

Current Status and Prospects of Demetallization of Heavy Petroleum Feedstock (Review)

R. N. Magomedov^a, A. Z. Popova^a, T. A. Maryutina^{a, b}, Kh. M. Kadiev^c, and S. N. Khadzhiyev^c

^aOOO “MFTI Engineering Center for Hard-to-Extract Minerals”, Moscow Institute of Physics and Technology, Moscow, Russia

e-mail: Magomedov.rm@cet-mipt.ru

^bVernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, Russia

^cTopchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

Received February 10, 2015

Abstract—Comparative assessment of the prospects of development of heavy petroleum feedstock (HPF) upgrading technologies in terms of the possibility of removal and recovery of metals contained in the feedstock is presented. It has been shown that HPF demetallization with different efficiencies can be achieved as a result of destructive thermal conversion of the feedstock and nondestructive mass transfer processes. Solvent deasphalting is characterized by simplicity of engineering design and operating flexibility and makes it possible to remove both asphaltenes and metals, whose deposition leads to irreversible deactivation of oil refining catalysts. Promising lines in demetallization by destructive feedstock conversion are associated with processes that provide the highest degree of HPF conversion and the lowest yield of the unconverted residue, in which the feedstock metals are concentrated. In this regard, the development and implementation of petroleum residue upgrading technologies based on the slurry hydrocracking, fluid coking or flexicoking, and supercritical fluid extraction processes creates real prerequisites for the organization of high-conversion comprehensive processing of heavy oils with the isolation of a metal concentrate.

Keywords: demetallization, petroleum feedstock

DOI: 10.1134/S0965544115060092

Heavy and high-viscosity oil reserves are known to make about 80% of the world oil resources [1]. By explored reserves of heavy oil, Russia ranks third in the world after Canada and Venezuela. The depletion of deposits of light and medium-gravity oils in Russia and the growing consumption of oil and oil products result in that the proportion of heavy oils involved in refining will inevitably increase [2]. As the gravity of the oil increases, the amount of resin–asphaltene compounds, heteroatoms, and metals in it increases [3] (Fig. 1). It is these components whose presence in significant quantities leads to a decrease in the H/C atomic ratio in petroleum feedstock, deterioration of its transport properties, a decrease in stability (growth of colloidal instability) and compatibility, an increase in carbon residue, the tendency to form solid deposits, and corrosion of equipment [4].

A high concentration of metals, in particular vanadium and nickel, is also a serious problem faced in the processing of heavy petroleum feedstock (HPF), as it leads to irreversible catalyst deactivation due to metal deposition on the active surface, blocking the pore space, and degradation of the catalyst structure [4]. In addition, inorganic vanadium compounds produced during the processing facilitate intense ash fouling and

high-temperature surface corrosion of equipment, reduction in the service life of turbo-jet and diesel engines and utility boilers, gas corrosion of active elements of gas-turbine engines, and growth of environmentally harmful emissions [5, 6].

However, metals including less-common and rare-earth metals are valuable associated components, whose content in crude oils and their refining residues is comparable to and can be even higher than their concentration in ores [7]. For example, heavy crudes of Russia are a potential vanadium source that is much superior to currently existing ore sources in quality [8]. Vanadium is one of the most important strategic metals because of its use in the manufacture of steels and nonferrous alloys, in which it is an essential alloying element [9]. According to published data [10, 11], the amount of vanadium contained in the metal-bearing industrial heavy oil extracted in Russia in 2005 is about 1/3 of the amount of vanadium produced by the Russian industry from its ore sources in the same year. However, no industrial-scale production of metals (in particular, vanadium) from petroleum feedstock has been launched in Russia, although oil refining technologies that allow obtaining concentrates with a high metal content are known around the world [11–13].

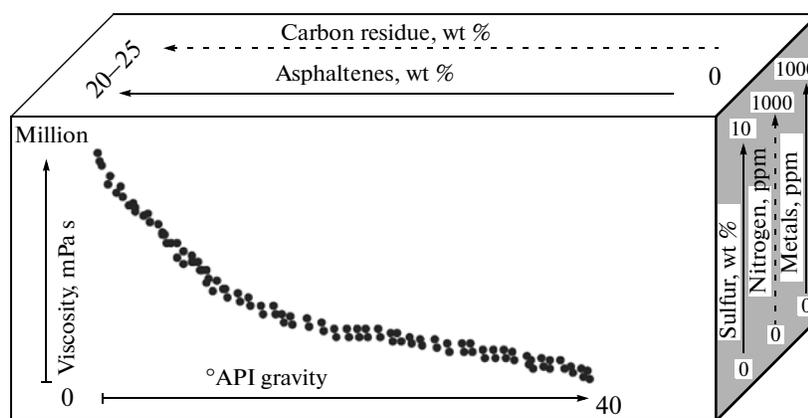


Fig. 1. Trend in the change of the average concentrations of some components and oil properties with increasing density [3].

In particular, about 8% of the world production of vanadium is from petroleum feedstock; in some countries, this percentage is as high as 20% (the United States) [14].

Thus, as the gravity of petroleum feedstock increases, a greater attention is focused on the problems of its demetallization for the purpose of increasing the efficiency and reducing the cost of oil refining on one hand and producing the metal concentrate as a commercial or intermediate product on the other hand. As a consequence, it becomes necessary to optimize the conventional processes of pretreatment and processing of heavy oils and heavy oil residues (HOR) to produce concentrates with a commercial concentration of particular rare metals (depending on their content in the virgin crude oil) without deterioration of the economics of production of target petrochemicals [13–15]. The choice of a sustainable technology for the processing of oils and oil residues is a quite complicated task. Its solution depends on the feedstock composition and properties, the range of required oil products, availability of the technology, availability of the relevant equipment, performance of industrial catalysts, use of recycled materials, and so on [11]. The possibility of large-scale extraction of metals from crude oil, inter alia, could be an impetus for the development of more efficient and cost-effective technologies for the production of rare metals.

The general line in the development of petroleum feedstock demetallization processes is the concentration of metals in the residues using known oil refining processes, in particular, the secondary noncatalytic thermdestructive and solvent–adsorption processes and/or catalytic cracking and hydroconversion processes. After obtaining the high-conversion oil refining residues enriched in metals or solid contacts (catalysts and adsorbents) with the metals deposited on them, special methods of metal recovery are used. At the same time, crude oil can be partially demetallized during its conditioning for transportation and refining.

In this paper, we survey the most widespread and promising processes of conditioning and processing of heavy oils and oil residues that involve their demetallization and the production of a metal concentrate.

DEMETALLIZATION IN OIL CONDITIONING PROCESSES

Crude oils are partially demetallized during their preparation for transportation in oilfield conditioning plants and, subsequently, in electrostatic desalters (EDS) at refineries [16–36].

In oil conditioning processes, alkali and alkaline earth metals and some acidic substances (fatty acids, naphthenic acids, and acid resins) pass into wastewater, as well as vanadium, arsenic, and nickel compounds, which are partially concentrated on the surface of water globules. The on-site conditioned crude oil is further subjected to secondary, more thorough treatment at a refinery to have a salinity of less than 5 mg/L and a water content less than 0.1 wt %. When the amount of chlorides is reduced down to 5 mg/L, metals, such as iron, calcium, magnesium, and sodium, and arsenic compounds are almost completely removed from the oil and the vanadium content is reduced by more than a factor of 2, a quality that is extremely important for jet and gas-turbine fuels, petroleum coke, and other petroleum products. Even more exhaustive desalination of oil to a chloride content of less than 1 mg/L is practiced at US refineries since the 1960s, thereby ensuring the continuous operation of crude oil distillation units for two or more years [16, 17].

If crude oil contains a large amount of organic acids, an alkali solution is added to the oil, usually in an amount of 1–5 ppm (to maintain the pH at 5.5–7.0) in the last stage of the desalter or after it. It was reported [18] that the desalting of Venezuela crude oil by treating with an aqueous NaOH solution followed by dehydration removed significant amounts of many trace elements, including the metals sodium, nickel,

and manganese (to 55 wt %). However, the desalted crude oil in this case contains almost unchanged amounts of vanadium, aluminum, and calcium. These results can be associated with the composition of the virgin crude oil from a particular area of its origin and the mode of the desalting process using a chemical reagent.

The increase in production of heavy high-viscosity oils (HVO) and natural bitumens (NB), which are an alternative source for production of valuable metals, brought about new dehydration and desalination problems due to their physical and rheological properties [19]. To dehydrate and desalt high-viscosity crude oil or natural bitumen extracted using special techniques, before sending to EDS the light solvent kerosene is often added to them in an amount of 10–15%, which significantly reduces the density and viscosity of the mixture and, being a nonelectrolyte emulsifier, dissolves a part of the solvation shells in water globules. In this case, the properties of the emulsion approach the properties of ordinary crude oil and water separation becomes possible in two to three steps according to the conventional electrostatic desalter flow diagram. A pilot ultraviscous oil conditioning plant (UPSVN) based on this technology in the Ashal'chinskoe oilfield of Tatarstan is described in a number of papers [17, 20–22]. To date, produced Ashal'chinskoe heavy, high-viscosity oil is being conditioned to group 3 quality in the UPSVN with a design capacity of 50 000 ton/year. Upon reaching commercial production volumes of high-viscosity oil, it is planned to build a UPSVN of a 1.0 million ton/year capacity.

However, deep demetallization of oils in conventional electric desalting plants is usually impossible because transition metals form rather stable organometallic compounds with hydrocarbon and heteroatomic petroleum components. Thus, research and development works on various modifications of desalination processes aimed to increase the recovery of metals [23–38] are of great current importance.

