7.2.1 Background and basics

Developments in environmental legislation in various countries have made it difficult to commercialize residues and heavy oils with high viscosity and high levels of contaminants (fractions with a high concentration of polynuclear aromatic hydrocarbons, asphaltenes, sulphur, nitrogen, and metals). This has created the right conditions for the development of hydroconversion processes suitable for transforming these residues into more valuable products, or at least making them more environmentally friendly.

The main objectives of residue upgrading processes are: pretreatment of feedstock for other conversion units, increasing distillates and the production of fuels with a low sulphur content (Le Page et al., 1992; Dickenson et al., 1997).

Traditionally, this type of process has been classified into two categories: technologies based on reducing the carbon content (carbon rejection), and hydrogen addition technologies. The first class comprises typically thermal processes, already developed in the first half of the past century, such as coking, deasphalting, and visbreaking. These processes, while having the advantage of flexibility and low cost, produce distillates of modest quality and residues of low value (fuel oil, coke, asphalt; see Chapter 7.1). The second class comprises more recent catalytic processes for the hydroconversion of residues, which increase the H/C ratio without simultaneously producing fractions with a higher carbon content; these have the further advantage that the contaminant content is also reduced.

Chapter 1.1 describes the place occupied by these processes in the principal refinery schemes. It should be remembered that conventional catalytic cracking processes may also be partially fed with residues (O’Connor et al., 1991). The hydroconversion processes available today differ mainly in terms of the typology of reactors, operating conditions and the catalytic systems used.

Reactions and catalysts

Hydroconversion processes for residues, both thermal and catalytic, are characterized by the fact that they generally operate under severe conditions, especially as concerns temperature and pressure. Space velocities, generally low, are obviously linked to the optimization of operating conditions, in accordance with the properties of the feedstocks and the products we wish to obtain.

Hydrodesulphurization (HDS), hydrodenitrogenation (HDN) and hydrodemetalization (HDM) reactions are catalytic, and of similar type to those described in other parts of this volume (see Chapters 3.1 and 6.2), with the difference that in this case the molecules are more complex molecules and have a higher molecular weight. Sulphur is present in residues mainly in the form of sulphides (sulphur links in asphaltenes) or thiophene compounds. The former are susceptible to thermal decomposition due to the low energy of the C-S bond, whereas the decomposition of thiophenes, still catalytic, may occur with or without a preliminary dehydrogenation stage. This stage is always present in the conversion of nitrogen compounds (see Chapter 3.1).

Hydrodemetalization is usually thermocatalytic, preceded by the partial hydrogenation and decomposition of asphaltenes and porphyrins, with the production of heavy metal sulphides, typically of vanadium and nickel. The life-span and performance of the catalysts used in hydrodemetalization are strongly conditioned by phenomena of inhibition and the physical obstruction of the pores.

Hydrogenation reactions, generally catalytic, are aimed at conversion, but also involve the olefins and free radicals which form due to thermal cracking,
significantly reducing polycondensation reactions (and thus the formation of coke) which, however, are always present. Also important are reactions which transfer hydrogen between the various hydrocarbon structures in solution (aromatics, cycloaliphatics, paraffins), and between these and free radicals.

Cracking and condensation reactions, by contrast, are mainly thermal, and lead to the formation of both light products and polyaromatic precursors of coke. Examples of reactions can be found in other parts of this volume (see Chapters 3.1 and 6.2 and Section 7.2.2), and in the literature (Leprince, 2001).

The catalytic reactions mentioned above are exothermic, whereas thermal cracking reactions are endothermic. The overall hydroconversion process, however, is exothermic.

The complex chemical and physical properties of residues, and the simultaneous presence of thermal and catalytic reactions, make the kinetic analysis of the chemical processes involved extremely complex. Thermal cracking and polycondensation reactions become significant above 400-420°C, especially with feedstocks rich in asphaltenes; under these conditions, high hydrogen pressures are needed to stabilize the free radicals and hydrogenate the aromatic rings.

The physical shape of the catalyst, in terms of particle size and structure, plays an important role both within individual processes, and in the different types of processes. The main distinction is that between supported catalysts (similar to those used, for example, in hydrotreating processes) with a diameter of between 0.8 and 3 mm, and catalysts used in the form of dispersed microparticles. Supported catalysts are used in fixed bed, moving bed and ebullated bed processes.

Very often, at least two different types of catalyst are used one after the other in a single process with different functions: a typical sequence consists of one or more HDM catalysts, placed to "guard" the efficiency of

<table>
<thead>
<tr>
<th>Table 1. Examples of supported catalysts for residue conversion</th>
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<tbody>
<tr>
<td><strong>Precatalyst</strong></td>
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<tr>
<td><strong>Filter</strong></td>
</tr>
<tr>
<td>Physical shape</td>
</tr>
<tr>
<td>Diameter (mm)</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
</tr>
<tr>
<td>Mean pore diameter (Å)</td>
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<tr>
<td>Active catalytic phase</td>
</tr>
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* more suitable for moving beds

<table>
<thead>
<tr>
<th>Table 2. Main types of process for the hydroconversion of residues (2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of Reactor</strong></td>
</tr>
</tbody>
</table>
| Fixed bed | NiMo-CoMo | Axens (Hyvahl)  
Chevron (RDS/VRDS)  
Exxon  
Shell (RHU)  
UOP (RCD/Union Fining) |
| Moving bed | NiMo-CoMo | Shell (Hycon)  
Chevron (OCR)  
Axens (Hyvahl-M) |
| Ebullated bed | NiMo-CoMo | Axens (H-Oil)  
ABB Chevron Lummus (LC-Fining) |
| Slurry  
(entrained bed) | MoS₂ | Veba (VCC)  
Petrocanada (Canmet)  
Exxon (Microcat)  
Eni (EST) |
subsequent catalytic processes. Often these are preceded by a bed of protection material with large porosity which acts as a trap or filter for the solid particles present in the feedstock: iron compounds, NaCl, carbonaceous or inorganic particles of various types, sediments, etc. Table 1 shows some of the properties of a typical catalytic material for industrial use.

