New Advances in Residue Upgrading Technologies to Maximize Conversion

by

Axens

Synopsis

As product demand continues to shift towards transportation fuels with a decline in Fuel Oil demand coupled with an increase in availability of Heavy Crudes, there is an economic incentive to invest in residue conversion units and maximize residue conversion. This trend has become the new standard for new refinery projects as well as for revamps of existing assets.

This paper discusses the latest technology development available to the refiners to achieve the goal of high residue conversion while ensuring high operation reliability through production of finished products.

After a review of the main features of the well proven Ebullated-Bed hydrocracking technology for residue conversion, the paper will focus on the combination with Solvent Deasphalting (SDA) Technology to further increase conversion without compromising the operability and reliability of the system. The challenges brought by increasing the conversion also include the nature of the feedstock processed in the unit. The paper will discuss several cases with different feedstock from benchmark Arabian Vacuum Residue (VR) feed to more refractory feeds such as Venezuelan and South American VR. Depending on the feed, the Ebullated-Bed Hydrocracking and SDA unit integration is optimized, providing a tailored and proven solution to the refiner according to their specific feedstock.

Market

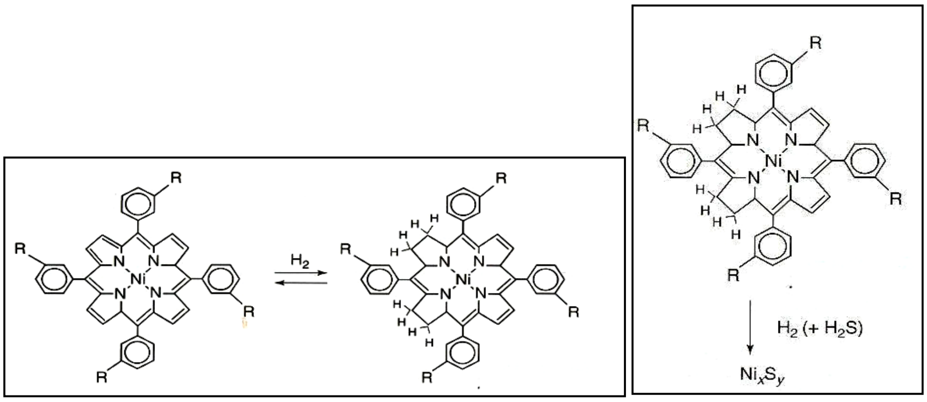
Despite recent booming of tight oils, it is well accepted that refiners will process heavier crudes in the future as they are becoming more available and at discounted price. Meanwhile, the world demand for high value products such as gasoline (+1.0% in 2030) and middle distillates (+1.6% in 2030) is increasing. The trend towards heavy feedstock and urgent demand for high quality products as well as more stringent fuel regulations will lead to a residual fuel oil decline (by about 1%). This presents new challenges for refineries. One of them is to find new ways to maximize yield of high-value products and maximize returns from bottom-of-barrel. In most regions, light crude oils availability is becoming scarcer and refiners need to adapt their plants to process heavier crudes, calling for increased residue conversion capabilities.

VR feedstock

Residue from distillation of petroleum contains large asphaltene molecules and heavy-metal contaminant, and is deficient in hydrogen content. This poor quality makes further processing of this material relatively specific and requires significant know-how.

Upgrading residues, either Atmospheric (AR) or Vacuum (VR) fractions, consists in lowering sulphur (HDS), nitrogen (HDN), metals (HDM), asphaltenes ($HDAsC_7$) and Conradson Carbon Residue (HDCCR) contents, through hydrogenation reactions, and/or cracking (thermally and catalytically) large molecules into smaller ones.

Residues are the most difficult feedstocks to refine and convert catalytically because they concentrate impurities like sulphur, nitrogen and refractory structures like resins and asphaltenes, containing themselves metals in their sub-structures (porphyrins). Metals (mainly nickel and vanadium, but also silicon, iron, sodium, etc…) are permanent poisons for catalysts. Those feeds represent a challenge for the Technology providers to design a plant that will consistently meet the expected process requirements over extended period of time.



Mechanism of hydrogenation and production of metallic sulfides

Another challenge to face when upgrading residues is to handle the asphaltenes, which are a heterogeneous mixture of highly poly-dispersed molecules, in terms of size and chemical composition, with a high content of heteroatoms (sulphur, nitrogen, metals…). Those heavy molecules are dissolved in the entire residue structure but can precipitate easily at high operating temperature or changes in composition of residues. Furthermore, asphaltenes are known to be coke precursors. Residue conversion is therefore a achievable goal as long as the unconverted fraction remains a manageable stream in terms of transport properties and stability.

Particularity of South American feedstock

As shown in the table below, depending on the origin and regions, properties of vacuum residues are very different, from sulphur to conradson carbon or metals contents. Crudes from South America (Maya & Zuata) are among the most difficult vacuum residues to process for different reasons.

