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Catalytic hydroprocessing of heavy oil feedstocks

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A grave problem of modern oil refining industry is continuous deterioration of the produced oil quality, on the one hand, and increase in the demand for motor fuels, on the other hand. This necessitates processing of heavy oil feedstock with high contents of sulfur, nitrogen and metals and the atmospheric residue. This feedstock is converted to light oil products *via* hydrogenation processes catalyzed by transition metal compounds, first of all, cobalt- or nickel-promoted molybdenum and tungsten compounds. The processing involves desulfurization, denitrogenation and demetallization reactions as well as reactions converting heavy hydrocarbons to lighter fuel components. The review discusses the mechanisms of reactions involved in the heavy feedstock hydroprocessing, the presumed structure and state of the catalytically active components and methods for the formation of supports with the desired texture. Practically used and prospective approaches to catalytic upgrading of heavy oil feedstock as well as examples of industrial processing of bitumen and vacuum residues in the presence of catalysts are briefly discussed.
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I. Introduction

The demand for motor fuels together with the ever deteriorating average quality of the produced oil stimulate enhanced processing of feedstock with high contents of heavy hydrocarbons, sulfur, nitrogen and metals. Most approaches to the processing of oil residues for the production of light products and removal of impurity components (desulfurization, denitrogenation and demetallization) are based on catalytic hydrogenation processes. Typical hydroprocessing catalysts are molybdenum (tungsten) sulfides promoted with cobalt (nickel). In fixed-, moving- and ebullated-bed processes, the nano-sized active component of the catalyst is supported, most often, on Al_2O_3. In slurry

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processes, suspensions of micro- or nano-sized sulfide catalysts are used without a support. Apart from the chemical composition of the active component, a significant factor affecting the catalyst activity in the heavy feedstock upgrading is the support texture, in particular, the size and the volume of meso- and macropores.

This review is devoted to catalytic hydroprocessing of heavy oils boiling above 350 °C under atmospheric pressure. The atmospheric residue of oil distillation can, in turn, be separated into fractions by vacuum distillation, namely, into vacuum gas oil and vacuum residue (b.p. > 565 °C).

Currently, the produced crude oils are classified in accordance with the GOST P 51858–2002. In this standard, the feedstock with the density (ρ) from 874.5 to 899.3 kg m^{-3} at 15 °C corresponds to type 3, or heavy oil, while crude oils with higher density are type 4, extra-heavy, or bituminous oils. According to the world classification, bituminous oils are divided into two subtypes. According to the US classification, heavy oil has a density of $934 < \rho < 1000$ kg m^{-3} (20–10°API).[1]

A specific feature of heavy and extra-heavy crude oils is a higher content of heteroorganic compounds containing oxygen, sulfur, nitrogen and metal atoms as well as high-molecular-weight compounds — resins and asphaltenes.[2,3] Since secondary catalytic and non-catalytic processing of oil feedstock (thermal cracking, catalytic cracking, hydrovisbreaking, delayed coking and reforming) occur at elevated temperature and pressure, the presence of these compounds in petroleum products obtained in the first refining stages (usually fractionating distillation) decreases the efficiency of the subsequent stages. Sulfur and nitrogen compounds poison the petroleum refining catalysts, while asphaltenes, naphthenes and their metal complexes, which are present in considerable amounts in heavy feedstock, not only block the catalyst surface but are also deposited on metallic reactor surfaces, thus substantially impairing their service performance.

The enhanced demand for motor fuels stimulates processing of heavy and extra-heavy oil feedstock, including vacuum distillation residues. The key goal of these processes is decrease in the density (viscosity) of the feed, which is equivalent to an increase in the H : C ratio. The major processing methods are either to remove excess carbon (coking, thermal and catalytic cracking, hydrovisbreaking) or to introduce additional hydrogen into the hydrocarbon feed (hydroprocessing).[4–6] Although the latter method requires considerable amounts of hydrogen and large capital investment, in recent years, the volume of heavy feed hydroprocessing has markedly increased. First of all, this is due to high yields of light distillates (> 85%), which can meet the growing demand for motor fuels.[7]

By the beginning of the present decade, 49 fixed-bed hydroconversion units for heavy feed with a total capacity of ~2.2 MMbpd operated all over the world.† In addition, 22 ebullated-bed hydroconversion units with a total capacity of > 0.6 MMbpd,‡ some industrial and pilot moving-bed units and slurry reactors were in operation. In Russia, the design of a pilot unit for heavy oil hydroconversion on nano-sized catalysts with the planned capacity of 50 thousand tonnes of bitumen per year, developed by the A V Topchiev Institute of Petrochemical Synthesis (IPCS) of the RAS, is being currently completed.

The selection of a processing method for heavy and residual hydrocarbon feed depends on the contents of asphaltenes and metals, first of all, Ni, V and some rare earth elements.[8,9] When the asphaltene content is < 8 mass % and the Ni and V contents are < 1–10 ppm, the feed can be processed directly at the catalytic cracking units. In the 8 mass %–20 mass % range of asphaltene concentrations and 10–100 ppm range of metal impurities, the process of choice is fixed-bed catalytic hydrocracking. When the asphaltene and metal concentrations are 15 mass %–30 mass % and > 100 ppm, respectively, ebullated-bed catalytic hydrocracking with feed recirculation and periodic replacement of part of the catalyst. Extra-heavy hydrocarbon feed with asphaltene content of 20 mass %–40 mass % and metal content of ⩾1000 ppm can be converted *via* slurry processes using nano-sized catalysts, for example, those formed *in situ* in the reaction medium from molybdenum complexes used as catalyst precursors.[10,11]

In Russia, industrial units for hydroprocessing of heavy feedstock are mainly at the stage of construction;[12] furthermore, there is no manufacture of the appropriate catalysts. Meanwhile, the plans for development of petroleum upgrading in Russia imply active processing of heavy crude oils and bitumens. This development strategy is due to the limited reserves of light crude oils and should lead to higher percentage of hydroprocessing and secondary processing plants upon commissioning of new plants for upgrading and increasing the quality of primary oil refining products.

Hydroprocessing is still little used in the Russian oil-refining industry and the scope of research and development works in this area is moderate. Therefore, the information on this subject is mainly concentrated in foreign publications that are not always available. Due to the high priority of this problem for oil companies, there are numerous patents on this topic; however, a substantial part of scientific and engineering works are confidential.

This review deals with the composition of heavy oils, the mechanism of reactions involved in heavy feed hydroprocessing, the assumed structure and state of the catalytically active component and the preparation of the desired texture of catalyst supports. The practically used and prospective catalytic processes of heavy feed conversion are considered in brief and examples of industrial processing of bitumen and vacuum distillation residues are given.

II. Composition of heavy crude oils

Heavy crude oils are complex multicomponent systems differing from intermediate oils by higher contents of arenes, including polycyclic (fused) aromatics (naphthalene, anthracene, coronene, *etc.*), alkyl-naphthenoarenes (mono- or bicyclic naphthenes with alkyl chains and so on) and heteroorganic compounds (thianaphthenes, thiophenes, thiophanes and their homologues, nitrogenous bases with annulated benzene or naphthene rings, indole and carbazole derivatives, cyclic amides, porphyrins and so on). The major part of these high-molecular-weight compounds are resins and asphaltenes. Depending on the predominant content of

† See *Residue upgrading using fixed-bed hydroconversion*. http://s03.static-shell.com/content/dam/shell/static/criterion/downloads/pdf/fact-sheets/criterion-fixed-bedfactsheethires.pdf

‡ See *Axens and Headwaters Technology Innovation* (*HTI*) *Join Efforts on Ebullated Bed Technology for Heavy Oil Upgrading*. http://www.axens.net/news-and-events/news/265/axens-and-headwaters-technology-innovation-hti-join-efforts-on-ebullated-bed-technology-for-heavy-oil-upgrading.htm

saturated, cyclic or aromatic compounds, crude oils are referred to as paraffin-, naphthene- and aromatic-base oils. For example, Venezuelan bitumens are known as 'naphthene-rich bitumens'. The vacuum residue obtained upon distilling off light fractions and vacuum gas oil consists mainly of resins and asphaltenes. Resins are fused cyclic compounds with long aliphatic side chains and molecular weight of 600–700, while asphaltenes are polycyclic aromatic systems with short aliphatic side chains and molecular weight of 2000–3000 and more. Asphaltene molecules tend to form aggregates and can be arranged into stacks of nearly planar molecules connected to one another. On heat treatment of oil, these aggregates serve as coke nuclei and give rise to a large number of carbonaceous deposits on all available surfaces. The presence of sulfur, oxygen and, first of all, nitrogen atoms in organic compounds, especially in asphaltenes accounts for strong coordination of vanadium, nickel and other metals to these molecules, which also hampers removal of metals during hydroprocessing.

Thus, judging by the elemental composition, heavy oils are characterized by higher hydrogen deficiency with respect to carbon and higher content of heteroatoms (sulfur, nitrogen, oxygen and metals) compared to light or intermediate oils. For example, some Canadian and US bitumens have the following elemental composition: carbon, 80 mass %–88 mass %; hydrogen, 8 mass %–12 mass %; sulfur, 1 mass %–7 mass %; nitrogen, 0.5 mass %–1.1 mass %; oxygen, 0.5 mass %–1.1 mass %; vanadium, 37 ppm–1480 ppm; nickel, 35 ppm–142 ppm.[3]

The development of advanced fractional separation and identification methods for heavy oils made it possible to define groups of compounds based on molecular weights and solubility in polar, aromatic and non-polar solvents.[13] For example, bitumens can be classified into the following groups: (i) n-heptane-soluble saturated hydrocarbons (HC); (ii) aromatic HC soluble in toluene or a methanol–toluene mixture; (iii) polar resins soluble in trichloroethylene; and (iv) n-heptane-insoluble asphaltenes. Quantitative characteristics of the Canadian bitumens of these groups are as follows: (i) 5 mass %–15 mass % of saturated HC with an average molecular weight (M_r) of 600 and H : C = 2; (ii) 30 mass %–45 mass % of aromatic HC with M_r = 800 and H : C = 1.5; (iii) 30 mass %–45 mass % of resinous substances with M_r = 1100 and H : C = 1.4–1.5; and (iv) 5 mass %–20 mass % of asphaltenes with M_r = 800–3500 and H : C = 1.15.[3] Currently, a heavy oil, including bitumen, is considered as a colloid system comprising a dispersion of 12–15 nm aggregates assembled from 3–4 nm asphaltene micelles stabilized by polar components of resinous compounds. The intense extraction or conversion of dispersion phase components leads to the loss of the colloid stability of oil, *i.e.*, enlargement of the dispersed phase components (asphaltene aggregates), which should certainly be taken into account in the hydroprocessing of heavy hydrocarbon feedstock.