The porosity of HDM catalysts must be sufficiently high, in terms of pore dimensions and adsorption capacity, in order to allow large molecules to enter and then trap the metal sulphides which form. Furthermore, the support (for example alumina) must have as low an acidity level as possible. Considering the mechanisms described, these catalysts can work at higher temperatures than HDS catalysts. The latter must also have the ability to encourage HDN reactions, hydrogenation and hydrocracking; for this purpose, the Ni-Mo system may be preferred over the Co-Mo system.

Catalysts in the dispersed phase, used in slurry processes (see below), consist of very small particles injected in a fluid phase or which form in situ from a precursor; the catalyst is entrained in the effluent which exits the reactor unconverted, and can be recycled with it.

One example is molybdenum naphthenate, which, due to thermal interaction in the reactor, turns into sulphide particles associated with a hydrocarbon matrix (about 1 µm in diameter). Despite the high surface area, activity is generally lower than that of supported catalysts. The use of these catalysts at relatively high temperatures causes fewer problems with agglomeration and loss of pressure; they also have a good ability to block free radicals, thus reducing polycondensation reactions.

---

**Fig. 1.** Typical operating windows for residue conversion technologies, including catalytic cracking (FCC) for the sake of comparison.

**Fig. 2.** Diagram of the RHU (Shell) fixed bed process. The HDM and HDS phases take place in reactors R-01/R-02 and R-03/R-04 respectively.
Processes

The various processes are differentiated on the basis of the type of reactors, their number and sequence, as shown in Table 2 (Leprince, 2001; Anonymous, 2002; Meyers, 2004). Fig. 1 gives an idea of the positioning considered optimal for the various technologies, as a function of the main contaminants (asphaltenes and metals) contained in the feedstock.

Fixed bed processes (the most common at the end of the twentieth century), though sound, do not appear able to adequately treat feedstocks with high contents of asphaltenes, metals and other heteroatoms, due mainly to problems relating to the deactivation of the catalysts.

Technologies of the ebullated bed type perform well even with relatively heavy feedstocks. Slurry processes, which operate with dispersed catalysts, ensure good feedstock upgrading performances, in addition to considerable flexibility.

Fixed bed and moving bed processes

Fixed bed processes are traditionally characterized by the presence of HDM stages and partial cracking, plus the HDS stage, as in the example shown in Fig. 2 (Giavarini, 1999).

The reactors, of trickle flow type, are normally large due to the low space velocities and the large quantities of catalysts needed. The temperature, which increases from top to bottom due to the exothermic nature of the reactions, is controlled by adding quench gas. The temperatures do not normally exceed 400-420°C, and pressures may be up to 160 bar. Space velocities, usually low, must be such as to ensure sufficient wetting of the catalyst.

In moving bed processes, which are relatively less common, the feedstock and hydrogen may circulate in equicurrent, as in the simplified diagram shown in Fig. 3, and in countercurrent. In these processes, too, the second stage reactors are generally of a fixed bed type. The catalyst moves towards the bottom only during operations to extract the depleted catalyst (from the bottom). The slight expansion of the catalyst, in the form of pellets, caused by the flow of the feedstock, creates some problems with friction and mechanical erosion. However, this disadvantage and that represented by more complex operating procedures is countered by the advantage of longer working cycles with respect to fixed beds.

Ebullated bed processes

Processes of this type are characterized by the fact that the circulation of the feedstock and hydrogen from bottom to top keeps the catalyst in suspension (Fig. 4); a recirculation pump for liquid products regulates the expansion of the bed. This pump may be placed inside or outside the reactor (Parkash, 2003).

These reactors are large, being up to 30 m tall and with diameters of up to 5 m; the volume must be suitably increased to take account of the expansion of the catalytic bed (about 30-50%). In this case, too, some friction between the particles of catalyst is unavoidable. The flow is agitated, rather than of piston type as in fixed bed reactors; the temperature profile is
isothermal. This, alongside the modest and controllable loss of pressure, represents one of the advantages of this type of process.

The catalyst may be added and removed either continuously or intermittently, thus avoiding variations over time in the yield and quality of products, typical of fixed bed processes. However, the consumption of catalysts is higher than for fixed beds, since the catalyst removed is found in varying stages of saturation and deactivation. Operating procedures are also more complex. With high conversion rates, furthermore, the quality of the residue is generally fairly poor.

Fig. 5 shows a diagram of the H-Oil process (Axens), which uses two ebullated bed reactors (Leprince, 2001). Since hold-up times are lower than for fixed beds, the temperatures (390-450°C) and above all pressures (90-240 bar) are higher; space velocities may range from 0.1-0.9 h⁻¹.