		Ural	**Maya**	**Athabasca**	**Shengli**	**Zuata**	**Buzurgan**
Origin		**Russia**	**South America**	**Canada**	**China**	**South America**	**Middle East**
Specific Gravity	-	1.014	1.0404	1.063	1.000	1.054	1.045
Sulphur	Wt%	2.81	4.23	5.62	0.61	4.45	5.56
Nitrogen	ppm	6300	5900	6000	1020	9900	3870

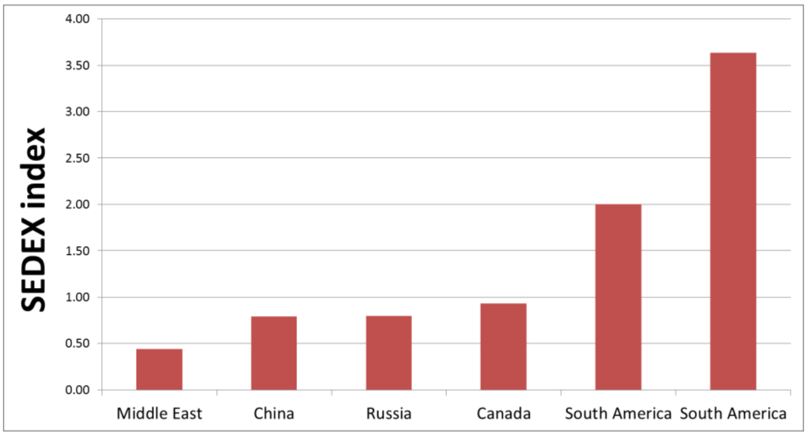
Asphaltene C7	Wt%	8.1	20.8	16.7	2.43	14.6	13.2
Conradson Carbon	Wt%	17.6	20.8	23.1	15	23.5	23
Nickel + Vanadium	ppm	229	566	485	64	875	251
Viscosity @ 100°C	cSt	457	10300	20597	482	44000	3500

Typical South American crudes properties are as follows (Marlim & Zuata):

- High nitrogen content
- High viscosity
- High metals contents

To evaluate the difficulty of a crude to be processed, one parameter often used by a experts in the Bottom-of-the-barrel field is the sedex index. This parameter correlates S/N ratio with CRR content, C7 asphaltenes and viscosity. It represents the difficulty of processing a feedstock and shows if one feedstock will tend to lose its stability faster (and thus form coke) or slower than another one depending on the conversion. Thus, a maximum level of conversion while maintaining good operability and reliability will be determined for each type of feedstock. For example, maximum conversion for a stream factor equal to 96%, is set in the range of 85-90wt% for an Arabian type of crude and 60-65 wt% for a South American crude. It is worth pointing out that these results are true for any kind of residue upgrading technologies.

As shown in the graph below, the sedex index for a South America type of crude is between 2 to 3.5 compared to 0.4 for a Middle East crude.



Different commercially proven strategies are available to process heavy residues containing asphaltenes, either non-catalytic (Solvent deAsphalting or Coking), or catalytic processes (hydrorefining or hydroconversion) or a combined system as presented in this paper. The optimal catalytic technology for a given service depends on several parameters: nature and contaminants of the feed, required level of conversion into lighter fractions, desired products slates, sulphur content of the residual heavier fractions, investment costs and of course operability and reliability.

As depicted in the following picture, Ebullated bed technology, such as Axens' H-Oil®$_{RC,}$ is the best option when targeting high conversion versus product refining.

In addition, the Ebullated bed technology can cope with any type of contaminants and poisons through catalyst addition and withdrawal. Also, thanks to the ebullated bed system, the exotherm is easily managed.
Thanks to these features the Ebullated Bed technology (such as H-Oil®) is the best one to upgrade residues.

H-Oil® history

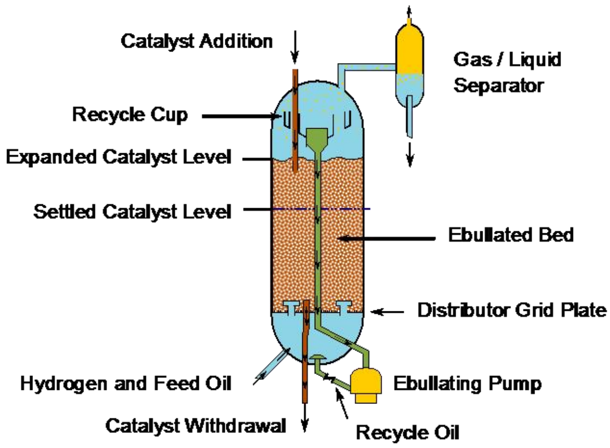
The H-Oil® process is a catalytic hydrocracking process which converts and upgrades heavy oil and petroleum residue. The process was invented by HRI and was first licensed jointly by HRI and Texaco development Company. It is now licensed by Axens. There are currently nine H-Oil® plants in operation. The first one started-up in 1968 and it is still in operation today. Additionally an H-Oil® plant licensed by Lukoil Bourgas is currently under start-up and 6 additional plants are in the Engineering Design phase or under construction phase.