III. Chemistry of hydroprocessing of heavy hydrocarbon feedstock

The catalytic hydroprocessing of heavy oil feedstocks includes heat treatment at elevated pressure of hydrogen, which serves as a reactant, in the presence of catalysts, resulting in a decrease in impurity concentrations (metals, sulfur and nitrogen compounds), an increase in the hydrogen proportion in the obtained products and increased yields of distillate fractions. The preliminary removal of all these components from the heavy residues to be processed is a necessary condition for residue catalytic cracking (RCC), which is often combined with hydroprocessing. The zeolite-based RCC catalysts are fairly sensitive to the content of metals (Ni + V) in the feed, as the catalyst active sites are blocked by V^{5+} ions[14] and the zeolite crystal structure is destroyed.[15,16] Therefore, the content of vanadium in the residues processed by catalytic cracking should not exceed 0.1 mass %.[17] The nitrogen bases present in oil are adsorbed on the catalyst active sites, thus also decreasing the overall rate of the catalytic cracking;[18] the stronger the base (the higher the proton affinity), the more pronounced the inhibitory effect.[19–21]

Catalytic hydroconversion of heavy feedstock in the presence of hydrogen at high pressure (up to 180 atm) and temperature (380–450 °C) involves quite a number of chemical reactions including hydrocracking, hydrodemetallization (HDM), hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The catalysts for hydroconversion of heavy feedstock should not only possess high activity but also maintain the balance between the above-listed reactions. A too low degree of HDM has an adverse effect on the catalyst activity in hydrocracking and HDS,[22] whereas high rate of hydrocracking of resins and oils may result in precipitation of asphaltenes and failure of the equipment.[23] The bifunctional nature of the used catalysts ensures that heavy component cracking is accompanied by hydrogenation and retardation of coking.

The hydrocracking comprises a number of sequential and parallel reactions: cleavage of high-molecular-weight hydrocarbons, hydrogenation of cleaved products, hydrodealkylation of alkylaromatic hydrocarbons and hydrocarbon isomerization. At pressures of < 150 atm, polymerization and condensation of hydrocarbons and coke formation can also take place.[7,24] This process is usually catalyzed by supported transition metal sulfides. The cleaving function of the catalyst is provided by the acid sites of the support, which is usually alumina or aluminosilicates. The behaviour of the hydrocracking catalyst is dictated by the balance between hydrogenation sites of metal sulfide and acid sites of the support.[25,26] At low relative contents of hydrogenation sites, secondary cracking reactions may proceed, resulting in the formation of light hydrocarbons as well as oligomerization and coke deposition on the acid sites. The deficiency of hydrogenating function of the hydrocracking catalyst leads to fast catalyst deactivation. Meanwhile, if the hydrogenating activity prevails, cracking is suppressed and isomerization becomes the major process.

A typical hydrocracking unit comprises two reactors, the first one containing a catalyst active towards removal of heteroatoms and metals and the second one containing the proper hydrocracking catalyst. Usually, an NiM catalyst removing sulfur, nitrogen, metals and hydrogenated aromatics is loaded into the first reactor, while a catalyst based on acidic supports (zeolites, mixed oxides), which run hydrogenation and hydrocracking reactions, is loaded in the second reactor. After separation of the products suitable as motor fuels, the residue is recycled to the hydrocracking reactor. However, in the early 1980s, the plants faced the problem of failure of hydrocracking reactors due to the formation of large amounts of a reddish deposit insoluble in

hot xylene, dichloromethane, acetone or other polar solvents.[27] These deposits were thoroughly investigated and it was found that during recycling to the hydrocracking reactor, carbon structures undergo condensation with the gradual formation of polycyclic aromatic compounds[28] and finally coke. Two condensation mechanisms are known. The first one is addition of one more ring to the molecule upon the attachment of two or four carbon atoms. For example, phenanthrene can be converted to pyrene after attachment of two carbon atoms, and then pyrene can transform into 3,4-benzopyrene upon the addition of two carbon atoms (Scheme 1). The second mechanism called Scholl condensation consists in merging of two aromatic molecules, for example, two coronene molecules with $M_r = 300$ form dicoronylene with $M_r = 596$, which is followed by hydrogenation and elimination of saturated hydrocarbon fragments, or two pyrene molecules can form dibenzo[*cd*,*lm*]perylene (**1**) and naphtha[8,1,2-*bcd*]perylene (**2**) (see Scheme 1).[29]

During hydrocracking of heavy crude oils, the structure of asphaltenes also changes. For example, in the hydrocracking of Venezuela heavy oil at 430 °C, an increase in the hydrogen pressure from 6 to 10 MPa results in an increase of the spacings between the layers in the asphaltene stacks and between the hydrocarbon chains but in a decrease in the stack size; simultaneously, the proportion of the aromatic and alkyl carbon diminishes, while the naphthene carbon proportion grows.[30] The conversion of asphaltenes upon hydrocracking usually does not exceed 60%. A hydrogen pressure rise induces dealkylation (elimination of aliphatic chains), formation of larger molecules of fused polycyclic compounds and aggregation and enlargement due to electrostatic or van der Waals attraction forces between colloid particles.[31, 32]

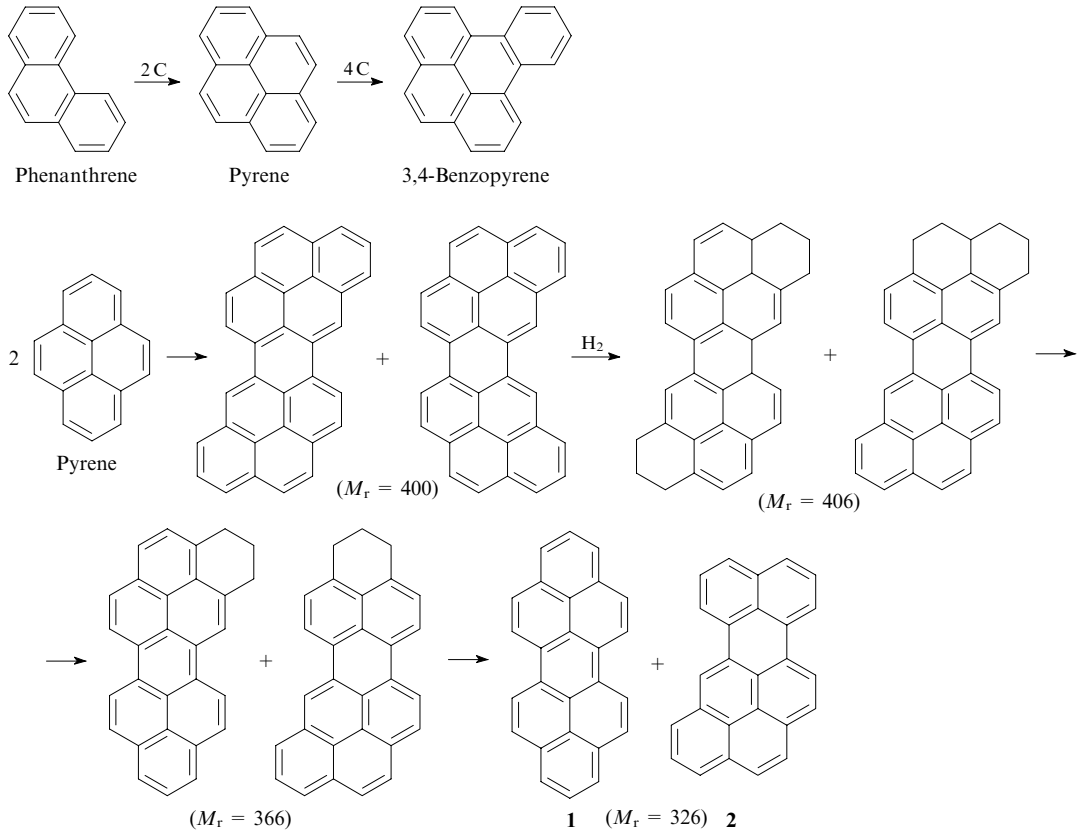
During hydrodemetallization, nickel and vanadium porphyrin complexes present in heavy oil react with hydrogen *via* a successive two-step mechanism on catalytic sites of two different types. In the first step, porphyrins are hydrogenated with tetrapyrrole ring cleavage, while in the second step, the liberated metal is deposited on the catalyst surface:[33]

$$\text{M-P} \xrightarrow{H_2} \text{M-PH}_2 \longrightarrow \text{M}_{\text{deposition}} + \text{hydrocarbon}$$

where P are the initial tetrapyrrole rings and M is metal. The metal is deposited from the intermediate metal complex $M\text{-}PH_2$. It is noteworthy that the transformation pathways of non-porphyrin metal complexes, which are also abundant in oil residues, have not yet been widely considered in the literature.

The removal of sulfur from heavy oil feedstock is needed to protect catalysts used in the subsequent transformations from poisoning and to decrease sulfur dioxide emission to the environment upon fuel combustion. Hydrodesulfurization eliminates sulfur from organic sulfur compounds to different extents depending on the nature of the compound. Alkane- and arenethiols, thioethers and organic disulfides are converted under milder conditions than thiophene and its derivatives.[34] Sulfur removal in sterically hindered reactions of hydrogen with 4,6-disubstituted dibenzothiophenes (DBT) is especially challenging.[35] Hydrodesulfurization of DBT derivatives follows two parallel pathways: (i) direct desulfurization to give biphenyls and H_2S (E_2 elimination);

Scheme 1



(ii) desulfurization *via* hydrogenation to give, first, tetrahydrodibenzothiophene derivatives and then cyclohexylbenzyl derivatives and H_2S. Depending on the nature of substituents in the DBT molecule, the contributions of these reactions to the overall HDS rate may considerably vary: for unsubstituted DBT, the contribution of the first reaction is 80%, while for 4,6-dimethyldibenzothiophene it is only 20%. It is noteworthy that the rate of the second reaction usually does not depend on the presence of an alkyl substituent in the DBT molecule. The differences in the reactivity of DBT derivatives towards HDS on heterogeneous catalysts are attributed to steric hindrance of C–S bond cleavage in the chemisorbed intermediates rather than to inhibition of adsorption of substituted DBT.[36] The coordinatively unsaturated molybdenum atoms attached to S^{2-} are considered as the catalytic sites of MoS_2 responsible for the first reaction, while the coordinatively unsaturated molybdenum atoms bonded to an SH group and adsorbed H atom are considered to be responsible for the second reaction. The role of the HDS catalyst promoter (usually nickel and/or cobalt) consists in acceleration of the C–S bond cleavage by endowing the sulfur atom, which forms the bridge between the molybdenum ion and the promoter, with more basic properties.[36, 37]

The HDN reactions involve conversion of nitrogen compounds of basic nature: amines and alkyl derivatives of pyridine, quinoline, acridine, *etc*.[38] Non-basic nitrogen compounds such as pyrrole derivatives and porphyrins are destroyed to be converted to basic products.[39] Nitrogen compounds are distinguished by high reactivity and are easily adsorbed on the catalyst surface; therefore, the adsorption of N-bases on acid sites results in fast catalyst deactivation. The removal of nitrogen compounds from oil is also necessary to maintain a low content of nitrogen oxides in exhaust gases.