**Slurry processes**

These processes, to an even greater extent than ebullated bed processes, are suitable for treating residues with a high impurity content. The unit consists of one or more reactors (which may be of fixed bed type) with the feedstock, hydrogen and catalyst (in the dispersed phase) circulating from bottom to top.

The catalyst generally consists of finely dispersed metal sulphides (of iron and/or molybdenum), generated *in situ* by the decomposition of a precursor. The catalyst does not promote cracking, which is of exclusively thermal type, whilst it activates the desulphurization, free radical quenching and hydrogenation reactions. The velocity of the liquids and gas must be sufficiently high to keep the catalyst dispersed; for the rest, conditions are similar to those of the preceding class of processes.

The processes under examination are often still in the pilot or pre-industrial stage (see again Tab. 2). A recent process, developed by ENI and named EST (ENI Slurry Technology), stands out for the fact that it combines the HDM/HDN/HDS stage using a MoS₂ catalyst with a deasphalting and asphaltene recycling operation, and the optional recycling of deasphalted oil. This process is also characterized by high conversion rates and high quality products, without the simultaneous production of fuel oil.

**References**


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7.2.2 LC-Fining process

The LC-Fining residuum hydroconversion process was developed to specifically target hydrocracking of the most difficult, heavy, lower-value hydrocarbon streams (petroleum residua, heavy oils from tar sands, shale oils, solvent refined coal extracts, etc.) at residue conversion levels of up to 80% and higher.

When coupled with an integrated, fixed-bed, wide-cut hydrotreater/hydrocracker, the LC-Fining process produces high quality finished products without significant quantities of undesirable by-products.

Residuum upgrading process requirements should include the ability to: a) handle high heats of reaction via efficient use of reactor volume; b) handle extraneous material without plugging; c) provide uniform distribution of reactants and efficient contacting; d) operate over extended periods without shutdown.

The nature of the LC-Fining process, makes it ideally suited for the conversion of residues to lighter, more valuable products. The process can be tailored for the feedstocks, the degree of conversion, and the product qualities required, especially for the production of high-quality residual fuel oil with a low sulphur content and good pipeline stability, or high quality synthetic crude oils.

The process is based on technology initially developed and commercially demonstrated by Cities Service, and subsequently improved and refined by ABB Lummus Global, BP (formerly Amoco Oil Company) and ChevronTexaco Corporation. With this process, heavy oil feeds – including gas oils, petroleum atmospheric and vacuum residue, coal liquids, asphalt, bitumen from tar sands, and shale oil – are hydrogenated and converted into a wide spectrum of lighter, more valuable products such as naphtha, light and middle distillates, and atmospheric and vacuum gas oils. Products can be used as fuel oil, synthetic crude, or feedstock for a coker, visbreaker, solvent deasphalter, or residuum catalytic cracker.

Operating conditions and catalyst type and activity can be varied to achieve the desired hydrocarbon conversion, Conradson Carbon Residuum (CCR) reduction, desulphurization, and demetallization of residual oil feeds.

Process chemistry

Residua and heavy oils differ from distillates in that they contain asphaltenes and other high molecular weight, highly polynuclear aromatic structures and coke-forming constituents including carbon residue and organometallic compounds (with nickel and vanadium). Asphaltenes have a marked effect on the chemistry of hydrocracking and result in the deposition of carbon and coke precursors on the catalyst. Such depositions seriously affect the catalyst activity due, primarily, to the condensation and polymerization reactions during residue conversions (especially at deeper conversion levels).

Residuum hydrocracking is accomplished at relatively high temperatures and high pressures in the presence of hydrogen, and of a catalyst capable to hydrogenate the products and prevent polymerization of the free radicals as cracking reactions proceed.

The catalyst consists of a combination of metals that promote hydrogenation (e.g., cobalt and molybdenum, or nickel and molybdenum) deposited on an alumina base.

The two most important reactions that take place in residuum hydrocracking, i.e. thermal cracking to lighter products and catalytic removal of feed contaminants, generally require operating temperatures between 385 and 450°C, hydrogen partial pressures from 7.50 to 15.00 mPa and space velocities ranging from 0.1 to 0.8 vol h⁻¹.

The chemical reactions in resid hydroprocessing are sub-divided into three main classes: cracking of large molecules followed by saturation (capping of free radicals); elimination of heteroatoms (S, N, O); demetallization (removal of vanadium, nickel and trace metals). Typical chemical reactions during hydroprocessing are shown in Fig. 1.

Traditionally, the compounds present in the residuum are generally classified as oils, resins, and asphaltenes. The asphaltenes are the high-molecular-weight material that typically contain a
large concentration of sulphur, nitrogen, metals, and highly condensed polynuclear aromatics.

Nitrogen removal is generally much more difficult than sulphur removal. Some nitrogen compounds in the cracking reactions are merely converted to lower boiling range nitrogen compounds rather than being converted to \( \text{NH}_3 \).

The highest concentration of metals (V and Ni) mostly reside in the asphaltene fraction with some in the resin fraction. The oil fraction tends to be nearly free of metals. Metals are removed as metal sulphides. Unlike sulphur and nitrogen, which are converted and “escape” as \( \text{H}_2\text{S} \) and \( \text{NH}_3 \), the vanadium and nickel removed are absorbed on the catalyst. These metals are known to plug the catalyst pores, and this pore blockage results in catalyst deactivation.