For example, a process for selective extraction of metals, sulfur, and other elements by means of radiofrequency thin-film electrolysis of crude oil in a flow electrolyzer reactor was proposed in [23]. Implementation of this technology reduces to the passing of oil to be cleaned through electrolysis cells. By changing the electrolysis conditions and current density, it becomes possible to successively recover contaminants (metals and nonmetals, sulfur inclusive) present in petroleum or petroleum products. The special feature of the electrolyzer is the design of the cells, which ensures a minimal hydrodynamic drag at a high ratio of the electrode surface to the treated volume, which intensifies the process and increases its energy efficiency. The impurities, including metals as well, accumulate in the receiver fluid, which is not consumed. The impurities are isolated from the receiver process fluid by mechanical filtration. The recovery of the impurities (vanadium, nickel, cobalt, molybdenum,

and sulfur, and other compounds) can be as high as 99%.

A number of oil demetallization processes using electrolyte systems was proposed [24–31]. Obratsov and Orlov [28] patented quite an effective process for demetallization and desulfurization of crude oil in a flow system, which provides implementation of the reagent-free electrochemical technology with regard to environmental requirements. According to this process, crude oil is electrochemically treated in flow using asymmetric alternating current. The products obtained as a result of demetallization, desulfurization, and recovery of the desired valuable components can be used as feedstock for industrial production purposes. Kremer et al. [29] disclosed a method for transferring metals and/or amines from the hydrocarbon phase to the aqueous phase in refinery desalting processes by introducing an additive of a certain composition into the hydrocarbon–water emulsion. This method makes it possible to transfer the majority of metals from the crude oil to the aqueous phase during the desalting process. Wu et al. [31] described a technique for crude oil demetallization using an electric desalting device [31]. In dewatering–desalting processes, a demetallization agent is fed together with an emulsifier and fresh water. The oil feedstock is further treated in an electric field with the use of special electric desalting cylinders, whereupon the next step of this demetallization procedure is carried out. The efficiency of isolation of metals such as calcium, iron, and manganese from the high-viscosity oil can approach 100% under certain process conditions. The main factors that affect the demetallization efficiency are the viscosity of the crude oil, the type and dosage of the demetallization agent, and the acidity of its aqueous solution. Reduction in the viscosity of the oil sample has a favorable effect on its mixing with demetallization agents and their interaction with metal ions formed during dissociation of metal salts, such as carboxylates and phenolates [31].

Problems of recovery of associated precious, nonferrous, and rare metals from petroleum feeds can be solved by introducing sorption on polymeric sorbents into oil conditioning (dehydration and desalting) processes [32, 33]. The method of extraction of metals is based on the results of studies of the sorption capacity of novel domestic redox ion exchangers for metal ions. According to the scheme proposed by the cited authors, the crude oil desalting and dehydration step before atmospheric–vacuum distillation of the oil is followed by the metal recovery step comprised of adding a polymer, forming a metal complex, and isolating the metals (to have the finished metal product and the polymer at the output). Using this scheme, it is possible to recover metals (zinc, copper, cobalt, nickel, vanadium, etc.) from petroleum or petroleum products at the conditioning and refining steps, thereby improving the quality of the petroleum products.

Samedova et al. [34–36] showed the feasibility of desalting, dewatering, deasphalting, and demetallizing of crude oils and their heavy residues using supercritical carbon dioxide (SC-CO₂) as a solvent (extracting agent). A new oil cleaning technology to remove water, salts, solids, and metals using SC-CO₂ was implemented on a pilot unit at the pilot plant of the Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan. This technology allows not only for the removal of water, dissolved salts, and suspended solids from oil, but also its deasphalting and demetallization. Supercritical fluid extraction of oil samples results in their dehydration (to 0.5% or even complete absence of water), desalting (from 40.5–54.9 mg of NaCl/L to zero level), and reduction in the solids content from 0.0348–0.0704 to 0.0102–0.0169% [35]. Simultaneously, the physicochemical properties of oils are altered, namely, the density and kinematic viscosity of the samples are decreased by the extraction. In the oil cleaning process for the removal of water, dissolved salts, and suspended solids, asphaltene and in part resins in which metals are concentrated are precipitated. Preliminary technoeconomic calculations showed that the energy demands of the process of oil extraction under supercritical CO₂ conditions are well below those of the currently used processes. The economic effect of the processing of 6.0 million tons of oil could reach \$25 million per year [36].

A unique method for concentrating metals from crude oil, based on the use of rotating spiral columns (RSC), which make it possible to implement the multistage liquid–liquid extraction process, was proposed in [37, 38]. One (stationary) phase is held in the RSC free of a solid support or sorbent medium, by the action of the field of mass forces emerging during column spinning and simultaneous rotation about the central axis of a planet centrifuge, while the other (mobile) phase is continuously pumped through the column. Due to the special design features of the rotating spiral columns, the method can be used to extract inorganic trace elements (including metals) from petroleum systems into the stationary aqueous phase. The composition of the aqueous phase is determined by the range of tasks to be resolved and depends on the values of the partition coefficients of the components of interest. The recoveries of valuable metals, such as zinc, manganese, iron, nickel, copper, cadmium, lead, and barium, are quite high, ranging within 75–95%.

Thus, partial demetallization of petroleum feedstock can be accomplished in the conditioning steps, typically, by removing the metal ions formed via dissociation of the corresponding salts of organic and inorganic acids. Application of the above-described methods of enhancement of the efficiency of metal recovery from oils makes it possible to concentrate the metals in the receiver fluid, metal complexes, resin–asphaltene substances, or the aqueous phase, from which they can

be further isolated in the direct way. However, the oil preparation step using either the conventional technology or the newly proposed processes generally does not suggest the recovery of metals as a final or intermediate product at present.

DEMETALLIZATION IN OIL REFINING PROCESSES

Depending on the quality of crude oil and its refining purposes, there are two basic ways of tackling the problem of demetallization of petroleum feedstock [13].

The first line is aimed at the realization of separate processing of commercially metal-bearing oils. It implies the use of geographically combined producing and refining process flow diagram in the development of heavy oil reserves. It should be noted that in most cases, the separate processing of metal-bearing heavy oils using special refining technologies that suggest the commercial production of petroleum vanadium and other metals is impossible in practice without special solutions on transport logistics, since heavy oil is necessarily mixed with light oil for technological reasons. This leads to a decrease in the concentration of valuable metals in the crude oil arriving at a refinery.

The scheme of separate refining of commercially metal-bearing oils was in part implemented in Canada in the extraction of Alberta heavy bituminous oils. Its principle is that the oil produced in the oilfield is preliminarily processed (upgraded) in situ in the so-called bitumen plants into synthetic and/or semisynthetic oil to reduce the density and viscosity and produce hydrocarbon mixtures that meet the pipeline transportation requirements. Plants for the processing of heavy crude into synthetic oil are often based on a combination of conventional refinery processes for upgrading of oil residues. The processing of vacuum residue, which can make more than 50 wt % of natural bitumen, to obtain lighter hydrocarbon fractions on site makes it possible to abandon the use or reduce the consumption of the expensive solvent and resolve the problem of lack of facilities for high-conversion oil refining at existing refineries [3, 39]. The quality of the products obtained in this case and, correspondingly, their price are substantially higher than those of the extracted raw material, and the vanadium-containing concentrate isolated as a byproduct can be used for the production of vanadium.

The second line suggests the use of technologies for the recovery of metals from refinery feedstocks that contain valuable metals in concentrations below current commercial levels.

For each of the lines in the development of petroleum vanadium reserves, its own value for the minimal commercial concentrations of vanadium in crude oil should be established. In the former case, the commercial V content will greatly depend on the conditions of a particular oilfield and the minimally com-

mercially viable concentration of V in the source oil will be determined by its technologically achievable content in the vanadium concentrate at which the transportation of the concentrate from the oilfield to the site of further processing will be economically viable. The lower limit of this estimate according to expert appraisal will be 30 ppm (V_2O_5). In the latter case, the minimal commercial concentration of V in crude oil arriving at a refinery will be determined by its technologically achievable content in the concentrate at which its further processing is profitable. If the V_2O_5 content in the byproduct obtained at the refinery is at least 1.0 wt %, the product will definitely be an economic raw material, since its V content is much higher than that in commercial ores. Regarding the technologically achievable concentration factor of 800–900, the minimal commercially significant vanadium content in refinery crude oils is about 12 ppm (V_2O_5) according to preliminary estimates [13].

The industrial oil processing at modern refineries involves complex, multistage physical and chemical processes on separate or combined high-production-volume facilities (plants, shops) intended for producing different components or market mix of products [16, 40–49].

Heavy petroleum feedstock with a high metal content can be upgraded in catalytic and noncatalytic cracking or solvent–adsorption processes. More than half (~57%) of heavy oil residues (HOR) in the world is being processed using noncatalytic destructive processes now, of which visbreaking, coking, and gasification are the most widespread. The thermal degradation processes primarily comprise the decomposition (cracking) reactions of feedstock molecules and cyclization and condensation reactions yielding high-molecular-mass condensation products.

Due to the increase in demand for high-quality motor fuels and their price, tightening the environmental standards, and the decrease in demand for boiler fuel oil, progressively increasing attention is given to the catalytic destructive processes, in particular, catalytic cracking and hydrocracking, whose proportion in HOR upgrading processes is about 27% and steady increases [4, 42].

