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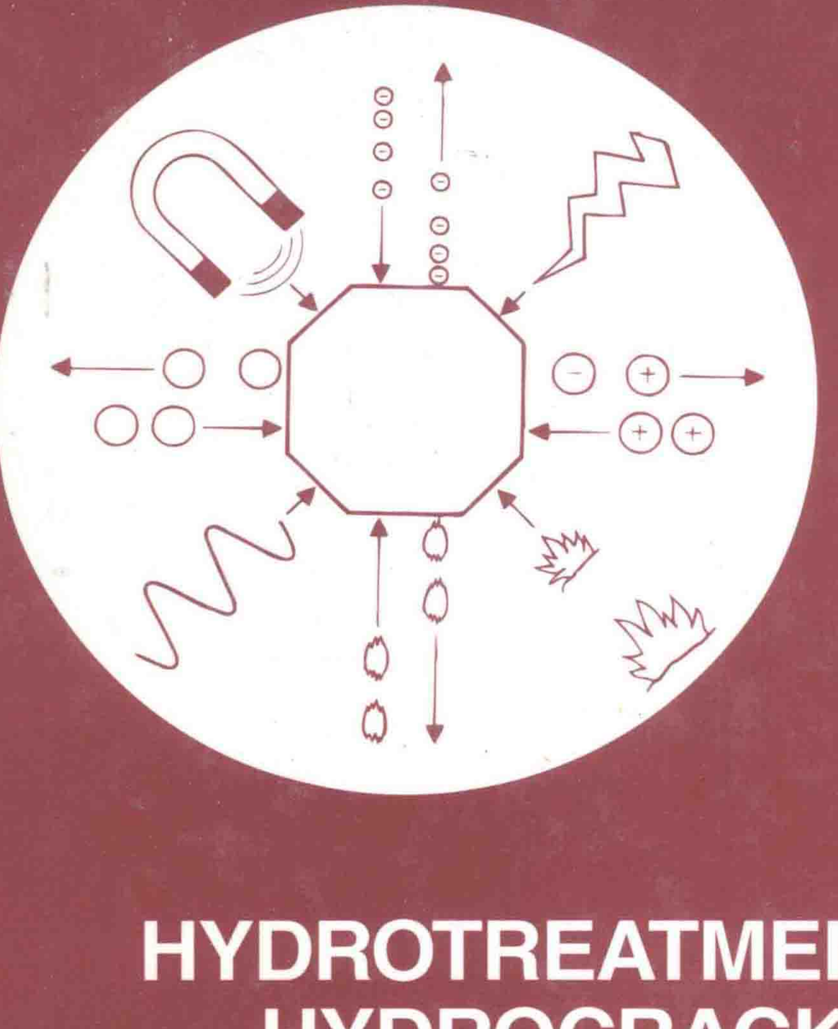

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HYDROTREATMENT AND HYDROCRACKING OF OIL FRACTIONS

G.F. Froment
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HYDROTREATMENT AND HYDROCRACKING OF OIL FRACTIONS

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INTRODUCTION

The new American, European and Japanese environmental regulations call for advanced hydrotreatment processes for HDS and HDN, the removal of S- and Ni-components from oil fractions. They will also alter the product slate of the oil refineries and the hydrocarbon composition of these products. Hydrocracking will play an important part in this shift.

Adapting the operating conditions will not suffice to reach the desired product specifications and yields. Adequate catalysts will have to be developed. Powerful tools are now available for this, among others surface science techniques, molecular modeling, new types of reactors operated in a non steady mode. Another instrument in the improvement of hydrotreatment and hydrocracking units is the availability of more realistic kinetic models. These are based upon a judicious insight into the reaction mechanism, also provided by the above mentioned tools. Progress in the analytical techniques has allowed to reduce the lumping of components in these kinetic models and first order kinetic equations are gradually replaced by equations accounting for the adsorption of the various components.

More detailed and more realistic reactor models are now based upon rigorous hydrodynamic models and their application has become possible through the rapidly increasing possibilities of computers.

A global perspective and an inspection of the state of the art are timely. This is exactly what this symposium on Hydrotreatment and Hydrocracking of Oil Fractions is aiming at. It is a worldwide extension of the 5 European Workshops held from 1981 onwards.

We have chosen a prestigious location for the Symposium, which will also favor the personal contacts between the participants.

We are grateful to Ms. R. Peys and her staff at TI-K VIV for the organization of the meeting and for the preparation of these Proceedings.

Prof.Dr. B. Delmon, U.C.L.
Prof.Dr.ir. G.F. Froment, R.U.G.
Prof.Dr. P. Grange, U.C.L.