The HDN, similarly to HDS, includes two key reactions: hydrogenation of nitrogen rings and hydrogenolysis of the C–N bonds to give ammonia and hydrocarbons (Scheme 2).[40]

The key parameters affecting the conversion of the compounds being removed in the above hydrotreating reactions are the pressure of hydrogen, the nature of nitrogen and sulfur compounds, temperature, the catalyst composition, contact time, $H_2S:H_2$ ratio and some other. For example, conversion of amines is initiated by addition of a proton from a catalyst Brønsted site.[41] Then the cation reacts with a base (another amine molecule, HS^-, S^{2-}), and, depending on the mechanism (E_1 or E_2 elimination or S_N1 or S_N2 nucleophilic substitution), one or another set of the intermediate and final products is formed (see Scheme 2).[40] In the case of E_2 mechanism, amines with NH_2 group at a primary or secondary carbon atom are converted to alkenes and ammonia, whereas amine disproportionation by the S_N2 mechanism affords dialkylamines, which are then converted to alkenes and alkanes with evolution of ammonia. Amines with NH_2 group at a tertiary carbon atom form more stable carbocations; in this case, HDN follows E_1 and S_N1 mechanisms.[42] A protonated amine decomposes to give NH_3 and a carbocation, which then reacts with a base to give thiol (S_N1) or alkene (E_1).

IV. Appropriate catalysts

IV.1. Supported catalysts

In most cases, fixed-, moving- and ebullated-bed processes are carried out in the presence of supported catalysts that comprise an active component dispersed on a porous support. A typical composition of a supported catalyst is as follows: 3 mass %–15 mass % of a Group VIb metal (tungsten, molybdenum) oxide and 2 mass %–8 mass % of Group VIII metal (cobalt, nickel) oxide deposited on a support and sulfided prior to loading into the reactor.[43, 44] Modern catalytic hydroconversion units, for example, those proposed by the Nippon Ketjen and Albemarle alliance use a family of highly specific catalysts with different properties arranged successively along the route of feed flow (Table 1). The combination and the weight ratio of the catalysts are determined by the processing conditions and the desired properties of the final product. Usually, at least, four catalysts are used, differing in the pore diameter, specific surface area and activity in particular reactions.[45]

Scheme 2

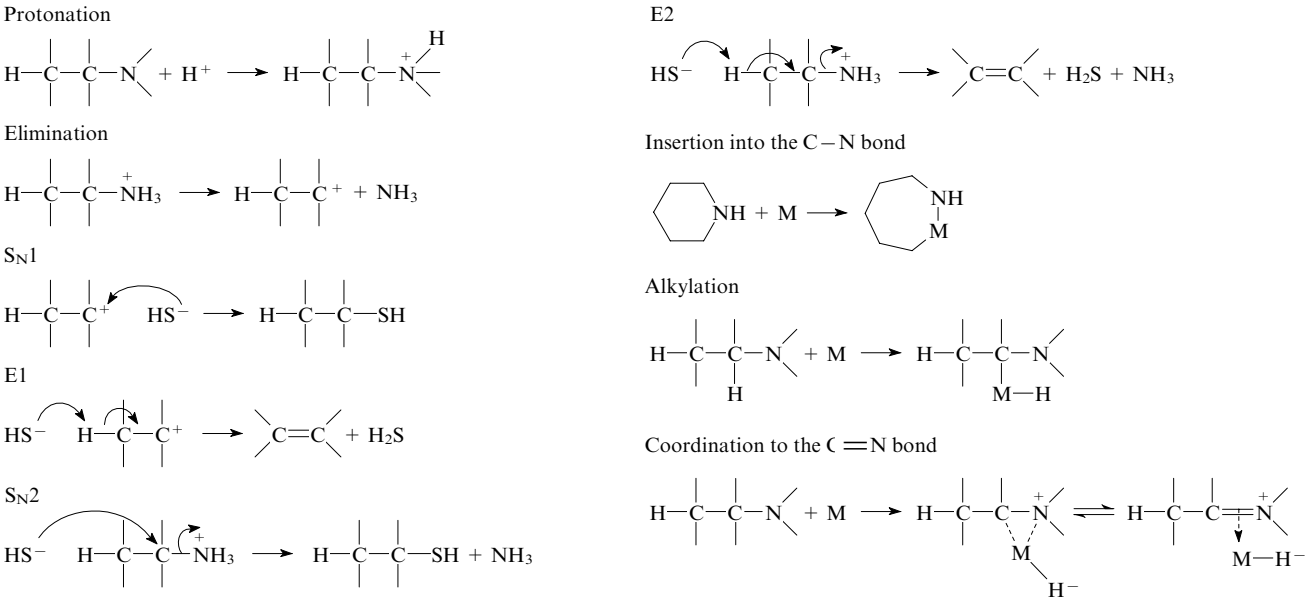


Table 1. Families of catalysts for oil residue hydroprocessing proposed by the Nippon Ketjen and Albemarle alliance.[45]

Bed	Catalyst name	Description and purpose
Guard bed	KG 55	pentagons for trapping large particles
	KF 542	rings for trapping medium-size particles
	KG 1	hollow spheres for trapping iron and particles > 1 μm in diameter
	KG 5	catalysts with HDM function
HDM catalysts	KFR 20	highly active HDM catalyst and low-activity HDS catalyst for low and medium pressures (< 15 MPa)
	KFR 23	frontal highly active HDM catalyst with high metal tolerance for high pressures (> 15 MPa)
	KFR 22	highly active HDM catalyst for high pressure (> 15 MPa)
HDM–HDS catalyst	KFR 33	bifunctional catalyst with relatively high metal tolerance
HDS catalysts	KFR 53	guard HDS catalyst with relatively high metal tolerance
	KFR 50	basic HDS catalyst with high activitiy towards HDS and HDN
	KFR 70	catalyst for outlet layers with high activity towards HDS, HDN and hydrocracking
	KFR 70B	specific catalyst with the highest activity towards HDS, HDN and hydrocracking

It is believed that NiMo catalysts are more active towards hydrogenation of N-heterocycles, while CoMo catalysts show higher activity in the C–N bond hydrogenolysis.[46] Hydrodenitrogenation involves at least four types of catalytic sites, including anionic sulfur vacancies, *i.e.*, coordinatively unsaturated metal atoms (Lewis sites), and SH groups, *i.e.*, Brønsted sites.[47] In the absence of hydrogen, only hydrocarbon polymerization to give coke takes place in the coordinatively unsaturated sites. The coordinatively unsaturated sites are located on the faces and edges of crystallites of metal sulfides, for example, MoS_2, these defects possessing different reactivity towards hydrogenation and hydrogenolysis reactions.[48] The presence of promoters (Co or Ni) changes the bonding energy between sulfur and the metal and thus regulates the activity of the catalytic sites, nickel being a stronger activator for molybdenum sulfide than cobalt.[49] From published data, it can be concluded that the weaker the S–metal bond, the higher the catalyst activity towards HDS. The transfer of electrons from Co(Ni) to Mo increases the occupancy of the molybdenum HOMO and, hence, the antibonding orbital of the metal–sulfide bond, which finally weakens the bond. It is noteworthy that the electron density transfer from Co to Mo strengthens the Co–S bond; therefore, the bonding energy of the sulfur atom coordinated simultaneously to both metals appears to be some average value. Presumably, this value lies in the optimal range of bond energies sufficient for high activity in HDS reactions.[50] Density functional theory (DFT) quantum chemical calculations provided the conclusion that the Ni-doped MoWS catalyst should be most active towards hydrodesulfurization.[51] Apart from the traditional mixed metal sulfides (CoMo, NiMo, CoW, NiW), metal carbides, nitrides and phosphides are considered as potential hydrotreating catalysts.[52–54]

Among various hypotheses on the mechanism of active component operation, most recognized is the theory developed by the Danish company Haldor Topsoe. This model describes the structure, positions and properties of catalytic sites performing hydrocracking, HDM, HDS and HDN processes. Presumably, the coordinatively unsaturated Mo atoms with sulfur vacancies, which arise upon modification of the major MoS_2 phase by the promoter atoms under the reaction conditions, are the hydrodesulfurization and hydrodenitrogenation active sites.[55] It was proven that the promoter is mainly located on the edges of MoS_2 plates and changes the particle morphology, in particular, it enhances the degree of packing of the active phase layers, *i.e.*, the height of crystallites increases. Two types of active particle morphology differing in the catalytic activity are distinguished, so-called M–Mo–S phases of types I and II (M = Co, Ni).[56, 57] The M–Mo–S phases of type I are characterized by incomplete degree of sulfiding and the presence of residual Mo–O–Al bonds with the support surface. These bonds are presumably formed during the annealing of the supported catalyst and give rise to a single-layer distribution of the active component, which in turn considerably decreases the catalyst activity. In type II phases, the interaction with the support is much weaker and these phases are much more sulfided. The MoS_2 phase, which forms the base of the catalytic site structure, is less dispersed and consists of 'multilayers' not bonded to the support. Detailed studies of the structure of type II phase demonstrated that it is possible to provide for the formation of small stable 'multilayers' of the MoS_2 phase by thorough control of the surface properties of the support and selection of active component precursors.[58] In a number of studies, high activity of the M–Mo–S phase of type II is attributed to S_2-bridged binuclear cobalt complexes.[59, 60]

The key point of the Halder Topsoe model is definition of two types of active sites: so-called rim (or brim) sites located in the upper layer and responsible for hydrogenation and cleavage of the C–X bonds (X = S, N) and the so-called edge sites located on the lateral surfaces of the intermediate layers and responsible only for the C–X bond cleavage.[37, 48] The activity of the rim sites in the hydrogenation reactions is due to their specific location in the outer layers, which enables the η^6-coordination upon adsorption of aromatic heterocycles by the plane.[58] According to DFT calculations, scanning tunelling microscopy and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) data, the rim sites possess 'metallic' nature, owing to which binding of the heteroatom becomes possible.[61] If the neighbouring atom bears a proton (as the SH group) or a hydride ion (M–H), hydrogenation of the substrate can take place. The effect of promoters on the hydrotreating rate in terms of the rim–edge site model is explained by the fact that addition of Co as the promoting agent increases the number of MoS_2 layers and hence, the number of edge sites, thus selectively increasing the rate of the forward desulfurization pathway, which is consistent with experimental data.[37] However, the increase in the number of MoS_2 layers can be a consequence or a 'side product' of the weak interaction between the supported component and the support, because single-layer

M–Mo–S phase of type II with high catalytic activity can also be obtained.[57]

Further studies at the atomic level demonstrated that M–Mo–S nanoclusters can be considered as single-layer MoS_2 truncated triangles, which are formed upon doping with metal atoms into particular edge sites. The catalytic activity of the clusters is determined by two factors: the shape of the cluster, *i.e.*, the length of the doped edge or the concentration of edge sites and the M–S bond energy. The cluster shape depends on the doping element: the length of the edge bearing the M and S atoms decreases with an increase in the number of valence electrons of M. The concentration of the doped edge sites is maximum upon the introduction of iron atoms and decreases in the series Fe > Co > Ni > Cu. However, as regards the activity towards HDS, the Fe–Mo–S catalyst is inferior to Co–Mo–S or Ni–Mo–S catalyst and is comparable with the undoped MoS_2.[62] The reason is that, apart from the geometric factor, an important role is played by the energetic factor: in the case of doping with iron, the M–S bond energy is too high and the hydrogen adsorption energy is too low. The optimal combination of these two factors is observed when nickel or cobalt atoms are introduced into the MoS_2 clusters.