In solvent–adsorption HOR upgrading processes, the components containing the majority of particular trace elements are nondestructively isolated into a separate phase. The most widespread among nondestructive HOR upgrading and refining processes is the solvent deasphalting (SDA) process, by which resin–asphaltene substances and organometallic compounds impairing to a large extent the feedstock stability and quality are separated using a light hydrocarbon solvent.

A special place is occupied by processes in which the chemical bonds of metals with the organic matrix of petroleum components are destroyed or altered by means of various physical and mechanical methods. These processes include some unconventional tech-

niques of metal recovery, in particular, methods based on the use of magnetic or electrical field, ionizing radiation, etc.

The decision on the choice of appropriate technology for upgrading or processing of heavy petroleum feedstock is a challenge. One of the main factors determining the operational and capital costs and the yield and quality of the final product is the feedstock composition and, above all, the content of undesirable components such as polyaromatic hydrocarbons, hetero atoms, and metals. An increase in the carbon residue and concentration of heavy metals in the HPF increases the rate of formation of solid deposits and catalyst deactivation during its processing, thereby leading to an increase in catalyst consumption and operating costs and impeding the feedstock conversion. However, the applicability of catalytic processes to the refining of heavy and extraheavy petroleum feedstock is directly related to their instrumental implementation and the composition and properties of the catalysts used. Although the processing of heavy petroleum feedstock with a carbon residue above 10 wt % and a metal content of more than 30 ppm by fluid catalytic cracking (FCC) is in general uneconomic, new catalyst systems developed to date and the engineering and technical solutions proposed for hydrotreating make it possible to organize the effective processing of feedstock with an API gravity less than 10 and a metal concentration over 700 ppm. In turn, heavy petroleum feedstock of almost any composition with very high metal and asphaltene contents can be upgraded using noncatalytic thermal processes. However, efficient disposal of the low-grade solid residue, whose yield increases with an increase in the feedstock carbon residue [4] (Fig. 2), should be taken care about in this case.

As a result of secondary oil refining processes, the metals for the most part appear in the residual products, such as asphalt, coke, and cracked residue, or (in the case of catalytic and adsorption processes) are deposited on the surface of adsorbents and catalysts, leading to irreversible deactivation of the latter [5].

The information presented in [5] on the basic processes for upgrading of heavy oil residues as applied to the removal of metals from their composition is complemented by other data in this paper and summarized in Table 1. None of the currently used processes for upgrading of HOR with a high metal content is absolutely preferable, since these processes are closely tied to the feedstock composition and particular conditions, primarily, economic aspects. Thus, the overview given below considers particular data for each of the lines in demetallization of petroleum residues. As regards adsorptive demetallization, it is usually carried out in thermofor or catalytic processes and, therefore, will be considered in the relevant sections of this paper.

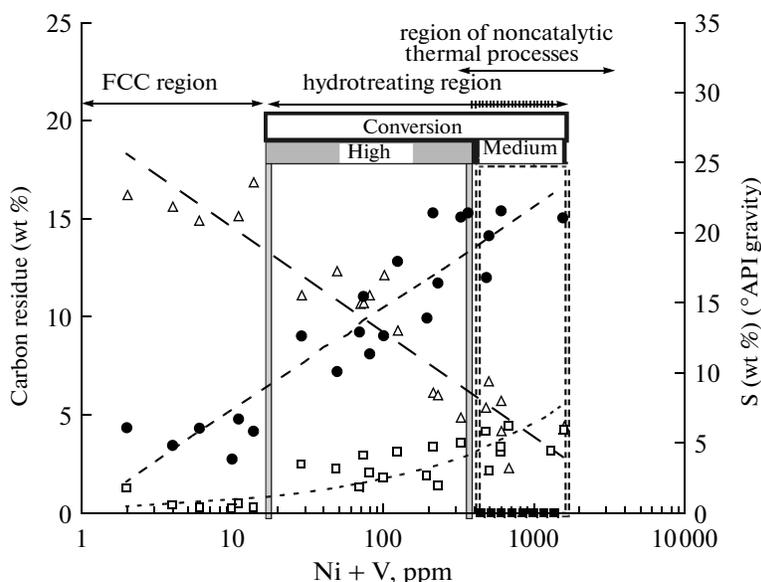


Fig. 2. General approach to the choice of HPF upgrading technology depending on the composition and properties of atmospheric residue (FCC fluid catalytic cracking: (□) sulfur content, (●) carbon residue, and (△) API gravity [4].

SOLVENT DEASPHALTING

Among extraction technologies that result in feedstock demetallization, solvent deasphalting (SDA) processes have found the widest use in the refining practice. They are based on the extraction of paraffinic and naphthenic components of HOR with light alkanes accompanied by coagulation and precipitation of high-molecular-mass polycyclic asphaltenic and resinous compounds in which the major amounts of heavy metals and hetero atoms of the starting petroleum feedstock are incorporated. An increase in the molecular weight of the solvent enhances the solvent power and increases the yield of deasphalted oil (DAO), but it simultaneously results in deterioration of the quality of the extract and a reduction in the degree of feedstock demetallization [16, 49, 50, 51]. For example, an increase in the yield of DAO from 66 to 90 wt % during SDA of Athabasca bitumens using *n*-pentane as the main solvent led to a decrease in the degree of removal of nickel and vanadium from ~90 to 47% [51]. One of the possible ways of resolving this problem is adding an appropriate modifier to the non-polar hydrocarbon solvent so as to change its solvent power and selectivity. For example, the addition of acetone to *n*-pentane to the level of its concentration of 20 mol % makes it possible to increase the yield of DAO by 4% with an insignificant change in selectivity for nickel and vanadium [51].

A promising direction in the solvent extraction methods for the recovery of desired components is the use of supercritical fluid extraction (SFE). Under supercritical conditions, solvents have specific properties that distinguish them from both gases and liquids. Supercritical fluids (SCF) have a density close to that

of liquids and the viscosity close to that of gases; thus, the diffusion coefficients in SCF are significantly higher than those in the conventional liquids.

The solvent power of supercritical fluids almost exponentially depends on the density, and small pressure changes can significantly change the solubility of the components in the SCF. This opens an opportunity to finely control solubility and selectivity and easily isolate and separate the components of interest [52, 53].

Modern SDA technologies, such as the Demex (UOP), ROSE—Residuum Oil Supercritical Extraction—(Kellogg Brown & Root), and Solvahl (Axens) processes, include the step of solvent regeneration under supercritical conditions. This can significantly reduce capital and operating costs for the implementation of the process [54–57]. Commercial ROSE units demonstrate cost reduction of up to 50% compared with the conventional SDA processes, which use evaporation, compression, and condensation of the solvent at its regeneration and recycle stages. Since there is no need to vaporize the most of the solvent from the extract solution, the size and complexity of the unit are reduced [55]. Depending on the purpose, the yield and composition of the deasphalted oil and asphalt in the aforementioned processes can be controlled by varying the composition and properties of the solvent and process conditions. It is noteworthy that along with a decrease in the degree of demetallization with increasing DAO yield, concentration of HPF metals in the residue (asphalt) increases. For example, in the Demex process intended for demetallization of HOR, an increase from 56 to 78 vol % in the yield of the demetallized residue from vacuum tower bottoms having a metal content of 98 ppm leads to a

Table 1. Comparative characteristics of the basic processes of destructive and nondestructive processing of heavy oil residues that result in their demetallization

Removal process	Extraction	Adsorption	Catalytic	Hydrogenation	Thermal	Combined
Principle of metal recovery	Recovery of metals in the composition of resin—asphaltene compounds separated from petroleum feedstock using coagulants	Recovery of metals from petroleum feedstock using adsorbents supplemented by thermal treatment	Destruction of metal compounds in the presence of a destructive catalyst and metal deposition on the catalyst	Destruction of metal-containing compounds by hydrogenation in the presence of catalyst	Thermal destruction of metal-containing compounds and concentration of metals in thermolysis residues and coke and on the surface of solid heat carrier	Destruction of metal-containing compounds by noncatalytic hydrotreating
Process name	Solvent deasphalting	Adsorption treatment; solvent treatment; adsorption and catalytic cleaning	Catalytic cracking	Hydrotreating; hydrocracking	Visbreaking; thermal cracking; delayed coking; fluid coking or flexicoking	Hydrovisbreaking; hydrocoking; hydrolysis; donor solvent cracking
Conversion of feed with to IBP > 350°C, wt %	0–50 (yield of deasphalted oil)	0–50	Up to 80	Up to 95*	5–75	20–90
Metal recovery, %	70–80	80–95	80–96	60–98	70–80	60–80
Kind of resulting metal concentrate	Asphalt	Metal-rich adsorbent	Metal-rich spent catalyst	Metal-rich spent heterogeneous catalyst, high-boiling-point fractions, and coke	Cracked residue, metal-rich coke, solid heat carrier	Heavy residue of process

* Degree of conversion of feedstock boiling above 550°C.

change in the concentration of metals in the material from 6 to 19 ppm and a simultaneous increase in their content from 201 to 341 ppm in the separated asphalt [54].

Among the emerging upgrading technologies based on supercritical fluid extraction, the SELEX-Asp (selective asphaltene extraction) process designed to remove undesirable components from natural bitumen should be mentioned [58]. The principle of supercritical fluid extraction of petroleum feedstock is based on a combination of nonsolvent with multicomponent phase equilibrium. The SELEX-Asp process makes it possible to selectively remove solid asphaltene particles from heavy oils and oil residues and extract valuable hydrocarbon components. In the case of deasphalting of vacuum tower bottoms having a Conradson carbon residue of 19 wt % and a metal content of 242 ppm, 21.55 wt % asphaltene residue with a Conradson carbon of 47% and a metal content of 1000 ppm is separated as a result of the process, which make 56 and 90% of the carbon residue and metal content, respectively, of the source vacuum bottoms. Solvent consumption in this process is lower by 20% than that in the ROSE process. However, since the extraction unit operates under the supercritical conditions for the solvent, the pressure in the SELEX-Asp process substantially exceeds that in the ROSE process and, as such, may lead to an increase in operating costs [3].

