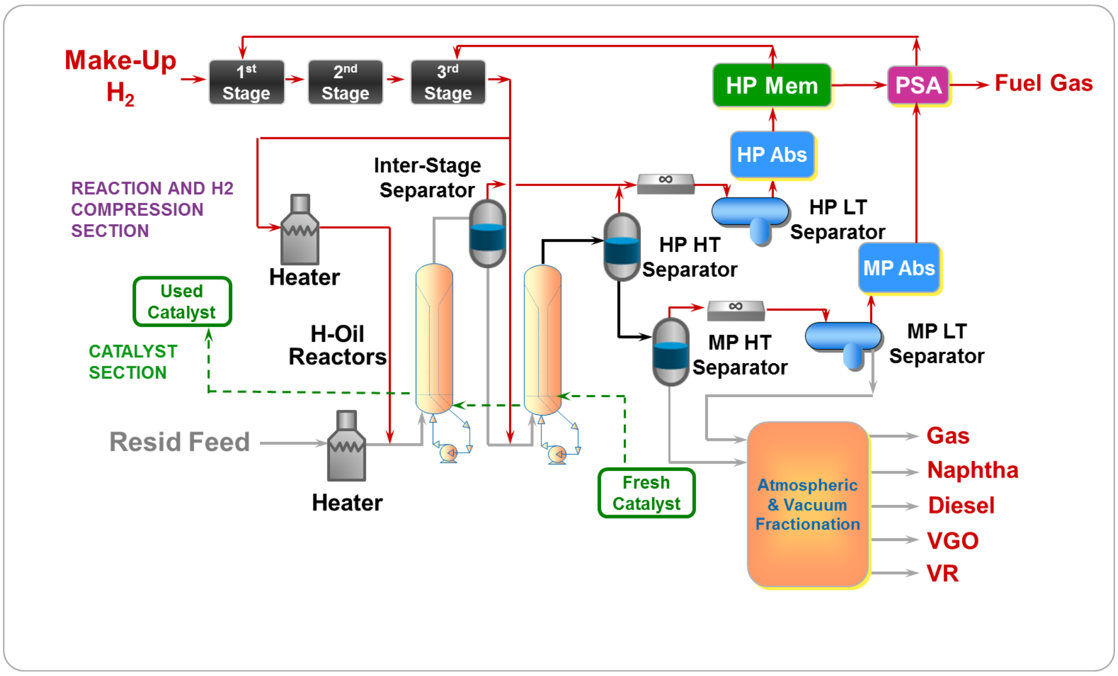

Exhibit 4: H-Oil® Simplified Block Flow Diagram

Some technology features used commercially inside the H-Oil® Process include the use of:

- Vacuum Bottom Recycle (VBR) to reduce reactor severity and conversion per pass thus reducing the formation of sediment downstream of the reactor
- A Low Space Velocity design that allows for deep hydrogenation and improved catalytic conversion while reducing the sediment levels in the unconverted residue
- H-CAT is a new liquid catalyst precursor that reduces product sediment and allows refiners to operate at higher conversion levels

The innovative technology features described above are gaining wide acceptance in the industry. Many of these features have expanded the slate of heavy crudes that can be processed in an H-Oil® unit as well as the conversion level. The VBR feature has been used at Shell's Convent, LA refinery in the USA since its startup in 1984. This unique application has allowed the refiner to run in several different modes including high conversion and maximum throughout depending on the market conditions.