The 1st International Symposium on Hydrotreatment and Hydrocracking of Oil Fractions was organized by : **The Technological Institute of the Royal Flemish Society of Engineers (TI-K VIV)**.

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Hydrotreatment and hydrocracking of oil fractions
G.F. Froment, B. Delmon and P. Grange, editors

Processes and Catalysts for Hydrocracking of Heavy Oil and Residues

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Atmospheric or vacuum residue can be converted into valuable distillates using high reaction temperature, high hydrogen pressure and low contact time hydroprocessing units. Various residue hydrocracking processes are now commercially employed using fixed bed, moving bed or ebullated bed reactors. The choice of process type depends mainly on the amount of metals and asphaltens in the feed and on the level of conversion required. Various improvements have been introduced in the last decade to increase run length, conversion level, products qualities and stability of the residual fuel. These improvements include on stream catalyst replacement systems, swing reactors, improved feed distribution, guard bed materials limiting pressure drop, coke resistant catalysts, complex association of catalysts using particle size, activity and pore size grading. Further improvement of the resistance of catalysts to deactivation by coke and metal deposits and of the hydrodenitrogenation activity are two major challenges for the development of new residue hydrocracking catalysts and processes.

1. INTRODUCTION

Hydrodesulphurisation of atmospheric residue is a well established residuum upgrading process which requires catalysts designed to remove and accumulate metals and to desulphurise the feed [1-3]. However, by increasing the reaction temperature and using appropriate catalysts, the conversion of a substantial fraction of the residue into distillates can also be obtained. The objective of residue upgrading is therefore more and more switching from hydrodesulphurisation (HDS) to conversion or hydrocracking (HDC) [1-3].

The HDC of atmospheric or vacuum residue lead to the production of valuable distillates and to the minimisation of the amount of unconverted residual fuel oil which is deeply purified and suitable for low sulphur fuel oil (LSFO).

Residue HDC processes are therefore able to satisfy a number of objectives driven by market tendencies and by more stringent environmental regulations such as a decreasing market for fuel oil, an increasing need for LSFO, an increasing need for clean transportation fuels (gasoline and diesel) and tighter requirements on the use or disposal of the worst refinery residues causing a trend toward "minimum residue" or "zero residue" refinery strategies.

Although very capital expensive and in competition with thermal conversion processes, residue HDC processes will develop in the future as they gain in maturity and as more and more synergy will be found with other conversion processes such as distillate hydrocracking, fluid catalytic cracking, coking and residue gasification for hydrogen, steam and power generation.

Today, commercially proven residue catalytic HDC processes use fixed bed, co-current and counter-current moving bed or ebullated bed reactors [4]. Several slurry reactor processes are also proposed and several demonstration plants have been operated, nevertheless, full scale units have not yet been built [5].

In parallel, many catalysts have been also developed over the years and in particular catalysts packages have been designed for fixed bed units specially adapted to minimise pressure drop and maximise metal retention capacity, HDS activity, run length and conversion level as well as unconverted residue stability.

In this paper we briefly review the recent major developments in residue HDC processes and catalysts.

2. RESIDUE HYDROCRACKING PROCESSES

2.1. Hydrocracking operating conditions

Atmospheric residue (AR) and vacuum residue (VR) are the most difficult feed to convert catalytically because they contain in a concentrated form most of the impurities contained in the crude oil and among them, asphaltens and metals (essentially nickel and vanadium).

Asphaltens are complex aggregates of large molecules containing heteroatoms (S, N, O and metals) which tend to inhibit all of the catalytic functions by coking and metal sulphides deposition during the reaction. In residue HDC one of the challenge is to convert as much asphaltens as possible into lighter compounds.

Metals are removed from their host molecules by catalytic hydrodemetallisation (HDM). It is known that metals deactivate the active phase and accumulate on the catalyst surface in the form of sulphide particles during the reaction. Eventually, a large accumulation of metal deposits lead to pore plugging [1,2,4,6-11].

Both catalytic and thermal cracking occur in residue HDC processes and the proportion of each type of reactions depends mainly on the reaction temperature. Catalytic hydrocracking is favoured by temperature and by hydrogen pressure. Thermal cracking involves free radical mechanism to convert large residue molecules to hydrocarbon gases, naphtha, distillates and gas oil. Thermal conversion is highly favoured by an increase of temperature and is nearly independent from hydrogen pressure. However, a high hydrogen pressure is useful for the hydrogenation of the highly reactive unsaturated compounds generated by thermal cracking preventing polymerisation reactions leading to coke formation. An increase of the hydrogen pressure also have a tremendous impact on the quality of the products by providing high level of desulphurisation and hydrogenation. Hence residue hydrocracking processes are high hydrogen pressure, high temperature and low contact time processes [2, 12].