The catalytic activity in the above hydrotreating processes is related to the metal sulfide phase distributed over the support surface. High specific surface area promotes a greater degree of dispersion of the supported phase and, hence, higher specific activity of the catalyst. The specific surface areas of commercial hydroprocessing catalysts vary from 80 to 400 $m^2\ g^{-1}$ (see Ref. 63). However, in the upgrading of heavy oil feedstocks containing high-molecular-weight asphaltenes, metal chelates and heterocyclic compounds, too large specific surface area of the support is undesirable because this is a result of developed microporous system the active sites in which are inaccessible to the listed macromolecules. A significant role in the hydroprocessing of heavy oil belongs to the texture of the catalyst support, in particular, pore size, pore size distribution, specific pore volume and the catalyst specific surface area.[7, 64, 65]

During hydroprocessing, metal and coke deposits block the catalyst pores, thus reducing the surface area and the catalytic activity and also decreasing the catalyst service life.[66, 67] Hence, the catalyst durability is to a large extent determined by the metal capacity and is inversely dependent on the metal content in the feed. It was shown that an increase in the characteristic pore size of hydroconversion catalysts for heavy feed in a fixed-bed process from 8 to 20 nm results in an increase in the capacity for extracted metals and sulfur irrespective of the chemical composition of the catalyst.[68–70] The catalytic hydroconversion of crude oil containing > 200 ppm Ni and V and < 2 mass % asphaltenes has been studied.[71] At this composition, catalyst deactivation was mainly due to blocking of the active sites by metal deposits and, to a much lesser extent, due to the coke formation from asphaltenes. The highest activity towards hydrodemetallization was shown by the catalyst with a larger pore volume (1.12 ml g^{-1}). A catalyst with the same pore size ($\sim$100 nm) but a smaller pore volume (0.45 ml g^{-1}) had the same initial demetallization rate but was rapidly deactivated. A mathematical modelling of deactivation of heavy oil hydrotreating catalysts Co(Ni)Mo/γ-Al_2O_3 revealed that the use of hierarchical[§] meso/macroporous supports with a macropore size of 215 nm and a macropore volume fraction of 30% doubles the catalyst lifetime with respect to that of the conventional mesoporous analogue.[72] Optimized hierarchical catalysts with a 15%–25% volume fraction of macropores and a $\geqslant$200 nm macropore size were also recommended[73] for hydroprocessing of heavy oils.

Apart from the pore volume and size of a supported catalyst, the pore size distribution is also an important factor for liquid-phase reactions at high pressure. The regular spatial structure of macropores is especially advantageous for the catalytic upgrading of heavy crude oils, oil products and oil residues. Indeed, in the catalysts with irregular porous structure, the transport pores differ in both the size and mutual arrangement. As a result, there are bottlenecks the blockage of which makes the inner part of the catalyst inaccessible for macromolecules. Furthermore, great pressure differentials appear throughout the catalyst, inducing fast catalyst destruction. Meanwhile, in the materials with a regular spatial structure, all of the pores, the relative positions of pores and the sizes of connecting channels are strictly defined. On the one hand, this makes it possible to perform selective reactions with heavy crude oil and oil product components with isolation of the desired component by molecular sieve effect. On the other hand, this ensures equal accessibility of the whole inner surface of the catalyst for molecules that are smaller than the connecting channel diameter and creates a more uniform flux of the liquid through the catalyst bed, which eliminates pressure differentials within the bed.

According to theoretical calculations and experimental data[74] on testing of catalysts with a regular unimodal porous structure, the effective diffusion coefficient (D_e) of a model porphyrin complex increases by 30% as the pore size increases from 10 to 70 nm, the pore volume being the same. What is especially remarkable, the D_e value increases by 60%–80% for catalysts with doubled porosity and a constant pore volume.

The traditional and widely used methods for the preparation of meso- and macroporous structure is to generate defects in the support lattice, for example, by thermochemical activation, hydrothermal treatment[75–78] or acid or alkali treatment.[79, 80] However, in these cases, pores with uncontrolled size and wide size distribution are formed in the final product.[81]

Since 1997, the method for the synthesis of macroporous supports using large (nano-sized) templates removed from the final product through burning-out or dissolution has been actively developed.[82–84] This approach called template synthesis is suitable for the preparation of a controlled material texture — a specified pore size distribution and 3D-structured porosity with a characteristic pore size from several nanometres to several micrometres — without a change in the chemical composition and properties of the surface.[85–87] Whereas the templates used for mesopore formation include surfactants,[88] various types of porous

§ By hierarchical are meant single-phase materials possessing a system of interconnected pores with polymodal size distribution in the range of up to 1 μm, for example, zeolites with an additional system of mesopores or meso/macroporous inorganic oxides.

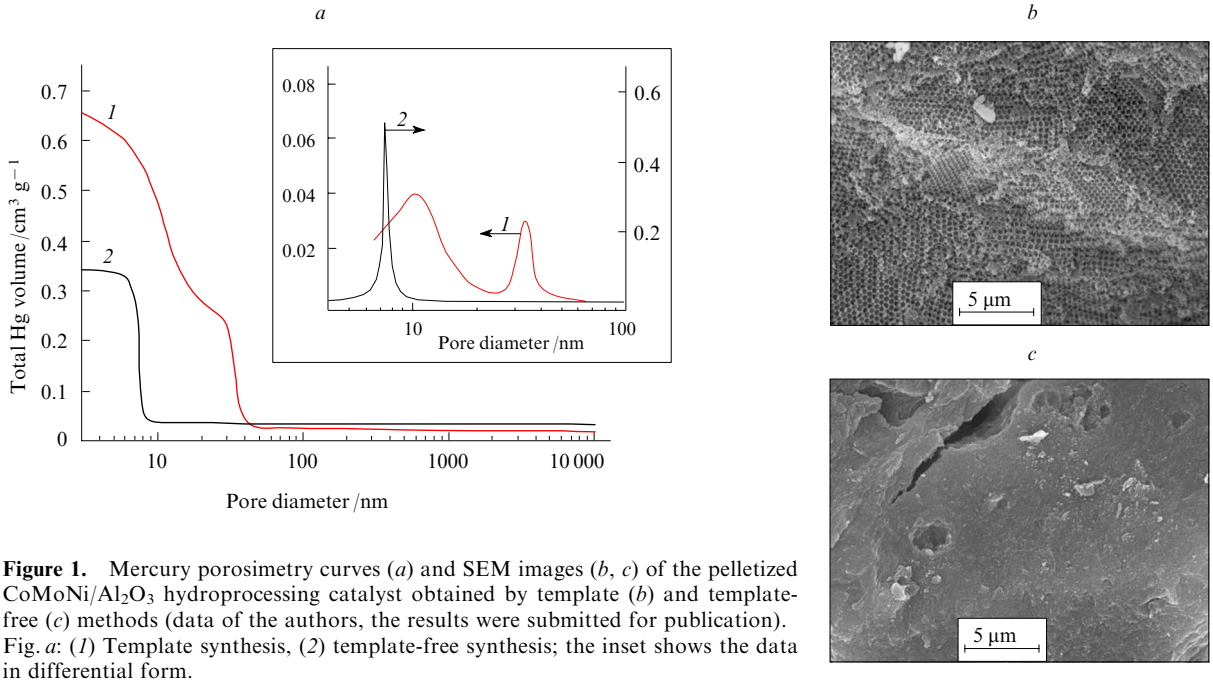


Figure 1. Mercury porosimetry curves (*a*) and SEM images (*b*, *c*) of the pelletized $CoMoNi/Al_2O_3$ hydroprocessing catalyst obtained by template (*b*) and template-free (*c*) methods (data of the authors, the results were submitted for publication). Fig. *a*: (*1*) Template synthesis, (*2*) template-free synthesis; the inset shows the data in differential form.

carbon [89] or organosilicon compounds,[90,91] for the generation of macropores, larger templates are used — polymeric microspheres,[92,93] ion exchange resins,[94] organic aerogels,[95] biological materials (bacteria,[96] wood,[97] starch[98] and so on). Figure 1 shows the differences between the supports obtained by traditional methods and the template method using the polystyrene (PS) spheres with a diameter of 250 nm. The mercury porosimetry curve of the pelletized $CoMoNi/Al_2O_3$ catalyst prepared by the template synthesis contains two maxima in the pore size distribution (at 10 and 40 nm) caused by the presence of meso- and macropores, respectively. The $CoMoNi/Al_2O_3$ catalyst of the same chemical nature obtained without a template has a narrow unimodal pore size distribution in the 10 nm range. According to the data of low-temperature nitrogen adsorption, the specific surface area of both samples of this catalyst calculated by the BET (Brunauer–Emmett–Teller) method is 89 $m^2\ g^{-1}$. Calculations of the diffusion coefficients of heavy oil fractions (vacuum distillation residues) in porous aluminosilicate catalysts prepared with and without a PS template was reported.[99] The diffusion coefficient for the extracted fractions of the vacuum distillation residue of Indonesian crude oil in the templated catalyst was found to be 2–3 times higher than those in the traditional catalyst, namely, $(1.5-5)\times10^{-8}\ cm^2\ s^{-1}$.

The template synthesis of supports of various chemical nature with a developed macroporous 3D structure, which has a large surface area accessible to macromolecules and imposes no limitations on the diffusion of reactants and products in the catalyst porous space, provides the unique possibility for the development of a new generation of efficient supported catalysts for the deep oil upgrading. For hydroprocessing of high-viscosity oil from Tatarstan, it was shown that the cobalt – molybdenum catalysts supported on a bimodal structured meso/macroporous alumina possess enhanced catalytic activity towards hydrodesulfurization and hydrodemetallization as compared with the traditional catalysts.[100] Table 2 presents data on the sulfur and vanadium contents in the products of Tatarstan heavy oil hydroconversion and in the catalysts before and after the

Table 2. Effect of the catalyst texture on cokability and sulfur and vanadium contents in oil refining products (authors' data submitted for publication).[a]

Catalyst	Catalyst composition (mass %)					Product composition			
		Mo	Co	Ni	V	cokability (mass %)	sulfur (mass %)	sulfur in bottoms (mass %)	vanadium in bottoms /ppm
$CoMoNi/Al_2O_3$	before the reaction	12.44	0.31	0.12	0.01	7.8	2.3	0.58	93
	after the reaction	5.73	0.14	0.78	0.63				
$CoMoNi/Al_2O_3$-T	before the reaction	11.10	0.24	0.11	0.01	6.7	1.7	0.34	74
	after the reaction	5.71	0.13	0.77	1.16				

[a] Crude oil: cokability, 8.6 mass %; sulfur, 3.4 mass %; sulfur in the bottoms, 0.54 mass %; vanadium in the bottoms, 335 ppm; process conditions: 420 °C, 15 MPa, LHSV 1 h^{-1}, H_2 : feed = 1000.

reaction, which illustrate the substantial difference between the templated ($CoMoNi/Al_2O_3$-T) and traditional alumina-based catalysts. The manufacture of new supported catalysts and heavy oil hydroprocessing processes on templated macroporous catalysts are protected by RF patents.[101, 102] Data on heavy oil hydrocracking were reported,[103] indicating that, as compared with the traditional hydrocracking catalyst, the PS-templated macroporous catalyst provides a 10%–12% increase in the oil processing depth and a 7%–10% increase in the yield of liquid products.