H-Oil® solution

The H-Oil®$_{RC}$ process applies ebullated-bed hydrocracking technology concept to process heavy residues containing high metals, sulphur, nitrogen, asphaltenes and solids. Conversion from 40 to 85 wt% can be achieved without any production of coke material and without any residue stability issues, while producing high quality distillates that can be used as feeds to hydroprocessing or hydrocracking units. Those finishing steps can be combined into H-Oil®$_{RC}$ unit system to minimize capital. Similarly to a fixed-bed reactor system, hydrocarbon feedstock and hydrogen are contacted in the ebullated-bed reactor using a specific hydrotreating catalyst.

However and unlike fixed-bed reactor system, the concept of the ebullated-bed reactor, is to maintain the individual catalyst particles in a state of constant motion or ebullated state, by recycling an internal liquid stream. The internal liquid recycle stream is obtained from an internal vapor/liquid separation device (recycle cup) which provides suction to the ebullating pump. The recycle liquid relative to the fresh feed ensures perfect back-mixing conditions resulting in excellent temperature control and low and steady pressure drop.

Spent catalyst withdrawal and fresh catalyst addition is managed on line on a daily basis, thus ensuring a constant catalyst activity. Constant yields and product quality over time are also achieved. Therefore, the run length for the ebullated-bed reactor system depends on the refiner turnaround strategy and is not dependent of catalyst activity or pressure drop issues that are typically experienced in fixed-bed systems.

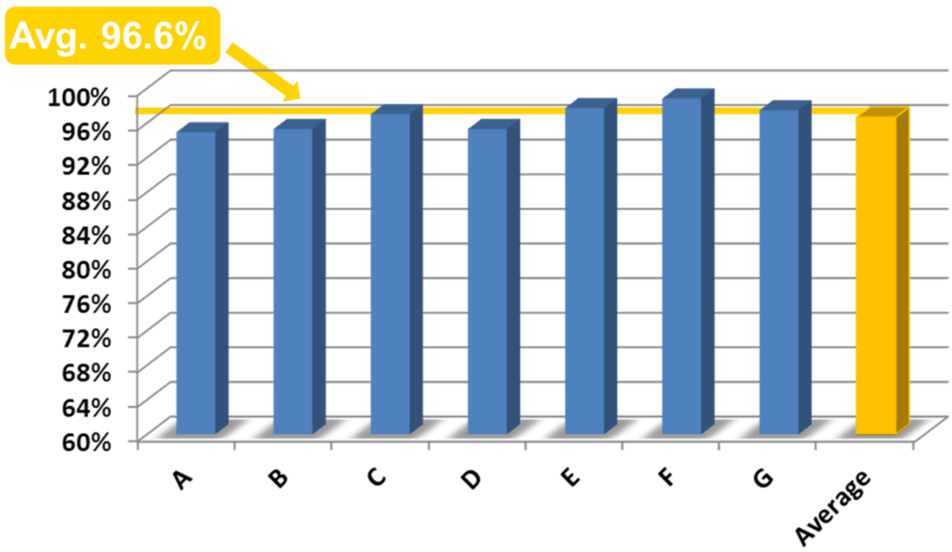


The ebullated-bed reactor scheme

The H-Oil®$_{RC}$ unit operates at relatively high severity: temperature from 400 to 440°C and pressure from 125 to 185 barg. Operating conditions can vary to achieve a range of conversion and product quality to meet seasonal demands or changes in crude slate. The design pressure, number of reactor stages, catalyst type, and catalyst replacement rate are selected to optimize the performances of the H-Oil®$_{RC}$ unit to meet refiners' objectives.

<u>H-OIL® PROCESS RELIABILITY</u>

H-Oil® Residue hydrocracking based on ebullated-bed technology is a mature technology with 17 licensed plants for a total capacity of more than 820,000 bpsd of vacuum residue in North America, Europe, Middle East and Far East. The reliability of the H-Oil®$_{RC}$ Technology has improved over the last 44 years since the start-up of the first plant for KNPC's Shuaiba Refinery in Kuwait. Over the past 10-years of operation the average availability of 7 commercial H-Oil®$_{RC}$ plants is above 96 %. This high level of reliability is the direct result of above 200-unit years of operating experience, automation of operations, pro-active reliability teams, improvements in the understanding of the chemistry of asphaltene conversion and stability through extensive R&D effort, and on-going improvements in critical equipment, components and process instrumentation.



The plot shown in the above figure reflects Unit Availability for 6 H-Oil® Commercial Operating Plants. Unit Availability is defined as the actual on-stream time less planned turnarounds (typically occurs once every 3 to 6 years) and outages due to external factors (i.e. hurricane on the Gulf Coast).