There are two major disadvantages to run at high temperature in residue hydrocracking. The first one is an increased rate of deactivation by coking of the catalysts reducing the cycle length and the second is the formation of highly unsaturated and insoluble compounds which tends to form dry sludge or sediments leading to a poor stability of the residual fuel. These sediments may simply be asphaltens or fragments of asphaltens precipitating as a result of the decrease of the ratio of resins to asphaltens obtained by hydrogenation and conversion [13].

A large number of technology have been developed to overcome the troubles generated by the use of high reaction temperature in the processing of heavy feeds containing metals contaminants like oil residua. Figure 1 indicates schematically the various combination of fluid and catalyst flows that can be found in commercial reactors. Various types of reactors are employed such as fixed bed, co-current and counter-current moving bed, ebullated bed and slurry reactors.

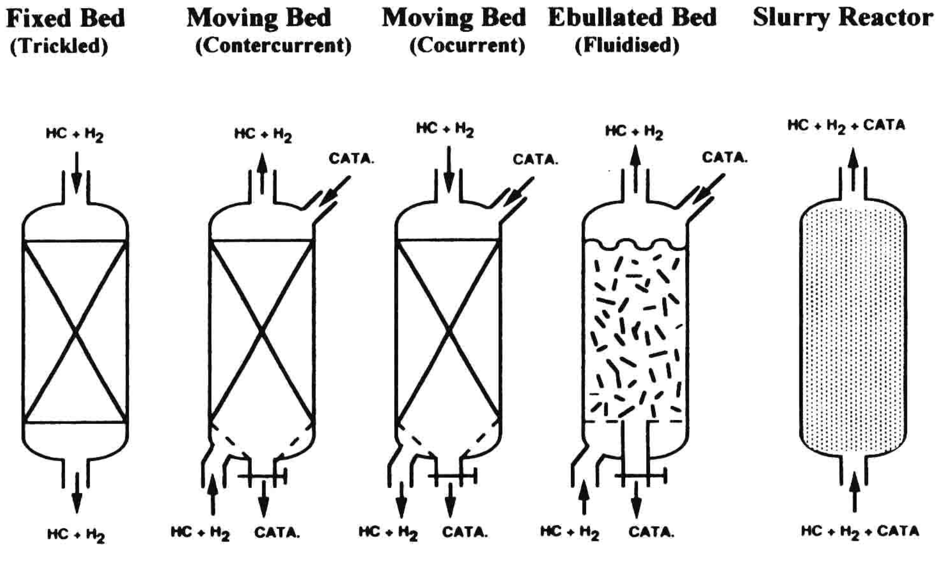

Figure 1. Residue hydroconversion reactors.

Table 1 summarises some of the main features of residue HDC processes using these various types of reactors. These processes are in general composed of several large reactors in serie and sometimes several parallel trains of several reactors in serie. For example, the Mina Abdulla unit in Kuwait has two trains of four fixed bed reactors each totalling about 1600 m^3 of catalyst [5]. The Amoco Texas City unit possesses three trains of three ebullated bed reactors in series each [2].

Table 1. Main Features of Residue Hydrocracking Processes.

	Fixed bed	Swing fixed bed	Moving bed	Ebullating bed	Slurry
Number of units (est'd)	40	1	3	9	3 demo
Ni+V max. in feed (ppm)	120	500	500-700	>700	>700
Pressure (MPa)	100-200	100-200	100-200	100-200	100-300
Temperature (°C)	380-420	380-420	380-420	400-440	420-480
Unit LHSV (h^{-1})	0.1-0.5	0.1-0.5	0.1-0.5	0.2-1	0.2-1
Unit Operability	good	good	medium	medium	difficult
Max. Conv. to 550°C^- (wt%)	50-70	60-70	60-70	70-80	80-95
Residue Stability	good	good	good	medium	bad
Unit cycle length (month)	6-12	12	CO+	CO+	CO+
RCC*	1	1	0.55-0.7	1.4-2	-
Catalyst part. size (mm)	~1.2x3	~1.2x3	~1.2x3	~0.8x3	~0.002
Particles/cm^3 [4]	~120	~120	~120	~250	~2.4 10^9
Vol. % Cat. in reactor [4]	~60	~60	~60	~40	~1

+ CO : Continuous operation

* RCC : Relative catalyst consumption for same feed for one year cycle

All five types of reactors shown in Figure 1 allow to reach the objective of converting a substantial fraction of the residue. Nevertheless as indicated in Table 1, a net advantage is obtained for ebullating bed and slurry processes which can process residues at higher reaction temperatures with no pressure drop. However these two processes produce lower quality products than fixed and moving bed processes as will be seen hereafter.