IV.2. Catalysts for slurry processes

The catalysts for slurry processes are prepared by dispersing solutions of water-soluble salts of a catalytically active metal, for example, ammonium paramolybdate, in the hydrocarbon phase to form a reverse emulsion (a micellar systems with the inner part of micelles being hydrophilic and containing water) or a reverse microemulsion (a stable reverse emulsion with a particle size of < 100 nm), which is further converted to a suspension by heat treatment.[104] The presence of surfactants in the system prevents the resulting particles of the catalytically active phase from aggregation and ensures the formation of more finely dispersed particles.[11] The average size of the resulting particles decreases with a decrease in the ammonium paramolybdate concentration, an increase in the water content in the initial solution and temperature rise and varies in the range from 80 to 950 nm, which is comparable with the average size of hydrocarbon macromolecules in bitumen (~ 10 nm).[105] As catalyst precursors, not only molybdenum compounds are used but also soluble salts of other metals, *e.g.*, aluminium, iron, cobalt and nickel nitrates as mono- or multicomponent systems.[11]

Data on nanoheterogeneous catalysts for upgrading heavy oil residues are integrated in reviews.[10, 106] The use of suspended nano-sized molybdenum disulfide particles markedly increases the degree of conversion as compared with pelletized or microspherical heterogeneous catalysts, first of all, owing to high accessibility of the catalyst particles to the heavy feed molecules. Under optimized preparation conditions, it is possible to obtain particles with a narrow size distribution in the 40–50 nm range.

The dependence of conversion of vacuum residue of the West Siberian crude oil on the amount of the catalyst precursor passes through a maximum at 0.05 mass % of the precursor (ammonium paramolybdate); the catalyst consumption is 0.1–0.2 kg per tonne of the feed.[11] The hydrocracking product is synthetic oil with the chemical composition resembling the composition of the overall liquid hydrovisbreaking product after hydrogenation of diene and a part of alkene hydrocarbons in it. According to the authors of a review,[107] this may indicate the involvement of free radical intermediates in the reactions.

Quantum chemical calculations attest to the promotory effect of hydrogen sulfide, which is formed upon hydrocracking of hydrocarbon macromolecules.[108] On the one hand, hydrogen sulfide can sulfide the molybdenum oxide obtained from the catalyst precursor, while on the other hand, it takes part in hydrogen transfer disproportionation reactions, thus increasing the hydrocracking rate.

During the slurry process, metals contained in the heavy oil feed are mainly concentrated in the coke residue and in the fractions boiling above 420 °C. The ashes and slag waste formed upon combustion of the latter are treated with an ammonia solution of ammonium carbonate for recovery of almost all molybdenum and some of nickel.[109] It was proposed to recover the vanadium and nickel that remain after the hydrometallurgical treatment by known industrial processes.[110]

IV.3. Combined catalytic systems

The hydroprocessing of heavy feed in the simultaneous presence of both fixed-bed and slurry catalysts has been reported in a number of publications. The mutual influence of the microspherical $NiMo/Al_2O_3$ hydrocracking catalysts and slurry MoS_2 desulfurization catalysts was studied in a laboratory reactor.[111] Molybdenum was injected into the solution as an oil-soluble carboxylate complex, which was subsequently sulfided by oil products.[107]

When the vacuum distillation residue of the Urals oil¶ was hydrotreated in the presence of both catalysts, the highest degrees of hydrodesulfurization and hydrodenitrogenation were achieved. In the absence of the MoS_2 catalyst, a very high activity of the NiMo catalyst towards hydrocracking and a low hydrogenation rate were observed, which resulted in fast coking of the catalyst. Conversely, if only the MoS_2 catalyst was used, the hydrocracking rate was the same as in the purely thermal process; however, the system was stable against coking. The combination of these catalysts produced a synergistic effect where the hydrocracking, desulfurization and denitrogenation rates increased and the coking rate was low.[112] A transmission electron microscopy (TEM) study of the NiMo catalysts after the reaction showed a coke layer with inclusions of MoS_2 on the surface of microspheres. Apparently, the presence of MoS_2 in coke nuclei increases the hydrocracking rate and prevents blocking of catalyst particles. The most pronounced effect was obtained in an ebullated-bed reactor with periodic regeneration of a part of the NiMo catalyst. The process productivity was 1.5 higher compared with the process catalyzed by only MoS_2 and the degree of desulfurization and denitrogenation was $\sim 90\%$ and remained constant for > 80 h.

It was assumed [111] that MoS_2 forms a protective layer on the catalyst surface, in which coke deposits are hydrogenated and the metal impurities are sulfided. The bulk of the NiMo microspheres thus remains free from deposits and the catalyst runs hydrocracking reactions at a high rate. An analogy can be followed between the bifunctional catalytic system in question [111] and the Hyvahl process† in which fixed-bed reactors connected in series are loaded with catalysts of different types, each catalyst bed being meant for a particular function.

V. Specific features of various catalytic hydroprocessing processes

As has already been noted, the extended use of hydroconversion of heavy feedstock is mainly driven by the increased demand for motor fuels. Non-catalytic thermal upgrading processes for heavy oil feedstock produce a large amount of coke with low application properties. Despite

¶ A Russian brand of export crude oil obtained by mixing heavy high-sulfur crude oil of Ural and Volga region with the Siberian Light oil.

† Hyvahl™ is a trademark of Institut Francais du Petrole (IFP) for hydroprocessing processes.

Table 3. Comparative fractional composition of delayed coking and hydroprocessing.[113]

Product	Yield (% of the initial feedstock weight)		
	delayed coking [a]	fixed-bed [b]	ebullated-bed hydrocracking [d]
LPG [d]	–	5.1	4.6
Petrol	4.0	19.3	18.1
Kerosene + Diesel	17.2	35.5	28.6
Catalytic cracking feed	84.1	28.8	29.9
Vacuum residue	–	20.2	–
Coke	–	–	28.6

[a] 134 m^3 H_2 (STP) m^{-3}; [b] 198 m^3 H_2 (STP) m^{-3}; [c] 332 m^3 H_2 (STP) m^{-3}; [d] liquefied petroleum gas.

Table 4. Characteristics of catalysts used in the Hyvahl™ process.[114]

Parameter	Catalyst application			
	guard bed	HDM	HDM/HDS	HDS
Pellet size /mm	3–10	1.2–6	0.8–1.6	0.8–1.6
Active component	none	Mo/NiMo	NiMo/CoMo	CoMo/NiMo
Specific surface area /m^2 g^{-1}	< 1	80–180	150–220	180–250
Pore volume /cm^3 g^{-1}	< 0.15	0.7–1.2	0.5–0.8	0.4–0.7
Average pore size /nm	10^4–10^5	20–100	10–20	8–12
Metal capacity (Ni, V) (mass %)	–	> 50	30–40	10–20
Load (% of the total catalyst weight)	< 5	30–60	10–40	30–60

higher capital investment to hydroconversion units as compared with thermal cracking units, the increased yield of distillates in hydroconversion (Table 3) shows that the potential of catalytic upgrading of heavy oils has not yet been exhausted.

The hydroconversion of heavy oil feedstock gives a vacuum residue co-product (see Table 3), which can serve as the feed for thermal cracking to give an additional amount of light distillates. The hydroconversion can be performed either as a single stage or as serial stages with removal of by-products such as ammonia and hydrogen sulfide. Hydroprocessing processes are conventionally subdivided into four key types: fixed-, moving- and ebullated-bed catalytic hydroprocessing and the slurry process; the possibility of combining different processes in one reactor or in several reactors in series has been actively discussed in recent literature.

Fixed-bed processes use a family of catalysts for HDM, HDS, HDN and hydrocracking loaded successively either into the same reactor or in several reactors in series. At the reactor inlet, there is a guard bed devoid of catalytic activity or having a low catalytic activity the function of which is to purify the feed from particulates and to retain and hydroconvert the largest molecules.[7]

A typical upgrading process for atmospheric and vacuum residues in fixed-bed reactors *via* catalytic hydrogenation is the Hyvahl™ process. The degree of conversion of heavy residues to distillates boiling at atmospheric pressure varies from 15% to 25%; furthermore, other products have low sulfur contents and can be used as low-sulfur furnace fuel oils or as a feed for the residue fluid catalytic cracking (RFCC). The Hyvahl products have low contents of metals (Ni and V), a low Conradson carbon value and a higher hydrogen to carbon ratio.‡ Currently, there are three Hyvahl units in the world, two operating on vacuum residues and one on atmospheric residues.

Feed is converted in a chain of reactors containing different types of catalysts (Table 4). The inlet bed in the pretreatment reactor contains a guard material without an active component. Then, along the feed flow, a HDM catalyst with an average pore size of > 20 nm is loaded. The wide pores are needed to transport large asphaltene and resin molecules towards the catalyst active sites where metal recovery and feed desulfurization take place together with thermal cracking.

As the feed moves along the series of reactors, the conversion increases, the concentrations of metals, sulfur and coke residue decrease and the average size of hydrocarbon molecules decreases. The order of catalysts is adjusted in such a way that the catalyst activity gradually increases as the feed moves along. The loading of low-activity catalysts in the inlet bed increases the process stability against coking and metal deposition. The high catalyst activity near the outlet ensures higher degrees of conversion of heavy molecules and more profound purification from sulfur and nitrogen.[114] This pattern of catalyst arrangement is also typical of other fixed-bed hydroconversion processes:[7] HYCON, RDS/VRDS and so on.§

The lack of possibility of easy replacement of fixed-bed catalysts imposes rather stringent restrictions on the metal content in the feed, which must not exceed 100 ppm. In order to extend the range of suitable feeds, modifications of the process are used, in particular, pretreatment reactor with periodic catalyst regeneration is installed (Hyvahl-S), the block diagram of which is shown in Fig. 2.[7, 114, 115]

According to this block diagram, atmospheric or vacuum residue is fed into pretreatment reactors in which particulates and large particles are removed and the feed is demetallized.[115] In the normal operation mode, reactors 1 and 2 are connected in series by a system of valves. As the flow resistance increases and the degree of purification is deteriorated, the first reactor is isolated for catalyst replacement, which takes about a week. The reactor with a fresh

‡ http://www.axens.net/product/technology-licensing/10091/hyvahl.html

§ HYCON is a Shell trademark for the hydroconversion process; RDS is atmospheric residue desulfurization; VRDS (or vacuum RDS) is vacuum residue desulfurization.