There are many factors that affect the sediment formation rate and, consequently, the reactor operability and resid conversion limits, including:

- a) asphaltene content;
- b) \( \text{CCR} \) reactivity;
- c) thermal severity (conversion);
- d) catalyst type and activity;
- e) hydrogen partial pressure;
- f) type and quantity of diluents;
- g) resin content;
- h) reactor temperature.

Of these, the first six have the most influence. Many pilot plant tests showed that sediment (i.e. coke) precursor formation is directly proportional to the asphaltene content of the feed and inversely proportional to the \( \text{CCR} \) reactivity.

The nature and origin of the coke precursors are often not precisely known. However, a mechanism of their formation in processes that involve thermal cracking in addition to hydrocracking and hydrogenation, such as the LC-Fining process, has been generally postulated as described by the following reaction chemistry:

- **Thermal cracking – formation of free radicals:**
  \[
  R_x \rightarrow R_y + R_z
  \]

- **Reaction of free radicals to form olefins or asphaltenes:**
  \[
  \begin{align*}
  R & \rightarrow \text{CH}_2 - \text{CH}_2 & \rightarrow & \text{R} - \text{CH} - \text{CH}_2 + \text{H}\cdot \\
  R & \rightarrow \text{CH}_2 - \text{CH}_2 + R_z & \rightarrow & R - \text{CH}_2 - \text{CH}_2 - R_y
  \end{align*}
  \]

- **Ermination or recapping of free radicals by hydrogenation:**
  \[
  R_y + \text{H}\cdot \rightarrow R_y - \text{H}
  \]

At elevated temperatures, thermal cracking reactions generate free radical species due to the rupture of carbon-carbon bonds. The free radicals may react with hydrogen in the presence of the catalyst to form stable products. This reaction predominates in the LC-Fining process where high hydrogen partial pressures are always maintained. If proper conditions are not maintained, the free radicals may also combine with other free radicals to form higher molecular-weight free radicals. This chain reaction can continue until very high molecular-weight, insoluble species (coke precursors/sediments) are produced. As the temperature is increased to obtain higher conversions, the rate of generation of free radicals, and consequently coke precursors, can increase, creating phase separation and potential instability in the reactor if it is allowed to exceed the solubility limit.

Control of coke precursors (organic sediments) can be accomplished in three ways: their formation is minimized or eliminated by using extremely high hydrogen partial pressures or very active catalyst; the coke precursors are maintained in solution by adding aromatic diluents; the coke precursors are removed from the system.

The catalyst and aromatic diluents used in the process have an excellent ability to control the formation of these coke precursors. The continuous physical removal of coke precursors (via filtration, centrifugation, etc.) from the reactor loop, can be accomplished by bottoms recycle and removal of the coke precursors from the recycle stream, an approach pilot tested and patented by Lummus for High Conversion LC-Fining.

**Catalysts and reaction kinetics**

A series of catalysts are available for use in LC-Fining units. The first-generation catalysts in
commercial use had adequate HDM (Hydrodemetallization)-HDS (Hydrodesulphurization) activity with acceptable sediment levels. These were less expensive than more recently developed, enhanced contaminant removal/sediment control catalysts. New generation catalysts are needed to produce low sulphur fuel oils (from vacuum bottoms) of 1 wt% sulphur or less, with minimum sediment levels (≤ 0.15 wt%) for pipeline stability. The other requirement of a good LC-Fining catalyst is to maintain improved reactor operability/stability at high temperature/deep resid conversions.

The residuum hydroprocessing catalysts are small (8 mm to 16 mm in size), extruded, cylindrical pellets made from an aluminium base. The pellets are impregnated with active metals (Co, Ni, Mo, W and other proprietary materials) that have good hydrogenation, demetallization, desulphurization and sediment control activity. Catalyst manufacturing processes are tailored to manipulate physical and mechanical properties such as: a) size (length and diameter); b) attrition resistance; c) crush strength; d) pore size distribution; e) pore volume; f) effective surface area. Catalytic performance is affected by the complicated nature of the “active site” and dispersion and distribution of activators and promoters.

Pore size control and distribution are key factors in the behaviour and formulation of residuum conversion catalysts. The pore sizes need to be sufficiently large to allow the diffusion of the large asphaltene molecules that require upgrading. Unfortunately, as the pore diameter increases, the surface area and the hydrogenation activity decrease. The diffusion of large molecules is reduced further because of pore mouth plugging due to carbon laydown and metal sulphide build-up from vanadium and nickel atoms that are removed from the resid feed. Metal sulphides are formed from the oxidative state of the catalyst in the reactor environment (presulphiding reactions with sulphur in heavy oils, etc.).

Catalysts are also optimized for specific functions – such as metals removal, sulphur removal, carbon residue reduction, and high conversion – while maintaining a clean product low in organic sediments. The catalyst system developed by BP for their LC-Fining unit at Texas City utilizes a proprietary demetallization catalyst in the first reactor, and a high activity Ni/Mo desulphurization catalyst in the second and third reactors.