Increasing conversion to high levels with the Ebullated bed Hydrocracking technology alone will hit some limitations due to asphaltene condensation and residue stability issue. To further increase conversion while maintaining excellent operability and reliability, and successfully displacing the conversion threshold is achieved by combination of H-Oil® technology with carbon rejection technologies such as Solvent DeAsphalting or Coking which are also well proved technologies .

<u>Technologies solution for grassroot projects: H-Oil® + SDA combination</u>

Solvahl™ is Axens Solvent DeAsphalting technology, which concentrates the asphaltenes, most of the metals and other impurities contained in the residue feed in an asphalt product and yields a DeAsphalting Oil (DAO).
Solvents used in the Solvent deasphalting process can vary from C_3 to C_6 depending on feed properties and downstream process objectives. The relative yields of DAO and asphalt, as well as the characteristics of both products, are linked to the nature of the feed, the operating conditions and the type of solvent.
The process extracts a maximum amount of high purity DAO at a low solvent/feed ratio, while producing asphalt with a high softening point.
This integrated scheme boosts conversion by as much as 15 to 20 wt%. Thus, the overall conversion goes from 75 to 90 wt%, as shown in the examples below.
Thanks to its expertise and depending on the refiner’s targets, project objectives, product requirements, feedstocks and site constraints, Axens will propose a tailored the configuration for each specific case. The Solvent desaphalting can be either implemented upstream (Option 1), between two H-Oil® reaction sections (Option 2) or downstream (Option 3) . Some case studies are presented in the following section to illustrate different configurations.

- Option 1:

For feeds with low asphaltenes content and low viscosity such as Ural crude, the configuration with SDA upstream of the H-Oil® would be optimum as the DAO lift is maximized in this case and acts as a guard bed for the downstream unit.

- Option 2

The first configuration consists in the integration of an H-Oil®$_{RC}$, SDA section, and H-Oil®$_{DC}$ .in sequence. The advantages of integrating the SDA unit downstream of the H-Oil®$_{RC}$ is to eliminate refractory asphaltenes (coke precursors for the 2nd step) that have not been converted in the first H-Oil® step. After removal of the asphaltenes in the SDA section through the pitch, the conversion can be increased in the second ebullated bed reactor (H-Oil®$_{DC}$ operating at higher severity & activity) to maximize the overall conversion level. In this configuration, the SDA acts as a guard bed section for the second H-Oil® stage. To minimise CAPEX investment, only one reactor is considered in the first step and another one in the second step.

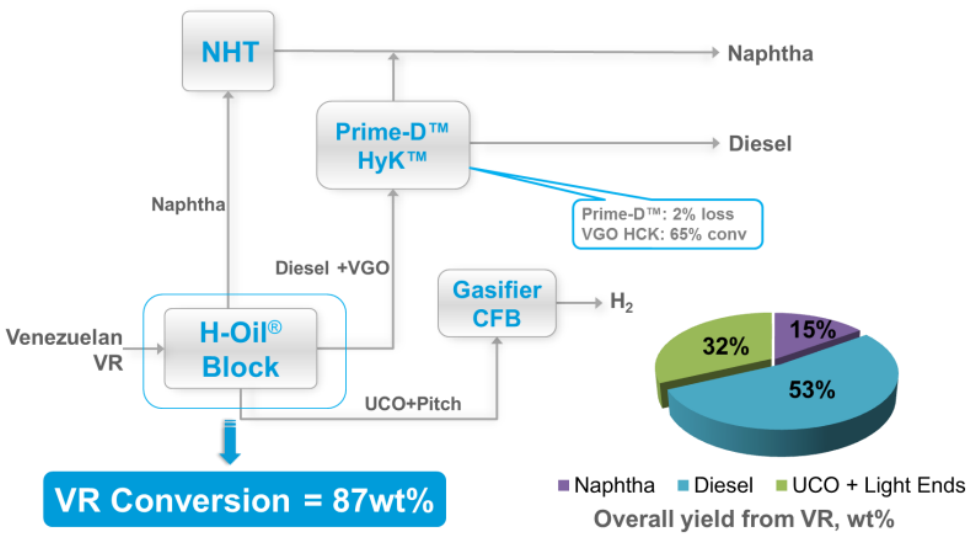
This configuration fits best for high viscosity and high asphaltenes content feeds such as south American. It can also be proposed to minimize revamping of are existing downstreams units as the vacuum gasoil is further hydrotreated in the second H-Oil® reactor improving its quality to meet specific feed requirements of the downstream units.

To highlight the advantages of this scheme an example is presented. The objective of the project was to maximize conversion of the Vacuum Residue towards middle distillate production.