Along with the use of organic compounds as a solvent or extractant, considerable attention begins to be paid to inorganic substances that have a simple structure and are readily available in the supercritical state. Supercritical water is an effective demetallization agent, a source of hydrogen, and a catalyst for hydrogenation and decomposition of vanadium and nickel porphyrins and is capable to remove up to 80% of the metals from the complexes and extract them into the inorganic phase [59, 60].

The most attractive of supercritical fluids is carbon dioxide (SC-CO₂), which is nonflammable, nontoxic, cheap, and readily available. Owing to high volatility, the solvent is easy to recover from the extract solution simply by pressure release. Supercritical CO₂ is an effective solvent for deasphalting and demetallizing of heavy petroleum feedstock, which makes it possible to reduce the solvent/feedstock ratio and the solvent regeneration cost, increase the yield of deasphalted oil, and ensure a high degree of removal of asphaltenes and metals from DAO, thereby eliminating the disadvantages of the existing SDA processes that use light hydrocarbon solvents [34]. The polarity, dissolving power, and selectivity of SC-CO₂ towards certain groups of feedstock compounds can be controlled by adding small amounts of modifiers to the solvent [61]. The use of suitable complexing and chelating agents as SC-CO₂ modifiers is quite effective for extraction of metal ions from solid matrices, such as furnace and gasifier fly ashes, and can hold promise for the recov-

ery of valuable components from heavy petroleum feedstock [62, 63].

It should be noted that there are numerous methods for isolating metals from HOR using various acids, alkalis, salts, and hetero compounds as solvents and reagents that have not yet received practical application [64]. Despite the fact that these methods are capable to extract metals, such as V and Ni, with an efficiency greater than 97%, their major disadvantage is often incapability or limited capability to precipitate asphaltenes, which requires to conduct further feedstock preparation processes for reducing its density and carbon residue and removing hetero atoms [51].

THERMAL PROCESSES FOR UPGRADING HEAVY PETROLEUM FEEDSTOCK

The most common thermal destructive processes for upgrading heavy oil residues are thermal cracking, visbreaking, delayed coking, thermoform catalytic cracking, and flexicoking. Being run at relatively high temperatures, all these processes lead to the formation of gaseous products, liquid hydrocarbons with low and medium molecular weights, heavy aromatic bottoms, and a carbonized solid residue in the case of coking and thermoform cracking [16, 46, 49]. Metals, including V, are concentrated in a small volume of this carbon residue (cracked residue, pitch, coke) and their concentration is substantially higher than that in the oil. The increase in the yield of liquid products and the decrease in the yield of the resulting residue of the thermdestructive process are accompanied by a rapid increase in the concentration of metals in the residue.

Thermal Cracking/Visbreaking

Thermal cracking is largely used at present as a process for thermal preparation of distillate feedstocks to coker units and production of thermally cracked gas oil at an elevated pressure (2–4 MPa) and a temperature of 500–540°C. As applied to heavy petroleum residues, only a version of this process known as visbreaking has remained to be of industrial importance in modern oil refining; this is a mild cracking process with a limited degree of thermolysis conducted at 1–5 MPa, 430–500°C, and a residence time of 2–25 min with the purpose of reducing the viscosity of fuel oil without regard for demetallization of the residue [16, 41].

Conventional visbreaking feedstock is vacuum tower bottoms, but heavy oil, fuel oil, and asphalt can also be processed in this way [40, 42]. Most commercial units operate in the residue conversion range of 20 to 30%; their basic limitation is a decline in stability of the product with an increase in feedstock conversion, which is associated with the deposition of asphaltenes and coke and the formation of olefins, whose subsequent secondary transformations can result in the formation of tar and hardly recyclable residues [3, 16,

49]. In the case of the use of visbreaking for upgrading heavy petroleum feedstock, the purpose of the process is to obtain a maximal yield of distillate fractions, which are then mixed to form synthetic oil. In this case, V and Ni, which largely concentrate in the high-boiling-point fractions and are bound to nitrogen in porphyrin and nonporphyrin structures remain in the residue of the thermal process, as well as relatively small amounts of sodium and iron [4].

The world's leading licensors of various embodiments of the process are considered to be Shell, whose technologies were used to build more than 70% of world HPF visbreaking capacity over the past 10 years, and Foster Wheeler and UOP, companies that designed more than 50 visbreaking units [65, 66]. The refineries in Pavlodar, Burgas, Mazeikiiai, and Omsk use the units designed by the Grozny Research Institute, and a number of other refineries employ the units designed by the Institute of Petroleum Refining and Petroleum Chemistry of the Republic of Bashkortostan.

Coking

Currently, coking becomes one of the most common processes for refining and upgrading HOR with a high metal content. Meant by coking is the process of thermal treatment of heavy oil residues at a low pressure (up to 0.2–0.3 MPa) for the production of distillates, which are feedstock for the manufacturing of motor fuel components and petroleum coke [46]. Unlike thermal cracking, coking is conducted under severe conditions (high temperatures of 430–560°C and residence times as long as several hours) with a high degree of feedstock conversion. Cokers can process various oil residues, straight-run vacuum tower bottoms, cracker resid, deasphalting asphalts from lube oil manufacturing units, pyrolysis pitch, etc. Abroad, heavy crude oil, shale oil, natural bitumen from Athabasca oil sands, and coal tar pitch are also used [16, 40, 41, 44, 45]. The process yields lighter valuable products, such as gas, naphtha, light and heavy gas oils, and solid residue (petroleum coke). Typically, the yield of coke increases with an increase in the carbon residue of the coking feedstock and its quality and properties depend on the sulfur, metal, and asphaltene contents and feedstock aromaticity [3, 4, 16, 49].

As a result of the process, metals of the petroleum feedstock almost completely concentrate in the petroleum coke [3]. Coker economy is determined to a considerable extent by the ratio and the cost of derived fuel fractions and high-sulfur solid residue of the process. The main drawbacks of the process in the case of HPF refining and upgrading are the formation of low-grade coke, a reduced yield of liquid distillate products, and limitations due to emissions of sulfur dioxide produced by burning coke. All of the resulting liquid fractions contain substantial amounts of unsaturated com-

pounds and require further catalytic hydrotreating to obtain components of commercial petroleum products [49].

Classification of the existing coking technology is based on modes of supplying the feedstock to the reaction zone and unloading the solid product. Regarding these modes, two different types of organization of the process have found commercial use to date: semibatch or delayed coking with continuous feed and periodic discharge of the coke in unheated coking chambers and fluid coking in a fluidized bed of coke as a heat carrier.

Delayed coking processes have become the most widespread, making it possible to obtain up to 40% coke depending on the composition of the petroleum feedstock. The degree of demetallization in the delayed coking process can reach 95–98% [5]. CB & I Lummus and Foster Wheeler (SYDEC (Selective Yield Delayed Coking) process), leaders in the field of efficient delayed coking technologies designed to achieve maximum yield of distillate fractions, commissioned more than 60 and 50 units, respectively [65, 66].

Among thermal demetallization processes, the Eureka process in which the thermolysis reactions also proceed in a system of two reactors operating alternately is interesting. This process is much similar to thermal cracking and visbreaking in conditions, although it differs in reduced temperature (360–420°C) and pressure (0.1–0.5 MPa), and to delayed coking in duration (0.5–10 h) and instrumental implementation. Thermal cracking reactions in the process occur in the presence of superheated steam, which is injected into the bottom of the reactor and regulates the temperature of the process, stirs the reaction mixture, and strips distillate cracking products. In such a reactor with direct contact of the feedstock with the heat carrier, the cracked products are rapidly removed from the reaction zone, thereby preventing the formation of coke. Owing to the development of polycondensation reactions, uncrackable hydrocarbons appear as petroleum pitch, which is liquid under the reactor conditions (softening point 130°C or higher). The Eureka process can result in concentration of almost the whole amount of feedstock metals in petroleum pitch, the residue of the process. The processing of vacuum residue with a metal (Ni + V) content of 338 ppm makes it possible to increase their total concentration in the resulting pitch to 1175 ppm, wherein the yield of the pitch is about 30% of the mass of the vacuum residue fed [5, 11, 13, 40, 49].

Fluid Coking or Thermoform Catalytic Cracking (TCC)

Rapid development of this process in recent years has made it possible to process the heaviest feedstock and provide a coke yield of 10 to 25 wt %. In turn, the use of gasification of the resulting coke powder led to creation of a combined flexicoking process. Fluid cok-

ing is carried out at higher temperatures (510–560°C) and shorter residence times (several minutes) compared to delayed coking, thus increasing the yield of liquid products and reducing the coke yield. Flexicoking is a modification of the fluid coking process and uses a coker reactor of the same design, except that it includes an additional gasification section in which excess coke reacts with steam and oxygen to be converted into a low-calorific-value fuel gas. The units designed are capable of gasifying 60 to 97% of the coke produced [4, 5, 7, 11, 13, 18, 40, 43, 46, 49, 67, 68]. The fluid coking and flexicoking processes were designed by Exxon Mobil Research & Engineering. Eight fluid coking plants operate since 1954 with a total capacity of 375000 barrels/day, whereas only five flexicoking units were built (with a capacity 179000 barrels/day) because of the necessity to use one more reactor and a high capital cost of its implementation [42].