One of the key features of the LC-Fining process is the use of counter-current catalyst addition to optimize catalyst usage. Fresh catalyst is added to the third reactor, then it is reused by withdrawing it and adding it to the second reactor. The catalyst can then be used a third time, by withdrawing it from the second reactor and adding that material to the first reactor. Catalyst cascading results in higher overall kinetics rate constants and, therefore, better overall catalyst utilization based on the concentration of metals in the spent catalyst discharged from the first stage. This mode of addition/withdrawal has the added benefit of exposing the most highly converted resid to the most active catalyst. This reduces the sediment formation in the last reactor and thus allows reactor operability/conversion limits to be extended.

The rate at which a catalyst deactivates during residual oil hydrocracking is a complex function of many parameters that can be categorized into three distinct classes: the first consists of physical and chemical properties of the residual feedstock to be processed; the second is concerned with the nature of the catalyst itself; the third is the effect of the operating conditions (temperature, space velocity, hydrogen partial pressure, etc.) used to obtain the desired levels of conversion and desulphurization.

The most significant causes of catalyst deactivation are metals and carbon laydown. Concurrent with the desulphurization of residua is a demetallization reaction. Products from the residual hydrocracking have nickel and vanadium contents markedly lower than the feed to the unit. The metals accumulate on the catalyst, causing deactivation. It has been proposed that the organometallics simply block the outer physical surface of the catalyst.

Carbon laydown on catalyst is influenced by feedstock characteristics and conversion severity. Carbon accumulation is high in all operating scenarios, ranging from slightly under 10 wt% for low temperature HDS of atmospheric residuum, to over 40 wt% for high conversion of vacuum bottoms. The residuum hydrocracking is, apparently, diffusion controlled. It has been found that 8 mm catalyst performs better than 16 mm catalyst.

Kinetics rate constants provide the fundamental basis for scaling-up from pilot plant to commercial conditions. As for hydrocarbon conversion, design from pilot plant data uses the back-mix-reactors-in-series model where kinetics is described in terms
of simple pseudo-first-order expressions; the rate constant is given by the following expression:

\[ k_{HC} = N \left[ \frac{1}{\frac{100}{100-C}} \right]^{1/N} LHSV \]

where \( k_{HC} \) is the first-order hydrocarbon conversion rate constant, \( LHSV \) is the Liquid Hourly Space Velocity, \( C \) is the residue conversion, and \( N \) is the number of ebullated bed reactors in series.

As for residue hydrodesulphurization, kinetics is considerably more complex than that related to hydrodesulphurization of model organic sulphur compounds or, for that matter, narrow-boiling petroleum fractions (see Chapter 3.1). In published studies of the kinetics of residue hydrodesulphurization, one of three approaches has generally been taken:

- The reactions can be described in terms of simple first-order expressions.
- The reactions can be described by use of two simultaneous first-order expressions – one expression for easy-to-remove sulphur and a separate expression for difficult-to-remove sulphur.
- The reactions can be described using a pseudo-second-order expression.

Referring to the latter approach and two back-mix reactors in series model, it is possible to obtain an expression for the second-order hydrodesulphurization rate constant \( k_{S} \). A similar expression is used to evaluate the second-order CCR reduction rate constant.

As for demetallization, the rate constant is given by a simple pseudo-first-order expression:

\[ k_{V} \cdot k_{Ni} = 2 \text{WDSV} ((C_{f}/C_{p})^{0.5} - 1) \]

where \( k_{V} \) and \( k_{Ni} \) are the first-order vanadium and nickel removal rate constants, WDSV is the Daily Weight Space Velocity \( (\text{m}^3/\text{g/day}) \), \( C_{f} \) and \( C_{p} \) are the concentrations of reacting species in the feed and product.

**Process description**

A simplified process flow diagram of an LC-Fining unit with a close-coupled, integrated, fixed bed hydrotreater/hydrocracker is shown in **Fig. 2**.

Oil feed and hydrogen are heated separately, combined, and then passed into the LC-Fining unit.
hydrocracking reactor (Fig. 3). Fresh feed and hydrogen enter the reactor at the bottom and pass up through a catalyst bed where, under the effects of time, temperature and hydrogen pressure, and aided by catalysts, the feed oil is cracked and hydrogenated to produce lighter, higher-quality products. A portion of the liquid product from the large pan at the top of the reactor is recycled, through the central downcomer, by means of a pump mounted in the bottom head of the reactor. This flow provides the velocity necessary to keep the catalyst bed in a state of motion somewhat expanded over its settled level (i.e. ebullated). Moreover, this flow aids in maintaining near isothermal reactor temperature. As a matter of fact, the hydrocracking reactions are exothermic, resulting in a temperature rise from inlet to outlet depending upon the reaction operating severity. However, because of the mixing effect of the internal recycle, the bed operates essentially isothermically. The catalyst level is monitored and controlled by radioactive density detectors, where the source is contained inside the reactor and the detectors are mounted outside. Temperature is monitored by internal couples and skin couples. The performance of the ebullated bed is continuously monitored and controlled with the density detectors and temperature measurements that verify proper distribution of gas and liquid throughout the catalyst bed. Temperature deviations outside the normal expected ranges that might suggest maldistribution will cause the Distributed Control System (DCS) to activate alarms or initiate automatic shutdown on the heaters, hydrogen feed, and/or reactor section, as required.