The feedstock considered is 100% of Merey crude with a cut point equal to 450°C+ to get an appropriate viscosity. Properties of the feedstock are shown in the table below:

Analysis	Units	Merey Crude 450°C+
Specific Gravity (20°C)	-	1.0276
Microcarbon Residue	wt%	219.8
Vanadium	wtppm	425
Nickel	wtppm	95
Sulphur	wt%	3.9
Nitrogen	wtppm	8000
Viscosity @ 100°C	cSt	7700
Asphaltenes content	%	15.8

With this difficult feedstock the residue conversion in the first step is around 60 wt%, the DAO lift around 80 wt% on feed and the conversion in the second step around 90 wt% which makes the overall conversion (100- pitch) over 87 wt%. At the outlet of the H-Oil® block, around 10 wt% of naphtha, 35 wt% of Diesel and 30 wt% of VGO are recovered. These last two products together with straight run diesel and VGO are routed to a VGO Hydrocracker unit and a Prime D unit for further hydrotreatments. With 65 wt% of conversion considered in the Hydrocarkers units, this configuration allows the production of more than 53 wt% of diesel plus 15 wt% of naphtha from a South America vacuum residue.



The unconverted effluents from the Complex are: the pitch from the SDA, the unconverted oil from the H-Oil® block and the Hydrocracker bleed. There are several options for the disposal of the unconverted effluents. One option is to use them as fuel in the refinery that can be burned directly inside the refinery with dedicated burners as the fuel that has a low viscosity when kept at high temperature. Another possible use is to route the unconverted streams to a gasifier. In any case, it is worth mentioning that there are no by-products left.

In summary, this configuration applies a moderate conversion in the 1st stage reactor in order to convert « easy asphaltenes » and reduce fouling issue. Most difficult asphaltenes are rejected thanks to the Solvent deasphalter which allows a high conversion in the 2nd stage reactor with a high reliability because feed is free from asphaltenes. Moreover two distinct separation sections are used to avoid stability issues of the products.

- Option 3

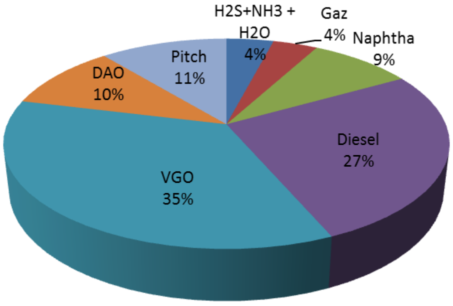
The second configuration consists in implementing a Solvent DeAsphalting (SDA) unit downstream of an H-Oil® unit. This configuration typically fits well for conventional type crude such as Middle East crude. But, it can also be a good option when the downstream units can process the DAO through either a grassroot design or when there is flexibility in the design of the existing unit. This configuration is best when quite a high conversion level is reached in the ebullated-bed technology, usually in one train of two reactors in series. In this case, the addition of the SDA unit allows the recovery of even more high value product from the unconverted residue coming from the ebullated-bed, coming from the DAO.

An example of this configuration is presented in the following section. (Example 1).

In this scenario, the objective is also to maximize conversion of the Vacuum Residue towards middle distillate production. The feedstock to the H-Oil® unit is a blend 50% Middle East and 50% of Merey crude with a cut point equal to 480°C+ to get an acceptable viscosity. The cut point is higher compared to the first example due to the presence of Middle East which helps reducing the viscosity of the blend. Properties of the feedstock are shown in the table below:

Analysis	Units	Arabian crude 480°C+	Merey Crude 480°C+	Blend
Specific Gravity (20°C)	-	1.0215	1.0429	1.0321
Microcarbon Residue	wt%	21.13	23.25	22.19
Vanadium	wtppm	142	504	323
Nickel	wtppm	48	123	86
Sulphur	wt%	5.39	3.73	4.56
Nitrogen	wtppm	4049	6763	5406
Viscosity @ 100°C	cSt	2746	64000	11000
Asphaltenes content	%	13.5	17	15.2

With this type of feedstock the conversion in the H-Oil® can reach 73.3 wt% which leads to a yield of 72 wt% of distillates (naphtha, diesel and VGO) and 21.6 wt% of vacuum residue. In order to maximize residue conversion and get more valuable products, the unconverted oil (UCO) of the H-Oil®$_{RC}$ unit is sent to a Solvent deasphalting unit where the DAO lift is set around 48 wt%. The limitation in the DAO lift is due to the hardness of the pitch. The overall material goes up to 85 – 88 wt% for the all complex. There is only 11 wt% of pitch which will be sent to the gasification unit to produce hydrogen.