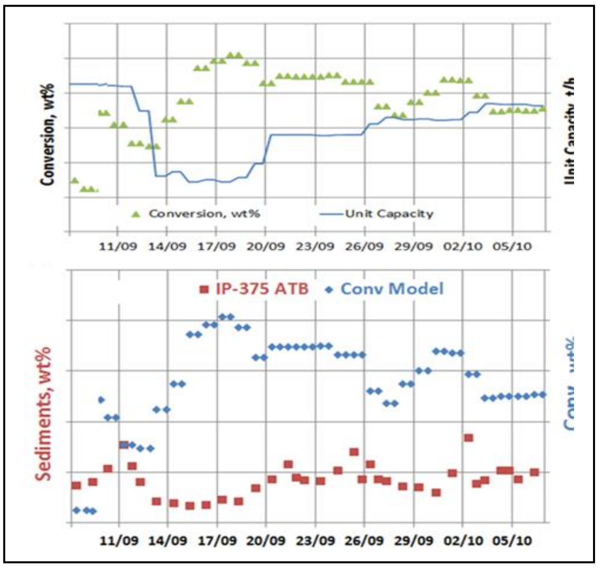

Exhibit 5: Low LHSV Demonstration

The Low Space Velocity design option is a powerful way to boost conversion and hydrogenation reactions. The effluent quality is improved and sedimentation / fouling levels are reduced downstream of the reaction section. In a recent industrial demonstration, the feedrate was reduced which allowed for a significant increase in conversion while the sediment levels in the downstream fractionator bottoms decreased as shown in Exhibit 5. This demonstration validated earlier research work which indicated conversions up to 95 wt% could be achieved with production of a stable UCO on an ebullated-bed pilot unit. As expected, the conversion of asphaltenes, CCR and HDS were also increased during this demonstration test.

Increasing the catalytic activity is another way to improve performance in both conversion and heteroatom removal. The classic way to achieve this improvement in activity is by either increasing the residence time (i.e. larger reactors) or by increasing the catalyst addition rate. The former increases capital investment while the later increases the refiner's operating cost through the use of more catalyst per day. An innovative alternative is adding a liquid catalyst precursor to the oil feed entering the reactor.

The HCAT catalyst complements the solid supported catalyst and allows the ebullated-bed reactor system to operate more efficiently by facilitating the transfer of hydrogen to the asphaltene molecule as shown in Exhibit 6. This liquid catalyst is finely dispersed in the feed oil to the ebullated-bed reactor by a specially designed mixing device. The hydrogenation of asphaltenes leads to higher asphaltene conversion at lower levels of sediment in the unconverted residue. The impact on sediment formation is shown in Exhibit 7. During a pilot plant

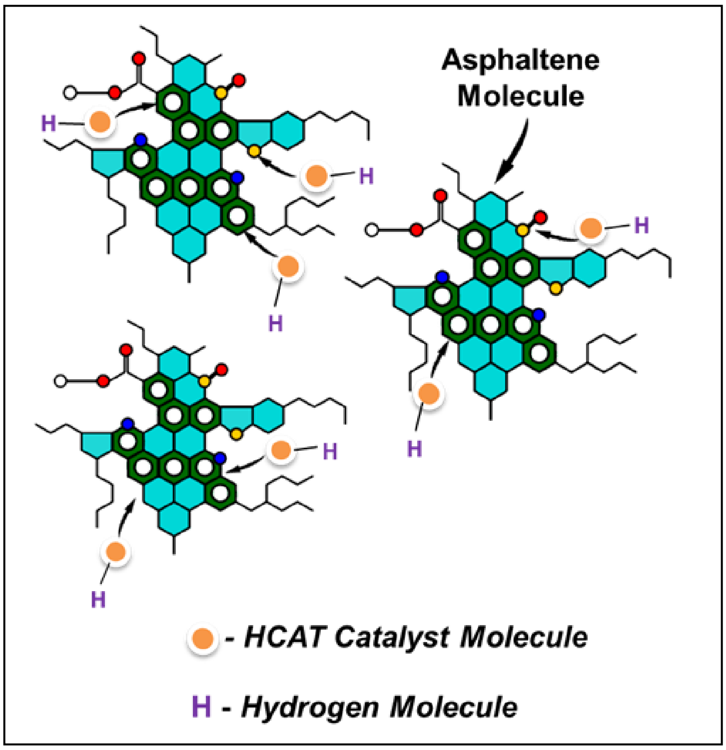

Exhibit 6: Hydrogen Transfer with HCAT

test in support of a commercial plant, the use of small concentrations of HCAT allowed for a 14 percentage points increase in conversion while maintaining the IP-375 sediment level at or below the standard level typically used in commercial operations. Sediment level measured downstream in the fractionator bottoms is used as an indication of fouling tendencies in the vacuum tower as well as the stability of the unconverted vacuum residue from the unit. HCAT is ideally suited for upgrading projects using residues from heavier opportunity crudes but it is also powerful to achieve very high conversion with easier feed. This novel catalyst additive is now in use at several commercial hydrocracking ebullated-bed plants around the world, including non Axens licensees.