Catalyst is added and withdrawn likewise to maintain an equilibrium catalyst activity without the need for unit shutdown. The reactors can be staged in series, where the product from the first reactor passes to a second reactor and, if necessary, to a third reactor. After the final reactor, the product goes to a high pressure/high temperature separator.

Vapour, effluent from the separator, is let down in pressure before heat exchange, removal of condensates, and purification. Handling the recycle gas at low pressure offers considerable savings in investment over a conventional high pressure recycle gas purification system.

After stripping, the recycle liquid is pumped through the coke precursor removal step (a physical means of separation such as centrifugation, etc.) where very small quantities of insoluble heavy hydrocarbons or carbonaceous solids are removed. The clean liquid recycle then passes to the suction drum of the feed pump. The net product from the top of the recycle stripper goes to fractionation; net heavy oil product is directed from the stripper bottoms pump discharge to vacuum fractionation.

The reactor effluent vapour, along with distillate recovered from the heavy oil stripper overhead, any virgin atmospheric gas oil recovered in the prefractionator upstream of the LC-Fining unit, and vacuum gas oil recovered in the vacuum fractionator, are all charged to a “wide-cut”, close-coupled, integrated, fixed bed hydrotreater/hydrocracker located immediately downstream from the last ebullated bed reactor. The inlet temperature to the first bed is controlled by adjusting the amount of heat extracted from the reactor vapour stream and the temperature of the distillate liquid is controlled by a combination of hydrogen and liquid quench.

The effluent from the hydrotreating reactors is separated into a vapour and heavy distillate liquid stream, with the liquid stream routed to the hydrotreated distillate fractionator. The vapour stream is amine treated, purified through a Pressure Swing Adsorption (PSA) or membrane unit, recompressed and recirculated to the LC-Fining reactors.

![Fig. 3. LC-Fining reactor.](image-url)
The high conversion (>80%) LC-Fining process differs from the basic process in that bottoms recycle is practiced. The recycle liquid is let down in pressure and passes to the recycle stripper where it is fractionated to the proper boiling range for return to the reactor. In this way, the concentration of bottoms in the reactor, and therefore the reaction products slate can be controlled.

**Technology features**

Several advances in the LC-Fining resid hydroconversion technology have significantly reduced the capital investment and have further extended the conversion limits and processing limitations. These include: a) H₂ purification systems; b) integrated fixed bed hydrotreater/hydrocracker; c) interreactor separator/stripper; d) modified liquid recycle pan; e) reactor bottom head feed distributor; f) improved reactor distributor design.

**Hydrogen purification systems**

In early designs, a lean oil system was used to purify the recycle gas and the maximum purity achievable was 82%. In 1984, Lummus developed and patented a low pressure H₂ purification system, which has been utilized in all commercial operating units since. With low pressure H₂ purification, the gas exiting the last reactor is immediately let down and cooled at low pressure and then purified in a PSA unit. This permits high hydrogen treat gas purities, generally exceeding 97 vol%. As a result, treat gas circulation rates were reduced by 50 to 60% and reaction system design pressure by 10%, while still satisfying the hydrogen partial pressure requirements. This change, in conjunction with the replacement of a certain amount of high pressure equipment with low pressure equipment, significantly reduced the unit investment cost. However, with this low pressure H₂ purification scheme the recycle gas had to be recompressed from low pressure back to reactor operating pressure, requiring an increase of 25 to 30% in the overall power consumption.

In 1998, the use of membranes was evaluated for purification of the recycle gas, and similar treat gas purities were achieved with membranes as with a PSA system. Membranes allow the same reduced reaction system pressure and lower treat gas circulation rates as with a PSA unit, but with the added benefit that the purified recycle gas is available at higher pressures. Consequently, the recycle gas can be recompressed in a single stage of compression versus the two or three stages of compression required with a PSA system, resulting in a 20% reduction in the overall unit power consumption. In addition, based on current high pressure equipment pricing, the unit investment is slightly less with membranes than with a PSA unit.

By using high purity recycle gas, it is possible to achieve the desired hydrogen partial pressure with much lower hydrogen gas rates. The low gas rates have two primary benefits: they reduce unit investment and velocity and, therefore, the gas hold-up in the reactor. This provides for more liquid residence time per unit reactor volume, thereby reducing the reactor volume. The use of low treat gas rates is utilized in all commercially operating LC-Fining units, which work with a total-hydrogen-to-chemical-hydrogen ratio of 2.5 to 3.

**Integrated fixed bed hydrotreater/hydrocracker**

Several designs incorporated a close-coupled, integrated, fixed-bed hydrotreater/hydrocracker immediately downstream of the ebullated bed reactors. In this design, the vapour stream from the ebullated bed reactors, plus the distillate recovered from the heavy oil stripper overhead and the straight run atmospheric and Vacuum Gas Oils (VGO), are fed to a fixed bed hydrotreater/hydrocracker operating at essentially the same pressure level.

Excess hydrogen contained in the ebullated bed reactor effluent vapour is used to hydrotreat the distillate fractions. Additional hydrogen, equivalent only to the chemical hydrogen consumed in the fixed bed reactor, is introduced as quench to the second and third catalyst beds.