Thermofor catalytic cracking is at present one of the key processes for territorial and technological combination of producing and refining heavy petroleum feedstock with recovering useful associated components. Upgrading of heavy oil residues in TCC processes makes it possible to increase feedstock conversion and achieve a high yield of distillate fractions (synthetic oil), and, unlike delayed coking, perform cracking in the continuous mode with a lower coke yield. Since almost all vanadium occurs in the fraction with a boiling point of >500°C, heavier residues are sequentially enriched in vanadium during processing to have a maximum of its concentration in the coke [7, 68]. An increase in the “severity” of the TCC process and a decrease in the yield of coke from the petroleum feedstock results in a maximum enrichment of coke in vanadium and other metals [13, 69].

The fluid coking process has been intensively developed in recent years, and various HPF upgrading technologies have been designed on its basis, which differ in instrumental implementation, heat transfer conditions, and the type of solid heat carrier. Among these new developments, the HTL (Heavy-to-Light) process intended for upgrading HPF to lighter synthetic oil of better quality that meets the requirements of pipeline transportation should be noted. The heat carrier in the HTL process is a moving, circulating bed of hot sand. Feedstock asphaltene is deposited on the contact surface to form a thin film covering the sand particles, thereby resulting in their high conversion. Because of a very short residence time of the slurry in the reactor, which does not exceed 2 s, a high yield of lighter liquid products and minimal gas and coke formation are achieved. The process was designed and patented by Ivanhoe Energy and is characterized by compactness and lower operating costs compared to conventional upgrading processes [70, 71]. As a result of the process, the API gravity of the upgraded product obtained from Athabasca natural bitumen decreases from 8.5 to 18.8; the vacuum resi-

due content, from 52 to 6 wt %; the V content, from 209 to 27 ppm; and the nickel content, from 79 to 15 ppm.

Viscositor, a similar thermal cracking process in a fluidized-bed reactor, was developed by the Norwegian company Ellycrack AS for the on-site refining of heavy oil [72]. In the Viscositor process, HPF is sprayed with superheated steam and cracked by contacting with heated fine sand particles in the cavity of the reactor in which a high linear velocity of the upward flow is achieved. The solid particles heated in a regenerator by fluidized-bed combustion of coke are driven to the reactor by means of pneumatic conveying with hot flue gases. The process occurs at low temperatures due to the low partial pressure of the feedstock, is autothermal, and requires neither the heat produced by burning the coke formed nor the presence of a catalyst, instead of which finely grained minerals act as a heat carrier. Thus, the metal content in the upgraded product is reduced by 90%.

A unique version of thermofor cracking was developed by ETX Systems. The technology is based on the thermal cracking of HPF in contact with hot solid particles fluidized by transverse gas flow and moved through the reactor by gravity. Entering the reactor, a heavy residue undergoes conversion to give liquid products, coke, and gas by heat transfer from the bed of solid particles. The coke is deposited on the surface of solid particles, while the fluidizing gas and other products of the process are withdrawn from the top of the reactor. The process is carried out under less severe conditions at relatively low temperatures, increasing the yield of liquid products, which is higher by 9% than the yield of hydrocarbons in the case of Athabasca bitumen processing in a delayed coker [73].

Thus, the thermal processes are quite effective for demetallization of heavy oil residues and metal concentration in the product coke (pitch) or on the surface of solid heat carrier particles from which the metals can be further recovered.

The known methods for the recovery of metals from petroleum coke, ash, and other products are described in more detail in [18, 74, 75]. For example, vanadium pentoxide is produced on the commercial scale in Canada, the United States, and Venezuela from the ash of TCC coke of Venezuelan oils and Athabasca bitumens using hydrometallurgical processes [44, 68], based on the conversion of ash and coke metals into water- or acid-soluble compounds and the subsequent selective precipitation of V and Ni. For materials with a high metal content, the use of autoclaved equipment and hydrothermal media is justified. A promising method is the recovery of metals from petroleum coke by reacting with chemical oxidants.

By 1988, eight units for V recovery from petroleum coke operated in Canada, Venezuela, and the United States, where the heavy viscous oil and natural bitumen processing technologies and are most developed

[19, 76]. In the ash produced by coke gasification, the vanadium content can be as high as 23000 ppm. The total output of V_2O_5 derived from petroleum feedstock in the Canadian units reaches 1660 ton/year, which is several times higher than the country's demand for this valuable metal.

GASIFICATION

Gasification today is an important intermediate step in integrated heavy petroleum feedstock processing schemes that, on one hand, makes it possible to concentrate the valuable feedstock metals in the mineral residue from which they can be directly recovered and, on the other hand, convert its organic part into synthesis gas, which a good fuel for power generation or feedstock for a variety of petrochemical processes. The desired product of the gasification process is the synthesis gas, which is a mixture of the main components carbon monoxide and hydrogen with carbon dioxide and methane. The feedstock of the process can be various solid and liquid carbonaceous materials including deasphalted asphalt, petroleum coke, and crude oil tank bottoms. Gasification is achieved by the complete decomposition of the carbonaceous feedstock at high temperatures (above 1000°C) in the presence of oxygen (air) and steam.

The other products are soot and bottom ash (BA). The soot may contain a significant amount of V. At a plant throughput of 800000 ton/year, 320 t/y of vanadium can be obtained. Soot is subjected to controlled oxidation in a multiport furnace. The product is a V concentrate containing about 75% V_2O_5 [40]. The majority of rare and rare earth elements concentrate in bottom ash, which can be regarded as feedstock for producing commercial compounds of a variety of elements [7].

Almost all of the gasification projects implemented to date prefer entrained flow gasification reactors because of their flexibility; the possibility of processing different carbonaceous raw materials (liquid and solid); a high unit capacity; and, hence, economic attractiveness. The best-known technologies based on entrained flow gasification reactor were developed by Texaco (TGP process), Shell (SGP process), Siemens-Future Energy, Prenflo (Krupp-Uhde), and Conoco Phillips (E-Gas process) [77, 78]. About 140 SGP plants and 90 TGP plants operate over the world [79]. A promising approach to gasification of various carbon materials is the process in a molten metal (iron) placed in a melting-furnace crucible blown with an oxygen-rich gas [80].

Table 2 collates data on the performance characteristics of the thermal processing of residues of light Devonian oil, which illustrate differences in the metal concentration efficiency depending on the thermal treatment process used. The characteristics of the crude oil are as follows: density, 0.86 g/cm³;

sulfur content, 1.6%; vanadium, 56 ppm; and nickel, 21 ppm [13].

According to the data in the table, the heat treatment-produced distillate fractions that boil up at temperatures below 500°C are almost deprived of vanadium and nickel. The highest vanadium concentration of 0.1–1.0 wt % is achieved in the fluid cracking coke and in the flexicoking coke ash concentrate. Note that the concentration of vanadium in the fluid cracking coke is almost two times that in the delayed coking coke.

These data indicate that refinery flow charts including coking or flexicoking processes are the most preferable from the standpoint of effectiveness of the commercial development of petroleum vanadium resources. It is in this case that a maximum concentration of petroleum vanadium in coke ash residue, one of the associated refinery products, can be achieved. The concentration factor defined as the ratio of vanadium concentration in the associated product to its concentration in the feedstock can be as high as 150–200. Further enrichment of the coke ash concentrate in vanadium in specialized utility boilers equipped with facilities for capturing particulate matter from the flue gas will increase the concentration factor to 800–900 [13]. It should be noted that the concentrations of vanadium in the fluid cracking coke and the coke ash concentrate are higher than in traditionally used vanadium ores. Moreover, these values can be achieved even in the case of refining crude oil that contains vanadium in an amount below the commercial concentration.

CATALYTIC PROCESSES OF REFINING HEAVY PETROLEUM FEEDSTOCK

Catalytic Cracking

Isolation of metals from the heavy fractions of petroleum feedstock is feasible in the case of the fluid catalytic cracking (FCC) process. In this process, the degradation of metal compounds in the presence of an acid catalyst occurs and the metals are deposited on the catalyst. The FCC process is one of the most common technologies that provide a high refining efficiency and manufacture of the base component of high-octane gasoline, the kerosene component, and lower olefins (propylene and butylenes). Simultaneously, the spent catalyst can be a raw material for the recovery of heavy metals deposited from the feedstock. In this process, which traditionally uses heavy distillates (vacuum gas oils) as a feedstock, oil residues (atmospheric and vacuum tower bottoms) preferably in a mixture with the distillate feedstock are increasingly involved. Oil residue feeds in the FCC process are used as received or after preparation. The immediate cracking of heavy feeds is the simplest process from the engineering standpoint. However, the presence in

Table 2. Comparative characteristics of various processes of thermal upgrading of residues (vacuum tower bottoms) of light Devonian oil from the Romashkino field [13]

Parameter	Process				
	visbreaking	delayed coking	Eureka	TFC*	flexicoking
<i>Feed: vacuum residue</i>					
Yield on crude oil basis, wt %	28.5	26.9	26.9	28.5	28.5
Carbon residue, wt %	17.7	18.0	18.0	17.7	17.17
<i>Contents:</i>					
sulfur, wt %	3.1	3.2	3.2	3.1	3.1
vanadium, ppm	200.0	210.0	210.0	200.0	200.0
nickel, ppm	60.0	90.0	90.0	68.0	68.0
<i>Obtained, wt %</i>					
C ₅ –500°C fraction	54.0	60.5	71.2	65.4	65.4
Cracked residue, pitch, coke	44.0	30.0	24.1	16.0	2.0
<i>Content in C₅–500°C fraction:</i>					
vanadium, ppm	0.5	0.2	0.2	0.2	0.2
nickel, ppm	0.4	0.2	0.2	0.2	0.2
<i>Content in cracked residue, pitch, and coke:</i>					
sulfur, wt %	3.1	4.0	4.1	4.8	2.1
vanadium, ppm	431	666	871	1052	10000
nickel, ppm	156	297	371	365	3400

* TFC stands for thermofofor cracking.

the feed of metals that deactivate the catalyst leads to rapid coking, reduces the process selectivity, impairs the product quality, and increases catalyst consumption. Pretreatment of the residual feedstock improves the yield and quality of the products of catalytic cracking, but it significantly increases the cost of the process.