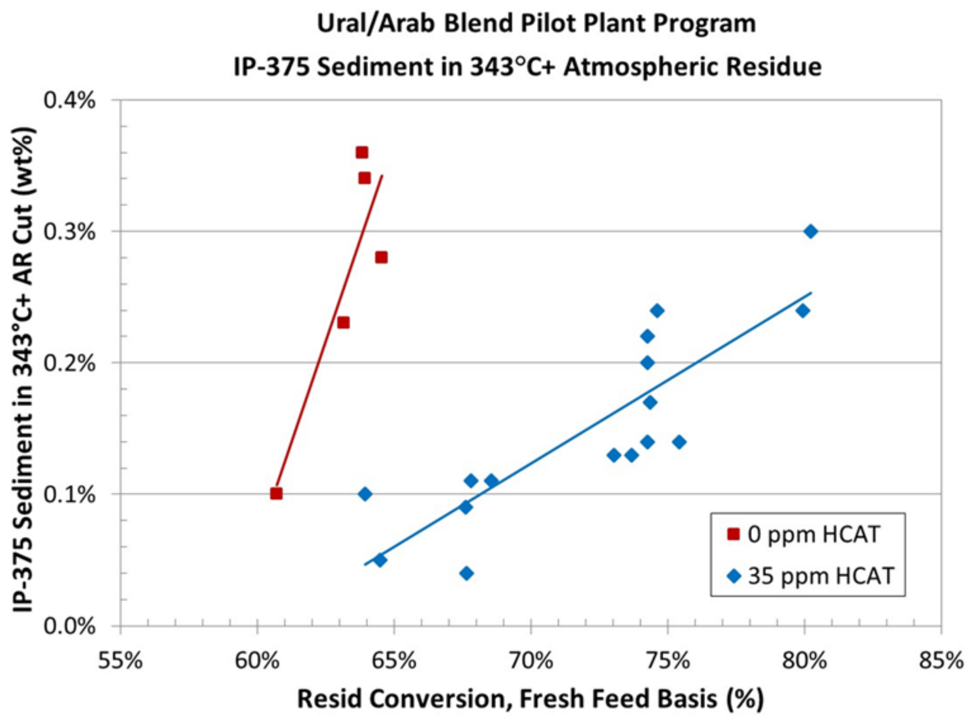

Exhibit 7: Impact of Sediment Formation when Using HCAT

Since 2010, market changes toward projects at high conversion. So Axens invested a lot in R&D for high conversion. Last H-Oil® reference awarded during this summer is a 2 trains configuration at 95wt% conversion guaranteed.

From Convent: 35 years ago and today, we made some design improvements, some catalyst improvements, with low LHSV & HCAT possiblity to go up to 98wt% conv with Arabian light and 95wt% with arabian heavy/medium.

The key features of the H-Oil® technology are the following:

- Demonstrated high conversion levels: the conversion of vacuum residue is set between 75 and 95 wt. % when production of a stable residual fuel oil is desired from the unconverted residue. Different leverages like, LHSV, use of dispersed catalyst are used to maximize conversion,
- No limitation on feed properties,
- Mature and reliable technology: more than 1.2 Mbpsd licensed capacity,
- High availability: higher than 96%.