The ebullated bed reactor effluent vapour is first contacted with VGO in a wash tower in order to remove any potential resid entrainment and entrainment of catalyst fines from the fixed bed reactor. By incorporating the fixed bed hydrotreater within the LC-Fining reaction system, the HP system service count is greatly reduced. In addition, since excess hydrogen in the LC-Fining reactor effluent vapour is used to hydrotreat the straight run and LC-Fining distillate fractions, the need for additional recycle gas compression is eliminated. As a result, the investment is significantly reduced compared to a stand-alone hydrotreater/hydrocracker.

**Interreactor separator/stripper**

Recently proposed process design configurations incorporate the use of an interreactor separator/stripper, which permits higher liquid capacities to be achieved for a given reactor cross-section. Gas superficial velocities
through the downstream reactors are reduced by separating the vapour between reaction stages and routing it to the final reactor effluent separator. This design provides for parallel flow of gas to each reaction stage while maintaining the benefits of series flow liquid operations. In a conventionally designed unit, the effluent vapour from the upstream reactor is combined with additional treat/quench gas and all the vapour is directed to the downstream reactors.

**Liquid recycle pan and bottom head feed distributor**

A modified, two-stage liquid recycle pan design has increased the conversion (about 4%) in the reactor and minimized upsets associated with the recycle pump bed expansion system. Subsequently, a new pan design has been developed permitting operation at still higher capacities and treat gas rates.

In 1985-86, a bottom head feed distributor was added to the LC-Fining reactors. It allows for better mixing of the feed oil, gas and recycle oil, while providing better distribution of oil and gas to the cap and riser assembly.

**Improved reactor distributor design**

The primary reactor grid distributor is a bubble cap type with slotted risers for distribution of vapour and liquid to each cap. Each riser contains a seat and ball to prevent back-migration of catalyst below the grid into the reactor bottom head should the recycle pump stop. The seat contains a small v-notch to permit oil to be drained from the reactor.

Amoco Oil Company performed substantial cold flow modelling of the distributor grid that led to the installation of catalyst slides. This was found to reduce instances of localized catalyst settling near the wall, maintaining a cleaner reactor environment and increasing the run length between turnarounds.

**Process flexibility**

The LC-Fining unit has great inherent flexibility to meet variations in feed quality/throughput, product quality and reaction operating severities (temperature, space velocity, conversion, etc.). This flexibility is a direct result of the ebullated catalyst bed reactor system. In an ebullated bed unit, if the metals or sulphur content of the feed increases, the product quality is maintained by increasing catalyst consumption.

The world’s first ebullated bed residual upgrader, operated by Cities Service Oil Company, utilized this flexibility to process atmospheric bottoms, FCC (Fluid Catalytic Cracking) heavy cycle oil, propane deasphalter bottoms, and vacuum bottoms.

Sufficient operating flexibility is also normally foreseen in the design to enable the unit to operate in the future with vacuum bottom recycle which provides for future options to increase either conversion or unit throughput.

A wide range of heavy oils have been processed in LC-Fining units. For example, the BP unit handles many of the poorest quality vacuum residua in the world, including Mexican, Venezuelan and Middle Eastern. Feed typically is under 5°API and has more than 4 wt% sulphur and more than 400 ppm metals. LC-Fining unit product yields for processing Arabian Heavy Vacuum Bottoms to conversion levels of 40%, 65%, and 80% are listed in Table 1. All of these conversions can be achieved in the same plant.

The plant and product properties are estimated from generalized correlations that were derived from extensive pilot plant and commercial data. Typical product properties for a 65 vol% conversion case are shown in Table 2.

**Operating variables**

The main operating variables in the ebullated bed residuum hydroconversion process are the following: a) feed quality; b) reactor temperature; c) hydrogen partial pressure; d) space velocity; e) treat gas to oil ratio; f) catalyst addition rate. Typical ranges of operating parameters are reported in Table 3.

**Feed Quality**

The quality of feed (gravity, S, N, CCR, metals, viscosity, C5 and C7, asphaltenes, ash content, trace metals, Na, Ca, Si, Fe, distillation, etc.) has a decisive effect on the choice of operating variables and the final processing objectives. Variations in contaminant levels influence the chemical hydrogen consumption and heat release.

Higher contents of asphaltenes, metals, CCR lead to a reduction in the catalytic activity. Higher viscosity/gravity feeds significantly affect the bed hydrodynamics resulting in higher gas hold-up.

Vacuum residua with varying paraffinic, aromatic, napthenic and unsaturated hydrocarbons contents have significantly different cracking/HDS/HDN (Hydrodenitrogenation)/HDM/ HCCR (Hydro Conradson Carbon Residue) reaction rate constants. Asphaltenes are difficult to crack and saturate and may
polymerize on the catalyst surface as carbonaceous deposits.