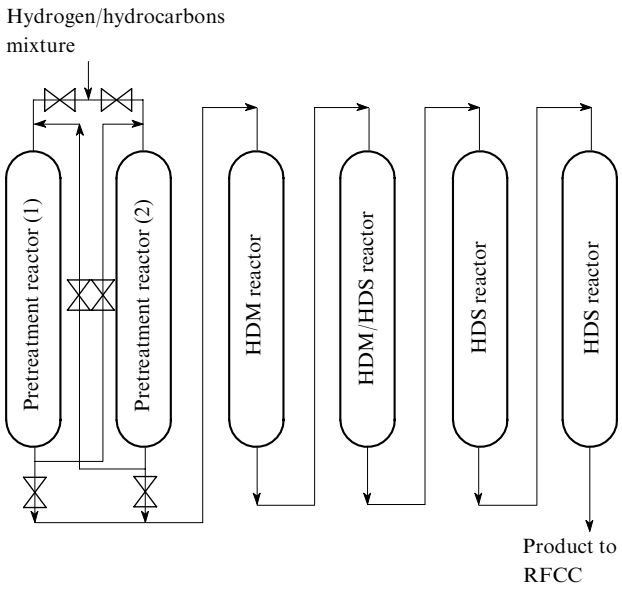


Figure 2. Block diagram of fixed-bed hydroconversion of heavy oil feedstock using pretreatment reactors with periodic catalyst regeneration (Hyvahl-S modification).[115]

catalyst is connected in the second position. Thus, at the beginning of the process, there is always the reactor in which the catalyst has already run for some time. The service life of the reactor with the same catalyst portion is about a year.[115]

One more method for processing feedstocks with higher contents of metals is to use moving-bed reactors. In the primary hydrotreatment of heavy oil in a moving-bed reactor, of particular importance is the HDM catalyst, which is located in the inlet bed and serves for preventing deactivation of HDS, HDN and hydrocracking catalysts located in the subsequent layers.[116] The first reactor is usually loaded with the HDM catalyst having a high porosity, wide pores and low specific surface area, which facilitates the diffusion of asphaltenes into the catalyst bulk. The use of mixed oxides that are more acidic than alumina is favourable for higher degrees of HDS and hydrocracking reactions.[117]

For 40 years, the Chevron Lummus Global (CLG) company has developed and has been licensing the RDS/VRDS process for catalytic hydroconversion of atmospheric or vacuum residues at temperatures of 350–430 °C and hydrogen pressure of 13–18 MPa.[118, 119] The Chevron Lummus Global tailored catalysts are suitable for both types of feed,¶ which enhances the possibilities for upgrading heavy oil feedstock.[120]

The RDS process is combined with the on-stream catalyst replacement (OCR) technology by using the upflow reactor (UFR).[121] The fresh catalyst is loaded from the top and the spent catalyst is withdrawn at the reactor bottom (Fig. 3).

The counter-flows of the stock and the catalyst provide the fullest utilization of the catalyst. The deactivated catalyst contacts with the fresh, most reactive feed at the reactor inlet, whereas the converted, least reactive part of the feed at the top of the reactor contacts with the fresh catalyst. The fresh catalyst is loaded at the top of the reactor. As stated by Chevron Lummus Global specialists, feed inlet at the bottom, even without using the OCR technology, is advantageous due to the lower flow resistance of the bed.

Combining the RDS reactor with OCR and UFR technologies makes it possible to operate on feed with metal contents of up to 200 ppm, which is twice higher than the usual value for fixed-bed reactors.

A similar process for hydroconversion of heavy feedstock with high metal contents (>500 ppm) using the bunker flow technology, called HYCON, has been developed by Shell.[122–125] In the HYCON process, both the catalyst and the feed enter the reactor at the top and the deactivated catalyst is withdrawn at the reactor bottom (Fig. 4).

The bunker reactor is mounted at the head of the unit, upstream of the fixed-bed demetallization reactor. The rate of catalyst replacement is chosen in such a way that the hydroconversion train can continuously operate for a year. At the appropriate flow rate of the catalyst supply, it is possible to upgrade heavy feedstock with metal contents of >500 ppm.[125]

The ebullated-bed catalytic hydrocracking occupies a special place among the upgrading processes of atmospheric and vacuum residues and heavy and extra-heavy hydrocarbons. The advantages of the process include the possibility of processing heavy hydrocarbons with Ni and V contents of >200 ppm, flexible tuning of the process parameters by on-stream replacement of the catalyst without shutting-down the reactor, and the possibility to control the degree of conversion of hydrocarbons according to the

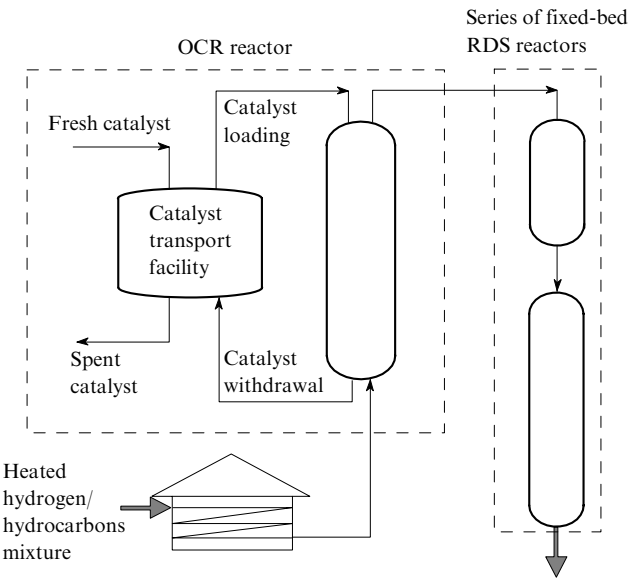


Figure 3. Flow diagram of anatmospheric residue desulfurization reactor (RDS) with on-stream catalyst regeneration (OCR).[121]

¶ See *Axens and Headwaters Technology Innovation (HTI) Join Efforts on Ebullated Bed Technology for Heavy Oil Upgrading*. http://www.axens.net/news-and-events/news/265/axens-and-headwaters-technology-innovation-hti-join-efforts-on-ebullated-bed-technology-for-heavy-oil-upgrading.html

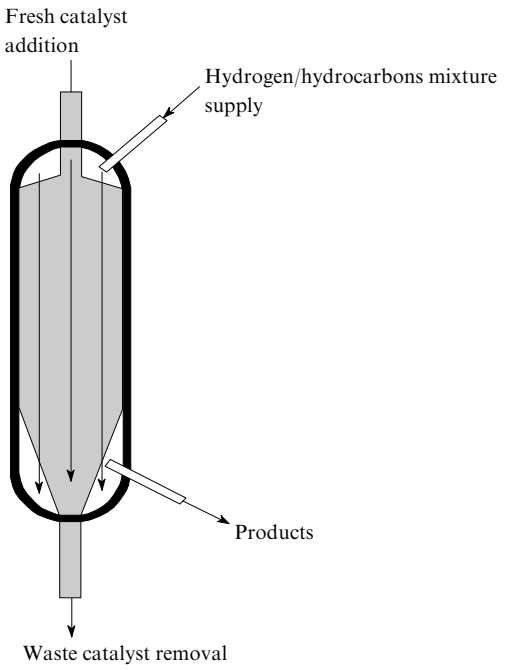


Figure 4. HYCON reactor.[125]

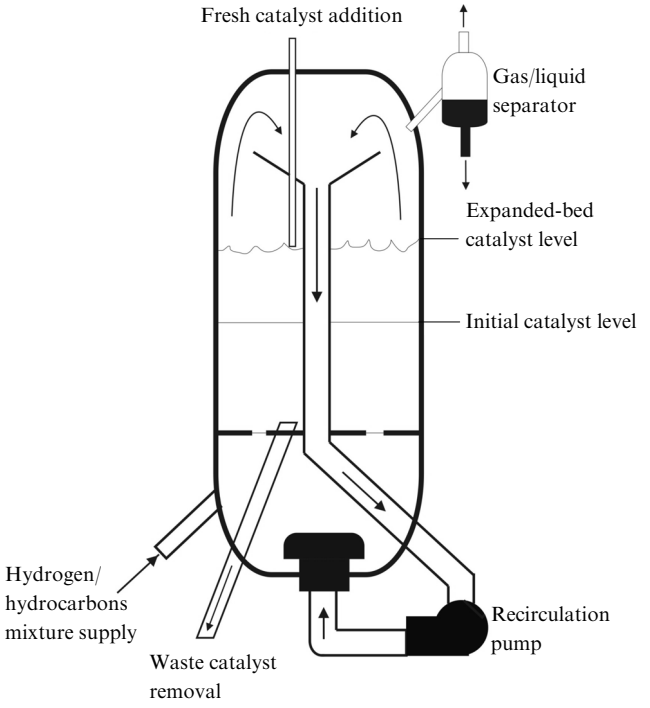


Figure 5. Expanded-bed reactor for extra heavy feed hydroprocessing to a high degree of conversion (LC-Fining).[8]

production objective and the type of feed.[8, 126] As a rule, the hydroconversion catalysts to be used in an ebullated-bed reactor are grains or pellets of $\leqslant 1$ mm size.[127]

There are several modifications of the process characterized by different feed conversions. Chevron Lummus Global is the licensor of the LC-Fining process, which uses an ebullated catalyst bed in a loop reactor. A specific feature of the process is regular (every 24 h) replacement of some of the spent catalyst by a fresh portion. The key process parameters are summarized in Table 5.[128]

At a high degree of conversion of heavy hydrocarbons, an asphaltene precipitate is usually formed. This is caused by faster conversion of high-molecular-weight resins and oils compared to asphaltenes. When the conversion is high, the amount of solvent (resins) becomes insufficient for dissolving asphaltenes, which precipitate and clog the pipelines. However, the addition of up to 10 vol.% of catalytically cracked light gas oil was found to reduce the asphaltene sedimentation.[129]

Table 5. Key parameters of the LC-Fining process.[128]

Parameter	Value
Reactor temperature	410–440 °C
Reactor pressure	110–180 bar
Conversion of hydrocarbons at 524 °C	55%–80%
Hydrogen partial pressure	75–125 bar
Hydrogen consumption	135–300 m^3(STP) m^{-3}
Hourly space velocity of feed	0.1–0.8 h^{-1}
Desulfurization degree	60%–85%
Conradson carbon removal degree	40%–70%
Demetallization degree	65%–88%

Figure 5 shows the schematic view of the LC-Fining reactor. A mixture of heavy hydrocarbons and hydrogen are fed from the bottom. As the mixture flows up, it is mixed with the recycled feed and comes in contact with the catalyst, thus maintaining the upper layer of the catalyst bed in the expanded state. The reactor design allows on-stream withdrawal of a part of the catalyst to be replaced by a fresh portion.