In Western Europe, Japan, and especially the United States, considerable experience of direct industrial processing of residual feedstocks on FCC units has been gained. In the United States, about 50% of FCC units process mixed feedstock containing a residual component, and 70 FCC units in Western Europe and the Middle East use 10 to 100% residues as feedstock [16, 40, 41, 43–46, 48, 81, 82].

The heavier the fractional composition of the cracking feedstock, the higher the vanadium and nickel content in it. The metal content of gas oil is up to 1 ppm, whereas that of fuel oil is 170 ppm. Accordingly, the amount of metals on the catalyst during the refining of such a feedstock can reach 10000–30000 ppm versus no more than 1000 ppm in gas oil processing. The metals adsorbed on the catalyst clog pores and block its active sites, resulting in catalyst deactivation, as well as accelerate the dehydrogenation reaction, thereby reducing the selectivity for the gasoline fraction and its quality. Along with a reduction in activity and selectivity, the formation of highly reactive metal oxides, such as vanadium pentoxide, contributes to the degradation of the crystal structure

of the zeolite catalyst during its regeneration [7, 68, 82–84]. Consequently, the immediate processing of heavy oil residues with carbon residue of more than 10 wt % and a metal content more than 30 ppm results in excessively high consumption of the catalyst and generally becomes uneconomical without pretreatment of the feedstock. For the cracking feed containing 50 ppm metals and a cat cracker capacity of about 2.7 million t/y, the amount of the fresh catalyst needed may reach 36 t/d (if metal content on the catalyst is 1 wt %) [46].

The development of affordable, highly active, and selective zeolite catalyst systems that are effective in cracking of high-molecular-weight hydrocarbon components of HPF and resistant to poisoning by heteroatomic and metal-containing compounds increases the practical applicability of FCC processes to HPF upgrading [85, 86]. The operation conditions of modern catalytic crackers for HPF processing are characterized by high temperature, high feed space velocities, and short contact times, which result in a decrease in the coke yield and increase in the yield of gasoline. To lower the temperature and partial vapor pressure of water during the combustion of large amounts of coke and to decrease the vanadic acid formation and zeolite dealumination rates, two-step regeneration and/or cooling of a microspherical catalyst with an external condenser are carried out in modern FCC units for oil residues. The most widely used FCC units for HPF processing have a UOP two-stage

regenerator or two Axens regenerators with separate air supply and flue gas withdrawal (R2R process) [46, 56, 57, 87].

To prevent catalyst poisoning with metals and recover them, preliminarily demetallization of the feedstock, continuous demetallization of a portion of the catalyst circulating in the system, and use of additives that passivate metal poisoning of the catalyst are practiced [40, 46, 81, 84, 85].

For example, Atlantic Richfield designed the Demet II process for the continuous recovery of metals deposited on a zeolite catalyst and, further, its new version Demet III, which is characterized by a simpler means of metal extraction from wastewater and a lower cost. The Demet III flow chart includes continuous withdrawal of 15% of the catalyst from the cracker and its treatment according to the following scheme: activating the metals deposited on the catalyst, chemical treatment of the catalyst, its washing with water to remove V and Ni, extracting the sludge from wastewater, and recycling water back into the system. The sludge isolated from the wastewater has a high concentration of metals and can be used to recover them [18, 68, 82].

Texaco patented a process for catalyst demetallization, in which vanadium and nickel are converted into volatile compounds and separated from a catalyst after special treatment of a portion (1/3) of the circulating catalyst. Less than 50% of vanadium and 60–40% of nickel are retained on the catalyst. The metals are removed as volatile chlorides and oxchlorides after treatment with chlorine. Gulf patented a process for demetallization of a zeolite catalyst by contacting with compounds of bismuth and manganese or oxides thereof [40].

Selective absorption of metal porphyrins directly during fluidized-bed catalytic cracking with separation of the catalyst for its subsequent regeneration and the recovery of the metals was proposed. Selective absorbers of metal porphyrins are alumina supported on activated sponge coke; magnesium salts; dolomite; sepiolite; carbonates; titanates; strontium, barium, or calcium zirconate in matrices consisting of 70–90% SiO₂ and 10–30% Al₂O₃; activated carbon; and aluminosilica gel [7, 68].

From the array of available data, it follows that feedstock for the catalytic cracking process should be only of relatively high quality, having a high H/C atomic ratio and a low metal content, to avoid the problems associated with a high coke yield and high catalyst consumption, which determine the profitability of the process. This is a major limitation on application of FCC units to refining heavy oil residues that makes it less attractive than hydrotreating.

It is noteworthy that a number of thermal adsorptive deasphalting (TAD) processes for preparing HOR to subsequent processing in FCC and hydrocracking units have been developed on the basis of the catalytic

cracking technology. Of the TAD processes, the ART (Asphalt Residual Treating) process is worth noting, in which a portion of the feedstock is vaporized and decarbonized and demetallized in fluidized bed. This resin–asphaltene portion of the feedstock is adsorbed on the catalyst sorbent with partial thermal degradation. Natural minerals, such as kaolin, bauxite, sepiolite, and manganese or iron ore are typically used as adsorbent catalysts for upgrading heavy oil fractions, which can be modified with vanadium, nickel, chromium, iron, or cobalt. The degree of removal of metals in TAD processes can reach 95%, and the concentration of vanadium and nickel on the sorbent can be as high 30000 ppm, so that the sorbents can be considered a source of recovery of valuable metals [46, 49].

Hydrogenation Processes

Demetallization of petroleum feedstock is also feasible in the course of hydrogenation refining processes. The principle of the removal of metals in hydroconversion processes is the destruction of metal compounds by hydrogen treatment and deposition of the metals on a heterogeneous catalyst or their concentration in the high-boiling-point unreacted fractions or coke in the case of using a homogeneous or nanosized catalyst [5, 7, 16, 18, 44, 46, 48, 49, 68, 88]. Quantitative assessment of the distribution and form of metal compounds in the hydroconversion products is reported in [18].

By their purpose, petroleum feedstock hydrogenation processes are divided into hydrocracking and hydrotreating. Hydrotreating processes are used to improve one or more characteristics of the feedstock and subdivided into hydrodemetallation, hydrodesulfurization, and hydrodenitrogenation depending on the narrower purpose. Using this group of processes can improve the quality by reducing the sulfur, nitrogen, and metal contents and prepare HOR for subsequent processing in catalytic cracker, hydrocracker, and/or coker units. Feedstock conversion in hydrotreating processes usually does not exceed 10%. In turn, hydrocracking processes are conducted under more severe conditions (pressure of 30 MPa and temperatures up to 450°C) resulting in quite deep (conversion greater than 25%) degradation of HPF components to decrease the size of the parent molecules. In contrast to thermal processes, HPF hydrotreating processes can significantly increase the quality and yield (85% or more) of the liquid products, but they require significant amounts of hydrogen and have high capital and operating costs. In addition, the possibility of their application to processing of heavy feedstocks is usually limited by enhanced coking, the need for frequent catalyst regeneration, a relative low maximum permissible concentration of metals in the feedstock, and a short catalyst service life. As a consequence, their use is not always cost-effective [5, 41, 42, 48, 64, 89].

In most cases, a catalyst is used for hydrotreating, but there are also noncatalytic thermal hydrogenation processes called hydrovisbreaking, hydroxyolysis, etc. [16, 49]. Selection of the composition and properties of the catalyst and type of a reactor or reactors for hydrotreating petroleum feedstock is largely determined by the feedstock composition, in particular, its metal and asphaltene contents, and the desired yield and composition of the final products [90–96]. In general, by the engineering design of the reactor block, hydrotreating technologies are divided into fixed-, moving-, ebullated/stirred-, and slurry-bed processes [91].

Fixed- and Moving-Bed Hydrotreating Processes

Catalytic hydrotreating of heavy oil residues in fixed-bed reactors is by far the most common industrially developed embodiment of the process [97, 98]. In the processing of heavy petroleum feedstock with high coking tendency and a significant metal content, the so-called guard reactors or guard catalyst beds are often used. This approach can minimize the poisoning of the underlying catalyst beds by deposition of coke and metals on their surfaces and preclude a sharp increase in pressure drop in the reactor in the presence of large amounts of solid deposits. The guard beds usually contain a catalyst with a large pore diameter, low activity, and high capacity for deposition of solid particles. The number of the catalyst beds to be used is determined by the objective of the process and the required product composition, but it largely depends on the feedstock quality [91]. According to published data [99], only petroleum feedstock with a metal content less than 100 ppm can be processed in a fixed-bed reactor. Moreover, narrow-pore catalysts with a high activity should be used at a metal concentration of less than 25 ppm in the feedstock. At metal concentrations of 25 to 50 ppm, a two-bed catalyst system should be used, in which the catalyst having a higher resistance to the deposition of metals is placed in the front bed. Finally, if the metal content is the range of 50 to 100 ppm, a three-bed system is needed, in which the hydrodemetallization catalyst with high metal capacity is placed in the front guard bed [99].