2.2. Fixed bed processes

The most standard residue hydroconversion processes use fixed bed catalytic reactors. The main process licensers are CHEVRON, UOP/UNOCAL, EXXON, SHELL and IFP.

Fixed bed hydroprocessing units can be operated in two modes, HDS and HDC by increasing the reaction temperature and using different catalysts [12]. Table 2 shows the products properties obtained from the two modes of operation on the same feed (Kuwait vacuum residue containing 5.51 wt% S) using the HYVAHL-F process from IFP.

In Table 2, the HDS mode allows to reach a conversion of the 550°C$^+$ residue of 35 wt%. The converted product is mainly a desulphurised vacuum gas oil. For the HDC mode, Table 2 shows that the conversion of the 550°C$^+$ residue reach 56 wt% and substantial amounts of gas oil and naphtha are obtained. In both mode of operation, the unconverted atmospheric residue is a desulphurised and stable high quality LSFO with 0.75 wt% or 0.8 wt% sulphur respectively. Results obtained on two other feeds and reported in Table 2 indicate that a conversion level of 63 wt % can be reached with a fixed bed process.

The fixed bed process is well adapted for feedstock containing less than 100/120 wt ppm Ni+V for a one year cycle length. This cycle length is determined by the HDM activity and the saturation of the metal retention capacity of the HDM catalyst. The operability of the fixed bed process is good.

Table 2. Hydroconversion of various residues in fixed bed HYVAHL-F Process.

Mode	HDS	HDC	HDC	HDC
Residue	Kuwait VR		AL/AH AR	Safaniya VR
Specific Gravity	1.031	1.031	0.988	1.035
Sulphur, wt %	5.51	5.51	3.95	5.28
Nitrogen, wt ppm	3600	3600	2900	4600
Conradson Carbon, wt%	21.8	21.8	13.8	23.0
Asphaltens C7, wt %	9.0	9.0	5.7	11.5
Ni+V, wt ppm	169	169	104	203
Yields /conversions MOR				
Gasoline, wt %	1.0	2.2	3.5	4.6
Gas oil, wt %	9.5	19.5	21.5	19.7
Vacuum gas oil, wt %	20.5	29.5	40.8	32.8
Vacuum residue, wt %	64.6	43.2	29.7	37.1
HDS, wt %	88	89	91	90
HDM, wt %	94	98	98	93
Conv 550°C$^+$, wt %	35	56	63	57
Hydrotreated AR				
Specific Gravity	0.963	0.965	0.934	0.970
Sulphur, wt %	0.75	0.8	0.50	0.70
Conradson Carbon, wt%	8.8	10.3	4.0	10.0
Asphaltens C7, wt %	0.7	1.3	0.3	5.3
Ni+V, wt ppm	11	4	2.0	20

For feedstock containing larger metal content (up to 250-300 wt ppm Ni+V), a new concept of fixed bed reactors including a swing guard reactors system has been developed by IFP (HYVAHL-S process, Figure 2). The process scheme includes swing guard fixed bed reactors which can be switched in operation and several downstream fixed bed reactors in serie. When the HDM catalyst contained in one of the guard reactor in operation is deactivated, a suitable procedure and technology allow to bypass this reactor, replace the catalyst with a fresh one and put back the reactor on stream. All these operations are done without shutting down the unit, avoiding any production loss.

The guard reactor volume and the operating temperature are optimised to achieve a high HDM rate while ensuring satisfactory cycle length in this guard reactor. The swing reactor system has all the benefit of fixed bed reactors, namely no catalyst attrition, no entrainement of fines and allows the unit to achieve a one year operation cycle in the main reactors for most available crude oils.

2.3. Moving bed processes

In moving bed reactors the catalyst circulates by gravity, in plug flow, inside the reactor and fresh catalyst is added periodically at the top of the reactor while spent catalyst is withdrawn at its bottom. The main advantage of the moving bed process is its capacity to process, with long cycle length, high metal content feedstock.