The LC-Fining process uses CoMo catalysts to maximize hydrodesulfurization and NiMo catalysts for predominant hydrodenitrogenation and hydrocracking reactions. The use of two types of catalysts in a series of two reactors is also possible. Catalysts for upgrading heavy hydrocarbons in ebullated-bed reactors are manufactured by several companies, in particular, CLG, Shell, Ketjen and some other. Table 6 gives typical parameters of commercial catalysts of this type.

Recently, CLG has subdivided the licensed ebullated-bed processes into two types, namely, upgrading of extra-heavy feedstock to high degrees of conversion, still existing under the trade name LC-Fining, and atmospheric residue

Table 6. Catalyst parameters for ebullated-bed hydroconversion of heavy hydrocarbons.[8]

Parameter	Catalyst	
	HDM	HDS
Surface area /m^2 g^{-1}	80–180	160–250
Average pore size /nm	20–100	8–20
Active phase	NiMo	NiMo–CoMo

upgrading process called IsoFining, which is distinguished by a lower degree of conversion.[128] The LC-Fining process implies hydroconversion carried out in two or more ebullated-bed reactors. In the first reactor, demetallization and primary removal of sulfur and nitrogen occur on NiMo catalysts. In the second reactor, the final treatment occurs on CoMo catalysts. The IsoFining process uses only one ebullated-bed reactor, often in combination with delayed cokers.

The differences in the product ratios obtained by feed processing upon severe (LC-Fining) and mild (IsoFining) hydroconversion are illustrated in Fig. 6. For comparison, data of the thermal delayed coking process are also presented. It can be easily seen that with increasing degree of conversion, the proportion of heavy hydrocarbons decreases, most of all, due to increased yield of middle distillates. Both processes do not give coke; however, if IsoFining is combined with delayed coking, the vacuum residue of hydroconversion products gives approximately twice less coke than present in the feed. Both processes are recommended in the case where the goal is to increase the manufacture of motor fuels and there is a possibility of additional investment to hydrogen production processes.

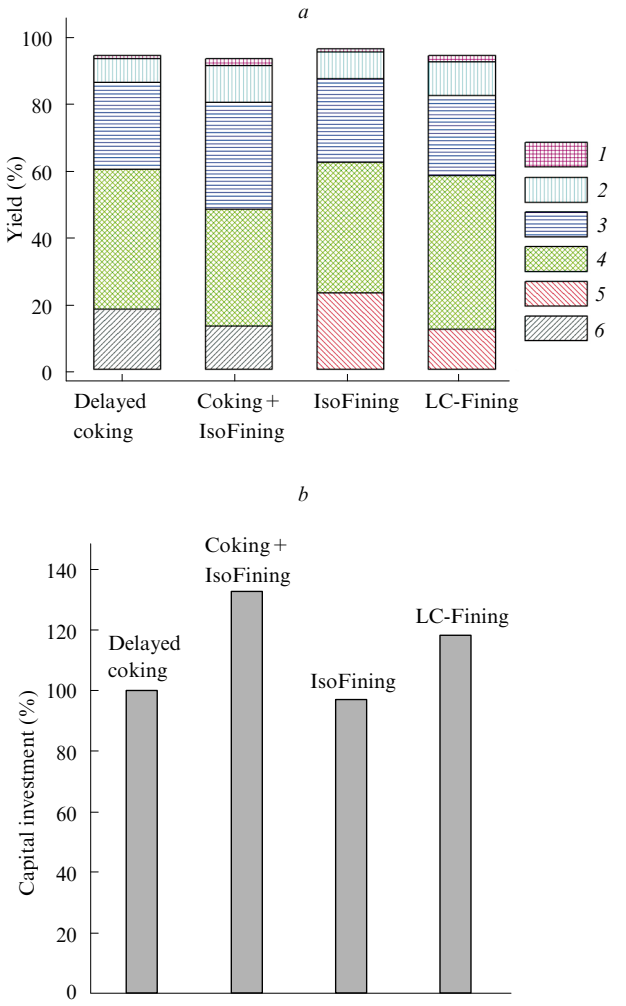


Figure 6. Product yields in severe (LC-Fining) and mild hydroconversion (IsoFining) in comparison with delayed coking (*a*) and capital investments to these processes (*b*).[128]
(*a*) (*1*) Gas, (*2*) petrol, (*3*) diesel, (*4*) vacuum gas oil, (*5*) fuel oil, (*6*) coke.

The Axens company is the licensor of the H-Oil process, which differs from the above-considered LC-Fining process mainly by the set of equipment.[130, 131] Conditions of the H-Oil process depend on the type of feed and fit into the range indicated in Table 5. A milder version of H-Oil for moderate hydrocracking to a degree of 40%–60% is licensed under the trade name T-Star. Although H-Oil uses the same catalysts as T-Star, the latter process has also been recommended for hydrocracking of vacuum gas oil.

A review of slurry-phase processes using solid catalysts that have passed pilot tests for the production of motor fuels from heavy oil fractions, natural vacuum residues and asphaltites was reported.[132] The authors state that solid catalysts have a low activity, hamper waste separation and disposal and are, most often, unprofitable due to low cost, whereas finely dispersed catalysts with large surface area-to-volume ratio exhibit higher catalytic activity and higher hydroprocessing performance.

Therefore, alternative processes that substantially intensify the catalytic hydroconversion of heavy and residual feedstock on molybdenum catalysts have appeared in recent years. For example, hydroconversion of heavy oil residues on nano-sized heterogeneous catalysts developed at the Institute of Petrochemical Synthesis of the RAS and Grozny Petroleum Research Institute[133, 134] proceeds at a temperature of 430–450 °C, a pressure of 5–7 MPa and hydro-

Table 7. Comparison of the vacuum residue hydroconversion products obtained in different processes.[136]

Parameter	Fixed/moving bed	Ebullated bed	Slurry process
Petrol			
Yield/feed (%)	1–5	5–15	10–15
Density /kg m^{-3}	710–740	710–720	720
Sulfur (mass %)	<0.01	0.01–0.2	0.06
Nitrogen /mass ppm	<20	50–100	200
Gas oil			
Yield/feed (%)	10–25	20–30	40–45
Density /kg m^{-3}	850–875	840–860	866
Sulfur (mass %)	<0.1	0.1–0.5	0.7
Nitrogen /mass ppm	300–1200	>500	1800
Vacuum gas oil			
Yield/feed (%)	20–35	25–35	20–25
Density /kg m^{-3}	925–935	925–970	1010
Sulfur (mass %)	0.25–0.5	0.5–2.0	2.2
Nitrogen /mass ppm	1500–2500	1600–4000	4300
Conradson carbon	<0.3	<2	<2
Vacuum residue			
Yield/feed (%)	30–60	15–35	10–20
Density /kg m^{-3}	990–1030	1035–1100	1160
Sulfur (mass %)	0.7–1.5	1–3	2.7
Nitrogen /mass ppm	3000–4000	>3300	11 000
Asphaltenes (mass %)	5–10	>20	26

gen-to-feed ratio of 800–1000 [m^3 (STP) m^{-3}] in the presence of 0.03 mass % – 0.05 mass % of the catalyst.

In 2013, the first commercial slurry unit implementing the EST (Eni Slurry Technology) process was commissioned in Sannazzaro (Italy) [135].† A specific feature of the process is recycling of molybdenum-containing heavy residues, which increases the concentration of molybdenum in the reaction mixture to 2000 ppm.[135] A part of the heavy residues (1%–3%) is removed from the process to avoid accumulation of coke and metals in the reactor.

A combination of an ebullated-bed catalytic process and catalytic hydrocracking on nano-sized catalysts is apparently the optimal choice to upgrade heavy hydrocarbons for Russian industry. Table 7 presents the results of comparison of hydroconversion processes using the same feed.[136]

The highest degree of conversion can be achieved in the slurry process, while the lowest conversion is observed in the fixed bed. However the degree of removal of sulfur and nitrogen is improved in the opposite order: fixed bed > ebullated bed > slurry process. In addition, the heavy fractions of the slurry process have markedly higher density and lower stability (see Table 7).

† Eni is Ente Nazionale Idrocarburi, Italian state oil industry association.

VI. Applications of catalytic heavy feedstock hydroprocessing

VI.1. Upgrading of natural bitumen

A mixed process for conversion of natural bitumens to synthetic light oil combining thermal cracking and ebullated-bed catalytic hydroprocessing is in operation at the Mildred Lake refinery (Canada). Bitumen is supplied to the facility as a mixture of extracted bitumen and naphtha, the latter being added to reduce the bitumen viscosity for pipeline transportation. After atmospheric distillation, the major part of atmospheric residues is routed to vacuum distillation. The smaller part is mixed with the vacuum residue and fed into the ebullated-bed reactor. The remaining part of the vacuum residue is delivered to delayed coker (Fig. 7).[137]

As follows from the data on the composition and properties of bitumen upgrading products summarized in Table 8, the hydroconversion stage introduced into the process flow diagram is meant to decrease the sulfur and nitrogen contents in the cracking products and, hence, the load on the downstream hydrotreating stages.[139]