The main problems with fixed-bed catalytic reactors for HPF processing are associated with a rapid decrease in the activity of the upstream catalyst bed by coke and metal deposition and adsorption of other undesirable compounds on the catalyst surface [100]. These problems can be partially resolved by the development of highly active catalysts resistant to solid deposits; optimization of reactor loading along height with several catalyst beds or inert particles, which vary in grain size and shape, pore structure, and activity; and use of special devices to ensure efficient mixing of gas and liquid and uniform flow distribution over the cross section of the reactor [91, 94, 96–98, 100]. However, the main achievements in this area to solve the

task of continuous operation of the units are associated with the use of swing reactors or guard moving-bed reactors, providing a continuous replacement of catalyst during operation [96, 100].

The concept of using a bypass guard reactor and a swing reactor system (SRS) was implemented in the Hyvahl-S process designed by IFP (Axens). In this design, one or more guard reactors are placed upstream of the main fixed-bed reactor. In the case of a significant drop in catalyst activity or too large pressure drops in the first reactor, it is quickly turned off and the stream is switched to the second operating reactor, thereby allowing catalyst replacement without stopping the process and loss of productivity. The process is conducted at high temperatures and hydrogen pressures and short contact times and can be used for deep processing to high feedstock conversions. The guard reactor with a hydrodemetallization catalyst removes most of the metals present in the feed, while the removal of hetero atoms is achieved in the subsequent reactor or reactors with a high-performance hydrodesulfurization catalyst. Optimization of the composition, catalyst load, and process conditions makes it possible to remove 95% of metals and 92% of sulfur from HPF with high concentrations of metals, asphaltenes, and hetero compounds and maintain an acceptable level of conversion within one year of continuous operation [96, 97].

Among the technologies employing moving-bed reactors, the OCR (On-stream Catalyst Replacement) process by Chevron Lummus Global (CLG) and the HYCON process designed by Shell are most widely used.

Placement of an OCR reactor upstream of a fixed-bed hydrodesulfurization reactor makes it possible to increase the throughput of the system and/or upgrade HPF with a high metal content (over 400 ppm), while maintaining high product quality and process economics. The presence of the OCR reactor in the hydroprocessing flow chart can increase the service life of the hydrodesulfurization catalyst and resolve problems associated with increased pressure drop across the bed. In this case, the fresh catalyst is fed from the top of the reactor and HPF enters from the bottom. The catalyst and feedstock move in the countercurrent mode, whereby the feed with a maximum content of impurities is contacted first with the most contaminated catalyst. At the same time, the upward feed flow fluidizes (expands) somewhat the catalyst bed, entraining its particles to the top of the reactor. This arrangement improves the contact of the catalyst with the feedstock, minimizes the problems of bed clogging with deposits and growth of differential pressure. The completely spent catalyst is withdrawn from the bottom of the reactor. Catalyst replacement in this way is performed once or twice a week, without interruption of the process [101].

Another example of a moving-bed guard reactor is the “bunker” reactor in the HYCON process.

Depending on the feed quality, one or more of such reactors are used ahead of the conventional fixed-bed reactor. In this process, the catalyst and heavy oil are fed in co-current flow from the top of the reactor. The catalyst particles descend under gravity at a much lower velocity than the linear velocity of the feed and are discharged from the bottom of the reactor. The movement of the catalyst ensures its continuous addition to and removal from the system through special gateways on the top and bottom of the reactor without interrupting the process. Replacement of the catalyst enables maintaining the desired level of activity, and its frequency depends on the catalyst deactivation rate. Feedstock metals and salts that are removed in the upper beds of the catalyst are discharged along with it at the bottom of the reactor. The bunker reactor system can be used for hydroprocessing of very heavy feeds with a metal content greater than 500 ppm. The process conditions in this case are more severe than those of the conventional fixed-bed hydrodesulfurization reactor. For example, the pressure may exceed 200 bar and the temperature ranges from 400 to 427°C. A HYCON unit at the Shell refinery in Pernis (Rotterdam, the Netherlands) with a throughput of 4000 tons of vacuum residue per day includes five reactors, of which three are the “bunker” demetallization reactors and the remaining two are fixed-bed hydrodesulfurization/hydroconversion reactors. More than 60% of the feed is converted into lighter distillate fractions with a low sulfur content, a FCC feedstock. An inexpensive, regenerable catalyst having a high capacity for metals, low activity, and attrition strength is the most suitable for HPF demetallization [91, 96, 102].

Ebullated/Stirred-Bed Processes

In ebullated/stirred-bed reactors, the feedstock and hydrogen are fed from the bottom of the reactor and passing through the dispenser ascend at a velocity sufficient for expanding the bed, causing erratic, turbulent flow and backmixing of catalyst particles with the gas–liquid stream. In the ebullated bed, only part of the solid particles occur in the suspended state. The density of the solid particles in the bulk of the bed and the bed height and properties are controlled by the speed of the pump, which provides a continuous circulation of the liquid in the reactor, and by the recycle gas and hydrogen flow rates. The products of the process and the catalyst are separated in the upper part of the reactor, and the catalyst circulates to the bottom of the bed, on which it is mixed with the fresh feed stream. The spent catalyst is discharged from the bottom of the reactor and a portion of the fresh catalyst is added to the top of the reactor without interruption of the process and disturbance of the operation mode. The presence of a sufficiently large free space between catalyst particles in the bed minimizes both clogging due to the buildup of solid deposit and a rise in pres-

sure drop. Intense stirring ensures efficient contact of the liquid, gas, and catalyst phases, minimizes temperature and concentration gradients in the bed, and facilitates operation in a mode close to isothermal at higher temperatures compared to fixed-bed reactors. In ebullated/stirred-bed reactors, a catalyst with a particle size of less than 1 mm can be used in some cases because of the absence of problems due to increasing pressure drop; thus, the rate of the process is increased by virtue of minimizing diffusion constraints and increasing the efficiency of utilization of the surface of catalyst grains. The most problematic heavy petroleum residues with high concentrations of asphaltenes, metals, and hetero compounds, such as vacuum tower bottoms and natural bitumens, can be used as feedstock. The technology is quite flexible, and the reactors can operate in either hydrotreating or hydrocracking mode with a low or high feed conversion [91, 96, 100]. However, operation at high feedstock conversions (>50–60%) is fraught with certain difficulties due to the formation of deposits on the interiors of the reactor, an increase in the deactivation rate and consumption of the catalyst, and a significant decrease in stability of the resulting residue. In addition, the high process temperatures (400–440°C) lead to deterioration in the quality of the products [103].

The most widespread hydroprocessing technologies using ebullated/stirred-bed reactors are the LC-Fining (CLG) and H-Oil (Axens) processes. These technologies are very similar in concept, but they differ in reactor operation mode and design features including specialized product separation and purification, catalyst transport, heat recovery, etc. systems. A multistage flow diagram using multiple reactors can be used to implement these technologies. As a rule, the flow chart of the process comprises three reactors, the first of which serves for hydrodemetallization and the second and third ones are intended for hydrodesulfurization and/or hydrocracking. The system of addition of the fresh catalyst and withdrawal of the spent catalyst enables controlling the catalyst activity and maintaining the yield and quality of the products at a constant level during the process and ensures continuous operation for as long as four years. Depending on the operation mode, the objective, and the flow chart, the conversion of residual feedstock can reach 65–80% with the degree of demetallization being as high as 98%. The unconverted residue can be used as a boiler fuel component or a feedstock to coker, gasification, and solvent deasphalting units [56, 96, 101, 104].

Slurry-Bed Processes

In slurry-bed (slurry-phase) processes, petroleum feedstock to which a small quantity of a catalyst or catalyst precursor (from 0.025 to 3 wt %) is usually added is fed together with hydrogen into the hollow shaft (slurry) reactor and rises by upward flow. The degree of backmixing in this case is much lower than in the ebul-

lated-bed reactor. The feed and the catalyst move concurrently, and the flow regime can be close to the plug-flow mode, reducing the time to reach high conversions of the feed compared to ebullated-bed reactors operating in modes close to complete mixing. As in the case of ebullated bed, catalyst particles are in motion, solving the problem of bed clogging and the growth of pressure drop and maintaining the catalyst activity at a constant level by the on-line addition of the fresh catalyst and withdrawal of the spent catalyst. This organization makes it possible to process extra-heavy feeds with a metal content of more than 700 ppm, and the use micrometer- and nanosized catalyst particles significantly enhances the rate of the process as a result of the increased surface area, better accessibility of active sites, and the lack of intradiffusion constraints. The process can be carried out under very severe conditions, at temperatures up to 480°C and pressures up to 300 bar in the feedstock conversion reaching 95 wt %. The catalyst, catalyst precursor, or additive can be carbon; iron-impregnated carbon; pure iron sulfate; ground spent heterogeneous hydroprocessing catalysts; iron-rich clays; and Group VI and VIII metal compounds, such as phosphomolybdic acid, molybdenum naphthenate, and ammonium par-molybdate [18, 91, 103, 105–107].

The slurry-bed hydrocracking process is a promising hydroconversion line because of the possibility of effective deep processing, upgrading, and demetallizing of heavy oils and residues regardless of their elemental or group composition. About a dozen of processes of this type at different levels of their development are known to date. Some of them are being commercialized now, and the others have passed the pilot testing stage only [105, 106].