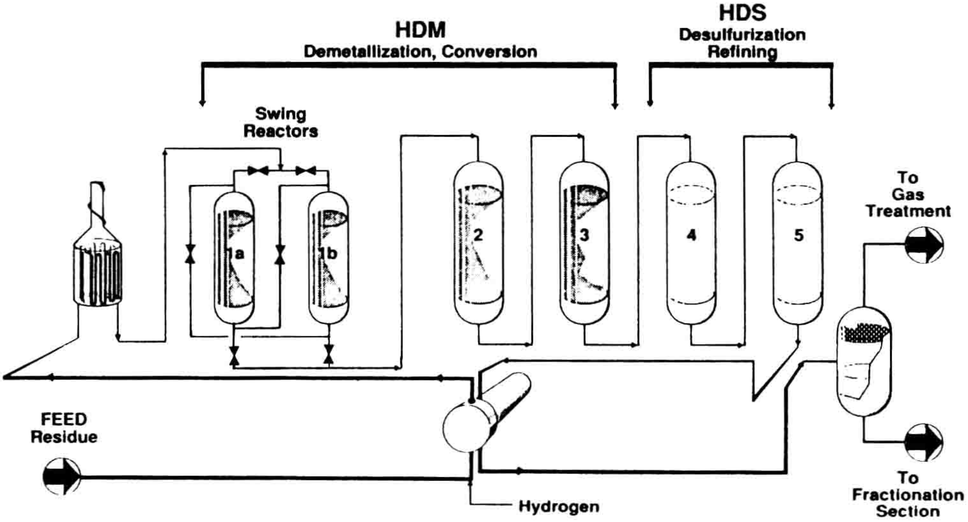

Figure 2. Fixed bed HYVAHL-S process with swing reactors.

Several processes are proposed by various process licensers such as the co-current down flow moving bed in the HYCON process (SHELL), the counter current moving bed OCR (On stream Catalyst Replacement) process (CHEVRON) and HYVAHL-M process (IFP).

The best configuration is the counter current mode because the spent catalyst saturated by metals meet the fresh feed at the bottom of the reactor whereas the fresh catalyst reacts with an already demetallised feed at the top of the reactor. This configuration results in a lower catalyst consumption than with other processes.

When moving through the reactor, the catalyst is submitted to high mechanical forces that may lead to attrition of the catalyst and therefore to bed plugging problems on the top of the first downstream fixed bed reactor. The catalyst attrition in moving bed can be reduced through optimal hydrodynamic conditions [14] and use of high attrition resistance catalysts.

Moving bed processes need however special equipment and procedures for a safe and effective catalyst transfer into and out of the high pressure and high temperature reactor. This involves several low and high pressure vessels as indicated in Figure 3 for the OCR process.

The product yields and qualities are similar to fixed bed process for the same operating conditions (Table 3). However, the operability is more difficult due to the operation of continuous catalyst renewal in high P-T conditions and to the entrainment of catalyst fines to the downstream fixed bed reactor.

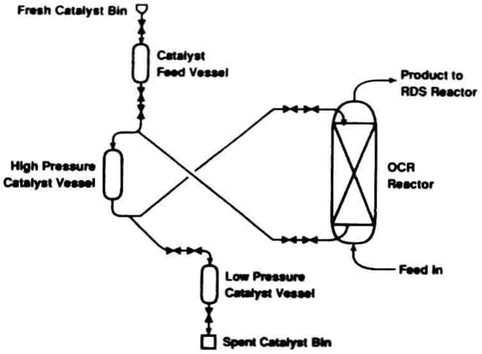

Figure 3. Moving bed OCR reactor.

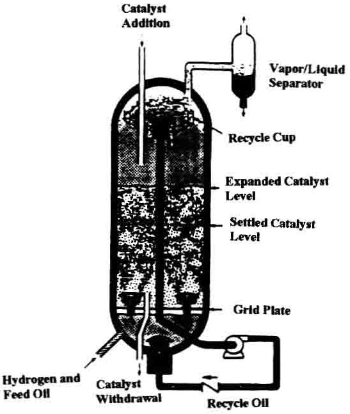

Figure 4. Ebullated bed H-Oil reactor.

With these processes the conversion can reach 70 wt % depending on the nature of the feed and the reactivity of the asphaltens. To reach a higher conversion level is difficult because increasing the reaction temperature induce an extensive coking of the catalyst and catalyst bed plugging.

2.4. Ebullated bed process

Two ebullated bed technology are currently licensed, namely the LC-Fining (ABB/Lummus Crest) and the H-Oil (IFP/HRI) processes.

In an ebullated reactor, the fluids circulate up flow in the reactor. A recirculating pump expands the catalytic bed and maintains the catalyst in suspension. The expanded bed volume is 30 to 50 % larger than the bed volume