In 2019, 2 new H-Oil® units high conversion start-up: ZRCC and Hengli

Hengli Project Example

The Hengli project in China is a perfect example of the option that integrates the upgrading of heavy oil at the refinery with a petrochemical plant downstream. This large complex was optimized by a team of engineers from Axens and Hengli that resulted in a configuration that includes the high conversion H-Oil® technologies; H-Oil® Process, SDA (Solvahl™), hydrocracking (HyK™) of the VGO and DAO, for the maximum yield of naphtha for processing in a downstream petrochemical plant. Hengli is able to maximize its overall margin by producing petrochemicals. This 110,000 BPSD plant uses 2 parallel trains with two ebullated-bed reactors in series for each train. The design feedstock is a blend of Arabian and Marlin crudes. The pitch from the SDA unit is routed to a gasification unit. Axens provided the major technologies for both the refining and petrochemical plants.

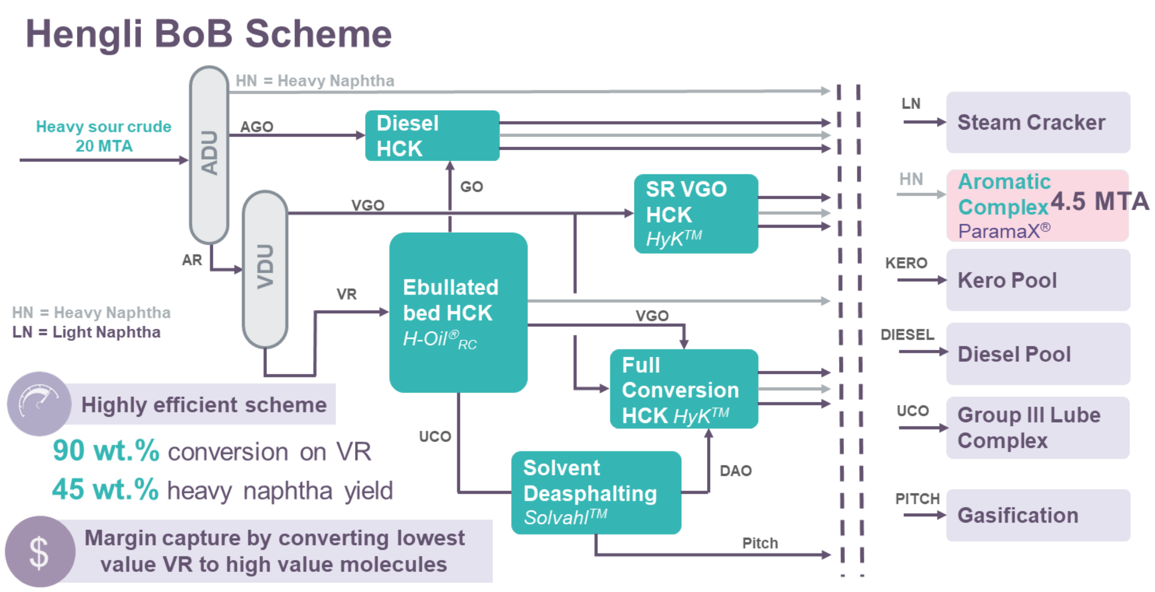

Exhibit 8: Hengli Simplified Refinery Scheme

After few months of operation only, major results are the following:

- VGO & DAO ex H-Oil® sucessfully process in full conversion HCK

- ParamaX® complex operates at nominal capacity
- High CCR reformers selectivity to aromatics
- Production of valuable octane contributors to gasoline Products on spec
- Naphtha ready to CCR
- On-specification paraxylene production
- High VR conversion

Conclusion

The petrochemicals demand growth higher than that of fuels. Crude to chemicals complexes offer many advantages such as expanding into higher growth markets, mitigating risks related to naphtha material and product price variations and improving asset profitability. For both the olefins route and the naphtha route, technologies benefit of continuous improvement and innovation to provide the maximum of services and productivities.

Crude to chemicals projects implementing advanced technologies is a way to catch these opportunities. Axens is your key partner to provide advanced and innovative solutions for both grassroots and revamps projetcs.

References

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3- World Energy outlook 2017, New Policies Scenario, IEA

Exhibits