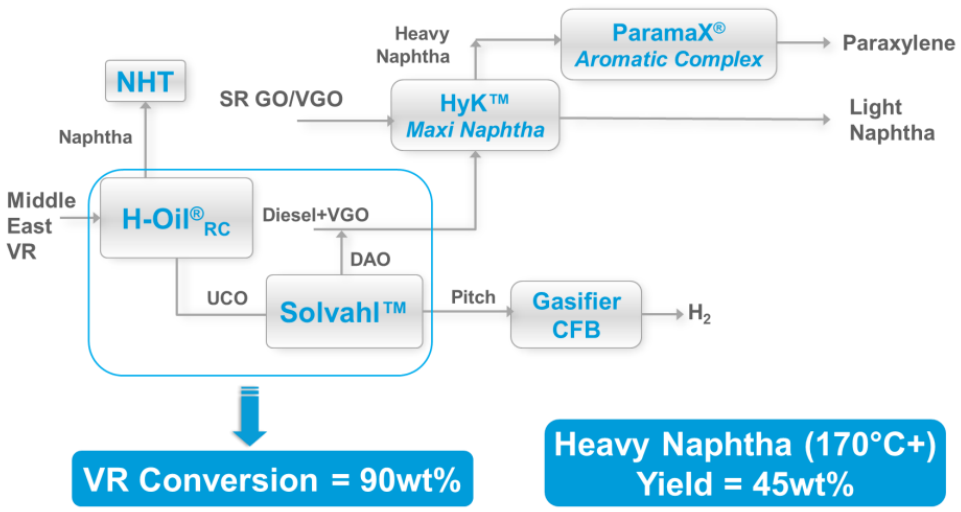
For a blend 50% Middle East / 50% Merey, it is possible to achieve around 88 wt% of conversion by implementing an H-Oil® unit followed by a Solvent Deasphalting unit. This residue conversion leads to a production of 9% of naphtha, 27 wt% of diesel and 45 wt% of VGO/DAO which neds to behydrotreated to produce Naphtha or Diesel on specification

<u>Example 2</u>

For comparison, the next example presents the same configuration for 100% Arabian type of feed. The objective of this project was to maximize heavy naphtha production for petrochemical application.

The vacuum residue is sent to an H-Oil® unit set at 80 wt% of conversion. The unconverted residue is then routed to the solvent deasphalting unit. A DAO lift around 55 wt% is achievable and allows a to recovery of DAO with properties in line for further hydroconversion in a VGO hydrocracker unit. The pitch from the Solvent deasphalting unit is sent to an exsiting gasifier unit to produce hydrogen. Within the battery limits of the H-Oil® and the SDA units, the yields for Naphtha, Diesel and VGO/ DAO are respectively 8 wt%, 36.2 wt% and 38.4 wt%. These yields areslihtly higher than that of the previous Example with Merey type of crude.

The Diesel and VGO cuts from the H-Oil® unit and the DAO from the SDA unit together with straight runs diesel and VGO are sent to a VGO hydrocracker unit operating in a max naphtha mode. This configuration allows an overall residue conversion equal to 91 wt% and a heavy naphtha yield equal to 45 wt% from crude.



In conclusion, these examples show that even if feedstock origins are completely different and the reactivity in the first H-Oil® is not similar, it is possible to achieve an overall very high conversion (from 85 to 90 wt%) for every kind of feedstock with a tailored combination H-Oil® + SDA unit.

H-Oil® / SDA solution in brief

- **Ebullated bed technology is well suited regardless of the feed quality** –The technology is proven for all kind of feedstocks such as Arabian type of crude to heavy South American feeds. Industrial experience is available from Pemex Tula and Salamanca units on South American feedstocks.
- **Novel but industrially proven high conversion scheme** - With **solvent deasphalting**, the molecules that are the most difficult to convertare rejected and allow the second stage reactor to operate at very high conversion. The overall conversion can be maximized. Every detail in the proposed diagrams is optimized for maximum reliability and therefore maximum on stream factor. Every section is made of equipment that are **fully industrially proven with decades of successful operation and continuous improvements with a high stream factor (>96%)**.
- **No by-products from residue hydrocracking:** Pitch from SDA can be burned in the circulating fluidized boiler or in a gasification unit.
- **High overall distillates yield**.
- **Less severe conditions** for each reactor section leading to **cheaper high pressure vessels**, and without fragile internal refractory lining
- **Tailored scheme** for each specific application depending on: Project Objective, Products Requirement, Feedstocks or Site constraints

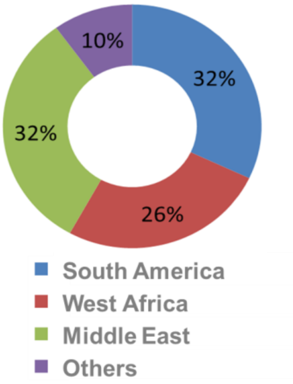
After describing the various options to increase the overall conversion thanks to a combination between solvent deasphalting unit and H-Oil® unit, the next section will focus on taking advantages of existing assets in the refinery (such as Coker Unit) to achieve the same goal and increase the conversion towards maximum distillates or maximum heavy naphtha production.

Solutions with existing assets: H-Oil® + coker

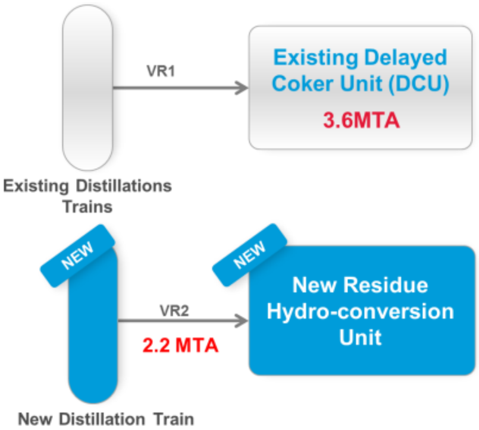
This section describes the configuration where the unconverted residue from the H-Oil®$_{RC}$ is routed to an existing Coker unit. The overall conversion will increase up to 90-95 wt%. Combining the H-Oil®$_{RC}$ with a Coker may also be used as a mean to debottleneck existing Coker units. The yield of petcoke will be lower than 10 wt%. Economics are greatly improved in Refinery with existing Delayed Coker.