Heavy metals, particularly nickel and vanadium, in addition to alkalis (such as sodium) and alkaline earths (such as calcium and magnesium) are strongly attracted to the catalyst and irreversibly destroy its activity. These metals are found predominately in

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**Table 1. Typical LC-Fining unit product yields**

<table>
<thead>
<tr>
<th>CRUDE SOURCE</th>
<th>ARABIAN HEAVY VACUUM BOTTOMS + CAT CRACKER HCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion level</td>
<td>40</td>
</tr>
<tr>
<td>Feed</td>
<td></td>
</tr>
<tr>
<td>Gravity (°API)</td>
<td></td>
</tr>
<tr>
<td>Sulphur (wt%)</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td></td>
</tr>
<tr>
<td>Ni/V (wppm)</td>
<td></td>
</tr>
<tr>
<td>CCR (wt%)</td>
<td></td>
</tr>
<tr>
<td>Product yields, vol.%</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1.07</td>
</tr>
<tr>
<td>C2-165°C</td>
<td>5.50</td>
</tr>
<tr>
<td>165-370°C</td>
<td>19.18</td>
</tr>
<tr>
<td>370-550°C+</td>
<td>30.77</td>
</tr>
<tr>
<td>550°C</td>
<td>48.00</td>
</tr>
<tr>
<td>Total</td>
<td>104.52</td>
</tr>
<tr>
<td>550°C + Sulphur, wt%</td>
<td>1.2</td>
</tr>
<tr>
<td>Hydrogen consumption S m³/m³ Fresh Feed</td>
<td>168</td>
</tr>
</tbody>
</table>

**Table 2. LC-Fining unit product properties**

<table>
<thead>
<tr>
<th>Boiling range, °C</th>
<th>ARABIAN HEAVY 65% VOL. CONVERSION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% on feed</td>
<td>C5-165</td>
</tr>
<tr>
<td>Wt% on feed</td>
<td>5.27</td>
</tr>
<tr>
<td>Vol.% on feed</td>
<td>7.60</td>
</tr>
<tr>
<td>Gravity, °API</td>
<td>61.2</td>
</tr>
<tr>
<td>Sulphur, wt%</td>
<td>0.01</td>
</tr>
<tr>
<td>Nitrogen, wt%</td>
<td>0.02</td>
</tr>
<tr>
<td>Aniline point, °C</td>
<td>50</td>
</tr>
<tr>
<td>Cetane index</td>
<td>41</td>
</tr>
<tr>
<td>Conradson Carbon, wt%</td>
<td>26.3</td>
</tr>
<tr>
<td>Metals: vanadium, wppm</td>
<td>48</td>
</tr>
<tr>
<td>nickel, wppm</td>
<td>26</td>
</tr>
<tr>
<td>Viscosity, cSt at 25°C</td>
<td>4.6</td>
</tr>
<tr>
<td>99°C</td>
<td>1.2</td>
</tr>
<tr>
<td>150°C</td>
<td>30</td>
</tr>
<tr>
<td>177°C</td>
<td>9.3</td>
</tr>
<tr>
<td>C7, Asphaltenes, wt%</td>
<td>9.3</td>
</tr>
</tbody>
</table>
asphaltenes; however, they are also present in porphyrins. Porphyrins are large, condensed-ring molecules that boil at a lower temperature than asphaltenes.

Iron, silica and calcium carried in with the feed can be troublesome trace metal contaminants. These may be chemically combined with the heavy hydrocarbon molecules. In either case, these result not only in deactivation of the catalyst through pore mouth plugging, but also plug the catalyst interstices causing excessive pressure drop.

### Reactor temperature

At a given space velocity, the ebullated bed reactor temperature influences the hydroconversion and contaminant removal rate constants. However, an increase in temperature also accelerates the secondary undesirable reactions of carbon laydown, catalyst deactivation, build-up of impurities on active sites, formation of hydrogen deficient coke precursors, pore mouth plugging, sintering, etc.

### Hydrogen partial pressure

Hydrogen partial pressure is of fundamental importance for the successful operation of the LC-Fining reactors. It has an important effect on catalytic activity and fouling rate. An increase in hydrogen partial pressure suppresses the coke fouling of catalyst and improves the reaction rates (first or second-order with respect to $H_2$ partial pressure) for the catalytic and non-catalytic reactions. For a given operation, hydrogen partial pressure can be increased by: increasing total system pressure, increasing make-up hydrogen purity and circulation rate, increasing recycle gas purity and circulation rate.

### Space velocity

The severity of reactor operation is established not only by the reaction temperature, but also by the Liquid Hourly Space Velocity (LHSV) which establishes the residuum conversion targets: a higher LHSV (feed rate) would require higher temperature for the same resid conversion and product quality.

### Treat gas to oil ratio

Higher hydrogen partial pressures are required for the completion of hydroconversion reactions. Higher treat gas to oil ratio improves the hydrogen partial pressures. However, optimum balance is required to reduce the compression costs and excessive gas hold-up at higher gas rates. Typically, the hydrogen circulation rates through the reactors are much higher than the stoichiometric (chemical) hydrogen requirements. In order to reduce the total make-up hydrogen requirements, the majority of the excess gas is purified and recycled with make-up being equal to chemical, solubility and mechanical losses. Typically, the excess over chemical treat gas to oil ratios vary between 2 to 4 depending on the purity of make-up and recycle hydrogen.

### Catalyst addition rate

Equilibrium catalyst activity influences two basic requirements. These are resid conversion to lighter material and hydrogenation severity. The hydrogenation reactions (heteroatom removal, demetallization and CCR reduction) are promoted by Co/Mo, Ni/Mo, Ni/W components. As the ongoing hydrogenation reactions proceed, the activity of the catalyst declines while metals and carbon build-up on the catalyst. Thus, in the LC-Fining reactors, the desired equilibrium catalyst activity is maintained by adding fresh catalyst and removing spent catalyst. The catalyst addition rate is an important variable to achieve desired product quality goals.

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THE HYDROCONVERSION OF RESIDUES


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