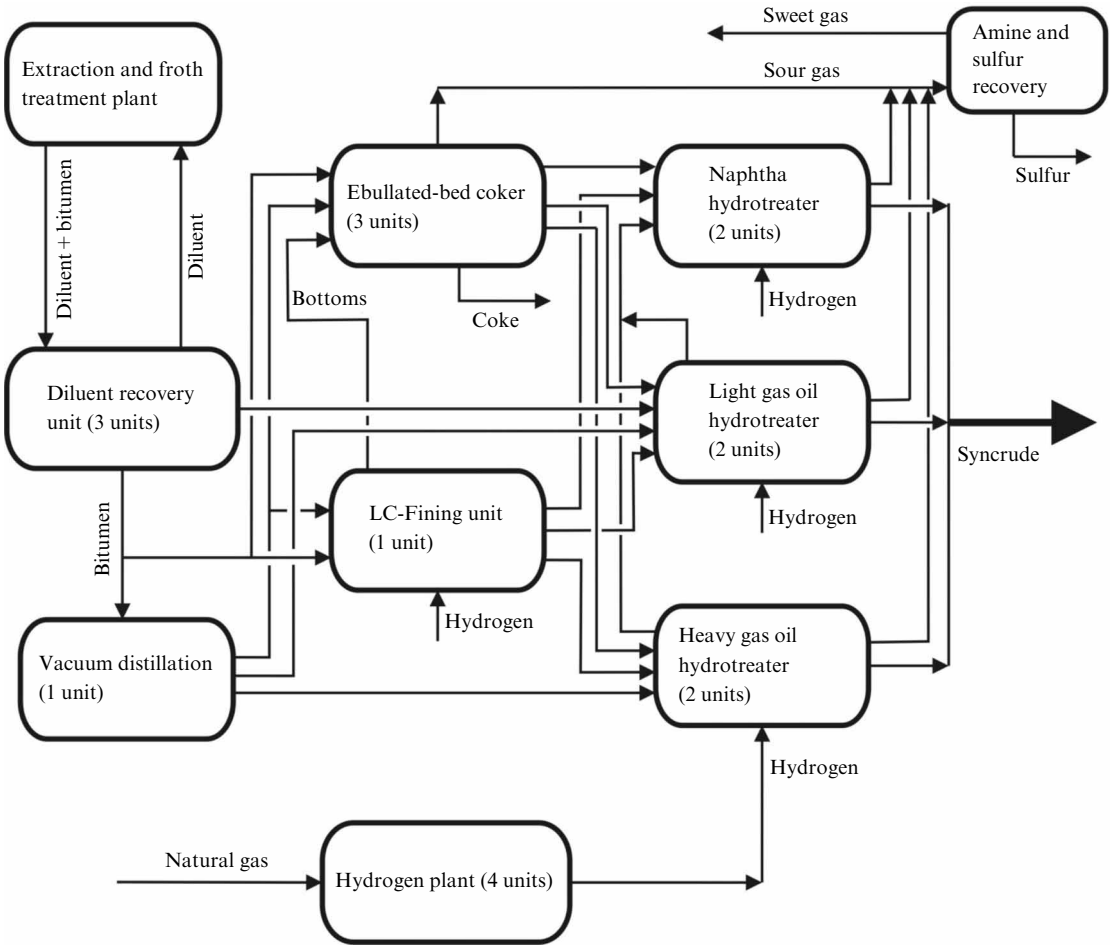


Figure 7. Flow diagram of the SynCrude plant in Mildred Lake (Canada) producing synthetic oil from bitumen.[137]

Table 8. Composition and parameters of bitumen and its hydroconversion and delayed coking products.[138]

Product	Yield (vol.%)	Density (15 °C) /kg m^{-3}	Contents		
			sulfur (mass %)	nitrogen (mass ppm)	hydrogen (mass %)
Bitumen					
Straight-run diesel (< 343 °C)[a]	13.5	898	1.6	200	12.31
Light vacuum gas oil	6.3	935	2.34	40	–
Heavy vacuum gas oil	23.8	969	2.92	1380	–
Vacuum residue (> 524 °C)	56.4	1057.2	6.42	9494	–
Hydroconversion products (IsoFining)					
Naphtha (light/heavy)	4.7/4.8	687/763	0.27/0.18	80/530	13.8
Light gas oil	30.5	876	0.68	1500	12.15
Heavy gas oil	4.8	943	1.3	3000	11.22
Bottoms	55.2	1018	2.7	5900	10.22
Delayed coking products					
Naphtha	34.1	782	1.68	237	12.36
Light gas oil	16.4	941	3.64	1600	10.87
Heavy gas oil	49.5	1002	4.33	3780	10.17

[a] Here and below, the values in parentheses are boiling points.

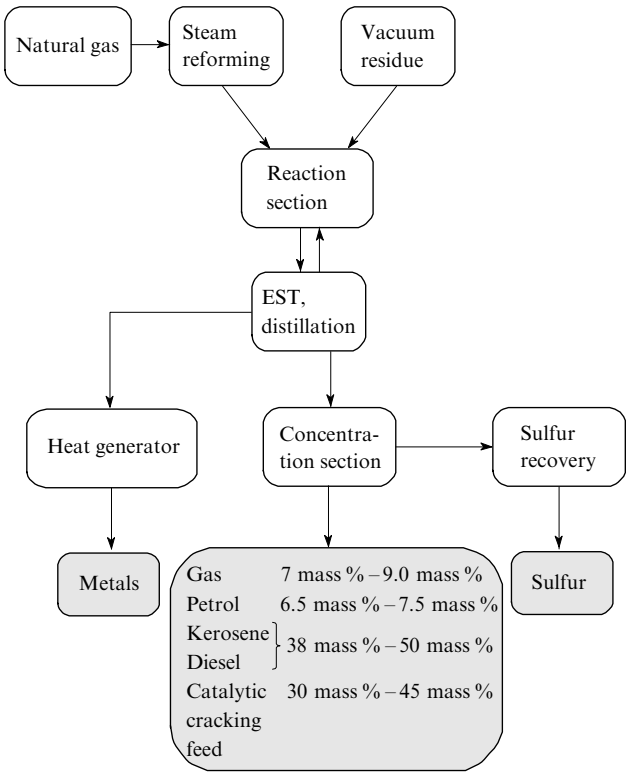


Figure 8. Flow diagram of the slurry unit at the Sannazzaro refinery (Italy).[140]

The Mildred Lake facility operates the world largest ebullated-bed hydroconversion reactor with a capacity of 50 Mbpd. This plant uses mild hydroconversion of heavy residues (~55% – 60%), which can be classified as the IsoFining mild hydrocracking process. The hydroconversion of heavy bitumen fractions is required to correct the properties of the final product of the plant — light synthetic oil. Owing to product hydrogenation, considerable decrease in the sulfur and nitrogen contents, together with the absence of vacuum residues, the synthetic oil product is superior even to natural light oil brands. The variation of the market price of a mixture of this synthetic oil demonstrates that it is 5% – 10% more expensive than the benchmark WTI crude oil.‡

VI.2. Upgrading of Urals vacuum residue in a slurry reactor

The first industrial catalytic slurry reactors were commissioned in 1929 for coal hydroconversion, while after the Second World War, they were switched to upgrading of vacuum residues. After 1964, only pilot and semicommercial plants were in operation. In 2013, an industrial slurry reactor, the only one in the last 50 years, using the EST technology (Eni) was put in operation in Sannazzaro (Fig. 8).

‡ WTI (West Texas Intermediate) is a crude oil produced in Texas (USA) for petrol production.

The goal of the EST is to decrease as much as possible the yield of side products from the processing of extra heavy feedstock — petroleum coke. The Sannazzaro plant will be the first one in the world meant for industrial hydroconversion of vacuum distillation residues of the Russian Urals oils and Basra refinery products.[140] The feedstock characteristics are summarized in Table 9. The plant comprises the EST section, a natural gas steam reforming unit for hydrogen production with a capacity of 100 000 m^3 (STP) per hour, a distillation unit, a product hydroprocessing section, a metal recovery section and an elemental sulfur plant with a capacity of 80 tpd.

The key part of the plant is a unique slurry reactor. The hydroconversion in this reactor occurs uniformly due to a small size of catalyst particles. The uniform temperature and the absence of hot spots are achieved due to vigorous bubble stirring of the feed and hydrogen in the reactor.[140]

The hydroconversion products are routed to distillation to separate gas components, petrol, middle distillates and catalytic cracking feed. The gas products run through amine treatment, then are mixed with hydrogen and fed back to the reactor. The vacuum residue, together with the catalyst, are recycled to the reactor for repeated processing. The degree of conversion is optimized to avoid the formation of carbonaceous deposits on the equipment walls that are in contact with the hydroconversion products. The stability of the vacuum residue increases upon mixing with the feed, which prevents the precipitation of asphaltenes. A minor withdrawal of the vacuum residue (3% of the initial feed amount) is necessary to maintain the steady-state process

Table 9. Feed specification for the EST process at the Sannazzaro refinery (Italy).[140]

Parameter	Used feed: vacuum residue of Urals	Alternative feed: vacuum residue from Basra
Content of 350–500 °C cut (mass %)	5	5
Content of 500+ °C cut (mass %)	95	95
Asphaltenes C_5 (mass %)	15	15.6
Density (1 bar) /kg m^{-3}	1004	1039
Density (1 bar) /°API	9.4	4.7
Viscosity /cSt	982 (100 °C) 159 (135 °C)	1126 (80 °C) 43 (100 °C)
Pour point /°C	51	51
Sulfur (mass %)	3	6
Nitrogen (mass %)	0.7	0.4
Nickel /mass ppm	68	46
Vanadium /mass ppm	214	164
Conradson coke (mass %)	20.2	18.5
H : C ratio	1.41	1.37

and remove the accumulated metals (Ni + V) from the reactor. The withdrawn vacuum residue is treated to recover the metals.

In the steady-state regime, the EST process provides a 98% degree of conversion for any type of residue, the yield of light products and distillates being 110% with respect to the physical volume of the feed due to the lower density of hydrogenation and hydrocracking products. The degrees of HDS, HDM and HDN can be more than 85%, 99% and 97%, respectively. Characteristics of the EST-hydrocracked products are summarized in Table 10.

It is expected that the real yield and mass balances for this process on an industrial scale will be published in the near future and then it will be possible to evaluate the real market potential and advantages and drawbacks of the new process, in particular, in comparison with other hydrocracking processes for heavy and residue feedstock operating in industry.

Table 10. Parameters of vacuum residue hydrocracking products in the slurry EST process.[140]

Products	Yield (mass %)	Content		Density (1 bar) /kg m^{-3}
		sulfur (mass %)	nitrogen /mass ppm	
$H_2S + NH_3$	3.2–4.0	–	–	–
$C_1–C_4$	7.0–9.0	–	–	540 (LPG)
Naphtha (C_5, 170 °C)	6.5–7.5	< 10	–	700
Kerosene + gas oil	38–50	< 10	–	840
Catalytic cracking feed (350–500 °C)	30–45	< 400	< 700	920
Feed to be processed at the waste treatment plant	2.5–3.8	–	–	–

VII. Conclusion

The increasing demand for motor fuels requires not only active upgrading of heavy oils and bitumens due to shortage of light oil reserves but also increase in the proportion of hydrogen-based and secondary processing processes.

Typical industrial catalysts for fixed-, moving- and ebullated-bed hydroprocessing are Co(Ni)-promoted Mo(W) sulfides supported on alumina pellets. A significant role in the upgrading of heavy feedstock is played by the support texture. Indeed, macroporous catalysts with an average pore size of 20–100 nm and a pore volume of at least 0.7 $cm^3\ g^{-1}$ have the highest capacity for metal removal from the feed, whereas for hydrodesulfurization, catalysts of a different type are more effective, namely, this requires small pores (8–12 nm) and, hence, high specific surface area of the support (up to 250 $m^2\ g^{-1}$). Thus, effective upgrading of heavy feedstock with high contents of sulfur and metals can be achieved only by using families of highly specific catalysts with different texture characteristics arranged in series along the feed flow.

The degree of feed conversion can be markedly increased by means of slurry processes catalyzed by a suspension of molybdenum and other transition metal sulfides in the hydrocarbon phase. However, in this case, the activity of catalysts towards removal of sulfur and metals from the products is much lower as compared with traditional catalytic processes.

In Russian industry, combined use of fixed-, moving- or ebullated-bed process and a slurry process appears to be the method of choice for upgrading the heavy and residue feedstocks.

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