Historically, refineries have added incremental Delayed Coking capacity using Coking Technology as part of refinery expansions because it was considered to be a low cost option and a well-known technology. But with the new changes in market prices (and lore particularly price of H2 in most regions) and the need for maximum conversion of residue, it begs the question; is implementing a new coker unit still the best option for refinery?
Axens has studied the expansion project of an existing refinery processing a blend of South America, West Africa, Middle East and others crude with properties shown in Table 1.

	VR 550°C+
API	7.1
Sulphur, wt%	2.5
Nitrogen, wppm	4900
Viscosity @ 100°C, cSt	9300
Vanadium, wppm	315
Nickel, wppm	110



The bottom of the barrel section is a typical refinery configuration with a Delayed Coker for processing the entire vacuum residue (3.6 mTA). The objective is to add a new distillation train of 2.2 mTA of VR associated with a new residue hydro-conversion unit in order to maximize the Diesel Euro V production while minimizing the revamping of the existing coker if any.



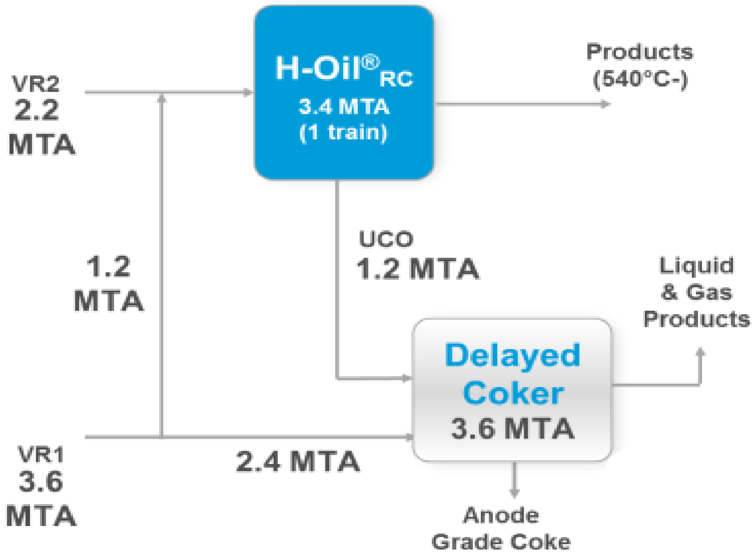
Two expansion configurations were investigated for this study. The first case assumed each train independently. The second configuration combined the new residue hydroconversion unit with the existing coker unit. The objective of the expansion was to bring the total vacuum residue throughput to 5.8 MTA.

The H-Oil®$_{RC}$ Unit was a single train plant with two reactors in series operating at 65% conversion of the 540°C$^+$ residue to distillates.

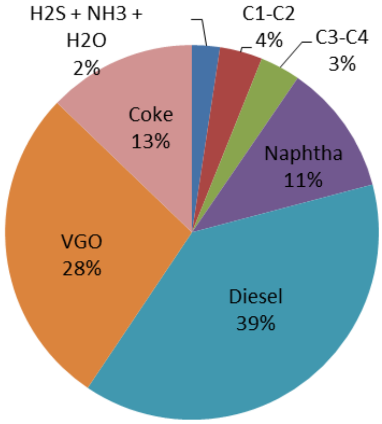
The first case showed that assuming two independent trains would lead to an average conversion close to 70 wt%.

In order to further increase the conversion a second case was studied where the unconverted residue from the H-Oil® unit was routed to the existing coker unit.

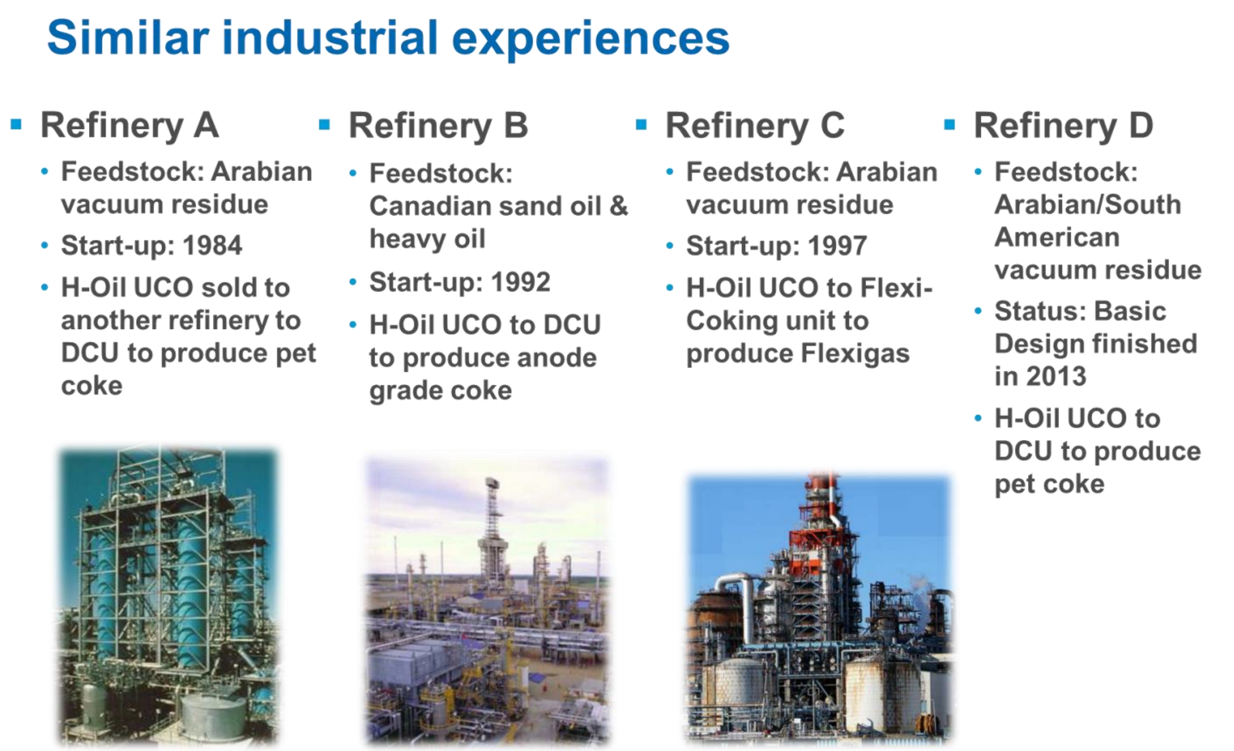
To minimize the revamping cost for the existing Coker unit, it was decided to keep the capacity of the existing coker constant and route a part of the vacuum residue from the existing distillation along with the vacuum residue from the new distillation to the H-Oil® unit, for a total capacity of 3.4 MTA. The coker feed was comprised of the unconverted residue from the H-Oil® unit and the remainder of the vacuum residue.



Yields are presented here below. This configuration allows the production of 39% of diesel, 11% of Naphtha and 28% of VGO. In residue hydrocracking, many of the coke precursors are hydrogenated which results in higher liquid yield compared to coking and reduced coke production. In addition, the addition of hydrogen into the liquid product increases the API gravity which in turn leads to greater volume swell and increased production of transportation fuels.



There are several advantages to this configuration. First, the overall conversion (100-coke) for both trains is significantly increased to a level of 79.5 wt% (on 5.8 MTA of VR). The conversion for the VR#2 itself reaches 87 wt% for the new train of vacuum residue (on 2.2 MTA of VR). Without the integration of both units, the overall conversion for both trains would have been around 70 wt%. Second, with this integration, there is no need to find an outlet for the unconverted product from the H-Oil® as it is routed to the existing coker unit. In addition, the coke produced can be sold as anode grade coke. Indeed, the coke produced with this configuration has a better quality thanks to the hydrotreatment achieved in the upstream H-Oil® unit. Finally, this configuration is industrially proven as shown in the next figure.



H-Oil® plus coker solution highlights:

- Enhance overall conversion
- Proven High Conversion with Combination of H-Oil®$_{RC}$ & Coker (>90wt%) with a high stream factor (>96%)

- Good VGO/Diesel Product quality which is easy to hydrotreat in downstream unit to meet final specifications
- H-Oil®$_{RC}$ & Coker: Coke can be sold as anode grade for Al production
- H-Oil®$_{RC}$ & Coker: High potential diesel Euro V production
- Combination : high profitability

Conclusion

Over the years, Axens, as a process licensor and catalyst manufacturer, has managed to develop an extensive knowledge and expertise in residue upgrading processesand in particular, on ebullated-beds HCK technologies. Axens also embarked in significant R&D activities and/or successful partnerships.
With 17 licensed H-Oil®$_{RC}$ units worldwide, among them three very recent projects, one in USA and one in China with an overall capacity over 810 kBPSD, Axens is the leader in ebullated-bed hydroconversion technology operating H-Oil®$_{RC}$ units have been running extremely well over the years, showing outstanding and stable performances. In particular, H-Oil®$_{RC}$ units achieve an average reliability above 96%.
By combining this technology with existing unit into the refinery or deasphalting unit, refiners can go beyond typical conversion levels and reach very high conversion levels even for difficult feedstocks.
With the increasing need for producing more motor fuels and less fuel oil, solutions proposed in this paper will certainly shape the refinery of tomorrow.