Among the processes at the commercialization stage, there is the heavy oil residue hydroconversion process designed at the Topchiev Institute of Petrochemical Synthesis and based on the use of catalyst nanoparticles of Mo compounds or Mo and Ni compounds formed in situ after preliminary dispersion of an aqueous solution of a precursor in the feed. The process is conducted at temperatures of 420–450°C, relatively low pressures of 7–13 MPa, and low catalyst concentrations in the reactor on the order of 0.05–0.10 wt % active metal on a feedstock basis. The catalyst consumption is no more than 0.05% of the feed mass. By this technology, more than 90% of the feedstock organic compounds are converted into light fractions that can be used for the production of motor fuels [18, 107–110]. In this process, V and Ni contained in the feedstock and Mo as a part of the nanosized catalyst concentrate in the heavy fractions (HBPF) having a boiling point above 520°C, produced by vacuum distillation of the liquid product of the process (hydrogenate) and largely recycled to the reactor. Based of this technology and using the input data as obtained at the Topchiev Institute and the Electrogorsk Institute of Oil Processing, Chevron

Lummus Global has developed a basic project of a pilot plant for processing heavy residue of bitumen oil with a capacity of 50000 ton a year at the TANECO refinery.

Another slurry process that has reached the stage of commercialization is the EST (Eni Slurry Technology) hydrocracking process designed by Snamprogetti and EniTechnology of the Eni Group. The catalyst of the process is ultrafine microcrystalline molybdenum sulfide dispersed in the feedstock in the form of irregular clusters with an average diameter of 0.5–2 mm, which is formed in situ by activating oil-soluble precursors. Compared with catalysts based on other transition metals, such as Ni, Ru, Co, V, and Fe, this catalyst provides the highest hydrogenating activity and lowest yield of gaseous hydrocarbons and coke during HOR conversion [111]. The catalyst does not accelerate cracking reactions in this process, but mediates rapid hydrogenation and saturates free radicals, impeding both condensation reactions and further β -bond cleavage and maximizing the yield of distillate fractions. The process is conducted at temperatures up to 460°C, hydrogen pressures up to 18 MPa, and molybdenum concentrations in the reactor of 1000 to 5000 ppm. The feedstock conversion and the degree of demetallization by hydrocracking can reach 90% at a degree of hydrodesulfurization of 85% [106, 112]. The catalyst consumption is yet unknown; most likely, it is on the order of 0.1–0.25 wt %. According to Bellussi et al. [106, 113], an industrial slurry reactor using the EST technology was launched in 2013 at the Sannazzaro refinery (Italy). In 2014, the company reported the successful start-up of the plant.

The CANMET hydrocracking process designed in Canada, which provides a high degree of demetallization as a result of the conversion of a high-molecular-weight residual material into products with lower boiling points, is also under commercialization. The process was initially intended for upgrading of heavy oil and natural bitumen. This technology uses an inexpensive iron sulfate-based additive (1–5%), which accelerates the hydrogenation reaction, inhibits the formation of coke, and makes it possible to attain high degrees of HPF conversion (>90%) into distillate fractions. The catalyst particles and almost all metals contained in the feed concentrate in the unreacted residue of vacuum distillation of the liquid products [114]. Based on the reactor block of the CANMET process and its industrially implemented Unicracking and Unionfining technologies, UOP developed a slurry hydrocracking process, called Uniflex, for heavy oil upgrading. The upflow reactor of the Uniflex process operates at moderate temperatures and pressures (435–471°C, 138 bar). The process is mediated by an ultrafine iron-containing catalyst, which has activity in hydrogenation reactions, thereby stabilizing the resulting cracking products. During the hydrotreating of heavy residue, a high conversion of asphaltenes is achieved, which ensures stable operation of the reac-

tor without precipitation of the insoluble sludge and deposit formation [115]. The main disadvantage of this process is a high catalyst consumption reaching 0.25–1.0% of feed mass and the necessity to increase pressure to 17–18 MPa during the processing of residues of heavy high-viscosity oils.

Commercialization of the hydrotreating process named Veba Combi Cracking (VCC) and licensed by KBR and BP [116] is also underway. In this process, a fine powdered coal additive is suspended in the oil residue, wherein the additive may contain iron and other transition metals whose primary role is to prevent coke formation as a result of high conversion of asphaltenes to lighter products and removal of the unreacted asphaltenes as feedstock metals. Typical working conditions are 440–485°C and 220–250 bar [106]. The conversion of the residual feedstock can exceed 95%. The VCC process is based on the Bergius coal liquefaction technology implemented in Germany in the 1920–1940s. Since the 1970s, the interest in the technology was revived with the aim of converting heavy oil residues because of the rise in oil prices during the oil embargo period, and a new plant with a capacity of 3500 barrels a day was built and launched in 1981 in the city of Bottrop (Germany). A further drop in oil prices and its retention at a low level for an extended period has led to the shutdown of the plant in Bottrop in 2001. Following the acquisition of Veba by BP in the United States in 2008 VCC technology was developed, built and launched a new pilot plant capacity of 1 barrel daily [116].

Headwaters Technology Innovations Group (HTIG) developed a process for upgrading of heavy oils and natural bitumens by hydrocracking in the presence of a homogeneous catalyst called HCAT/(HC)₃. The active phase of the catalyst is formed in the reaction system of oil-soluble precursor additives, such as iron pentacarbonyl or molybdenum 2-ethylhexanoate. The catalyst is homogeneously dispersed in the heavy petroleum feedstock TNS, forming a colloidal system with the particle size close to the size of asphaltene molecules. The colloidal or molecular catalyst is primarily associated with asphaltene molecules, whose conversion increases linearly with the conversion of the residual feedstock as a result of their effective hydrocracking, which prevents coke precursors from coalescence. In the pilot plant operating at different degrees of conversion of the residue of the atmospheric distillation of HPF, including Cold Lake natural bitumen, the consumption in molybdenum disulfide in the colloid form or 0.3 wt % molecular form was 0.03.

Thus, the hydrogenation processes along with deep demetallization results in purification and/or conversion (cracking) of heavy petroleum feedstock into lighter distillate fractions that can be used to produce high quality motor fuels and/or mineral base oils. The recovery of metals from petroleum feedstocks can reach 99% depending upon the catalyst type and pro-

cess conditions. When solid catalysts on porous supports are used, metals contained in the feedstock are deposited on the catalyst surface, whereas the feedstock metals in the case of unsupported homogeneous catalyst dispersed in HPF pass into the high-boiling-point liquid product fractions and coke. The recovery of metals from the products and solid residues (waste) in which they are concentrated is usually carried out using conventional hydrometallurgical and pyrometallurgical methods.

ALTERNATIVE PROCESSES

Among alternative processes that promote the demetallization of petroleum feedstock, the main place is occupied by processes in which energy is supplied to the system using a variety of physical methods usually accompanied by or combined with the processes of adsorption, heterogeneous catalysis, or extraction with various solvents and reagents.

For example, Trutnev et al. [117] proposed a process for demetallizing crude oil and device for its implementation that makes it possible to recover metals (V, Ni, Cr, W, etc.) during thermal cracking of crude oil. The process consists in the hydroacoustic treatment of the liquid residue, obtained by thermal cracking (e.g., radiation-thermal cracking) and heated to a temperature of 380–420°C, containing uniformly dispersed fine metal or metal oxide particles. This treatment results in separation, localization, and sedimentation of the fine particles by gravity, with the sedimentation being controlled by varying the acoustic field parameters and followed by separate removal of the cracked residue and the precipitated particles from the vessel, wherein the organic portion of the particles is calcined and fired in the kiln. After calcining and firing, the residue as the metallurgical sludge is sent for recovery to specialized plants. The oil distillation, cracking, and demetallization residue can be sent to further processing in catalytic crackers.

The prospects of the contact demetallization of heavy petroleum feedstock in a wave field was demonstrated by Giniyatullin [118]. The process results in partial thermal degradation of HPF and simultaneous deposition of metals on the contact surface. The cited author proposed a method for enhancement of sorption of organometallic compounds on the outer surface and in the pores of the contact catalyst and the mechanism for demetallization in the case of iron ore concentrate used as the adsorbent. In addition, the possibility of selective demetallization of petroleum feedstock without significant deasphalting was shown. During pilot testing, the degree of deasphaltization of atmospheric residue of one of the West Siberian crude oils was 19% at its demetallization degree of 72%. This demetallization process was recommended as a feedstock preparation step for the catalytic cracking, hydrocracking, and hydrotreating processes to preclude poisoning of the relevant catalysts.

In [119, 120] it was shown that rare metals can be concentrated using plasma-assisted pyrolysis of petroleum residues. The authors cited developed a new process for the catalytic pyrolysis of vacuum residue in the plasma jet of steam and hydrogen-rich gas. Plasma pyrolysis is a powerful destructive process for use in industrial chemistry, as high temperatures and high energy of plasma can accelerate the degradation of molecules of vacuum residue compounds. The plasma jet is both a heat carrier and a reactive catalytic medium in this case. Carbon black containing nickel and vanadium sulfides was used as the catalyst. Vanadium and nickel, the rare metals of the feedstock, were deposited on the surface of carbon black, which is used as a raw material in metallurgy.

Punanova's group [11, 68] developed a demetallization process based on the use of vibration and cavitation effects in the presence of available and reusable surfactants and the subsequent centrifugation and accumulation of high-molecular-weight precipitate containing the most of vanadium concentrated in crude oils. As a result, the recovery of petroleum vanadium reached 50%.

Petrosonic Energy designed Sonoprocess, a simple and efficient process for upgrading heavy oil. The implementation of the process makes it possible to reduce the API gravity of HPF by 5–10 degrees with a simultaneous decrease in viscosity by 99%, in the sulfur content by 40%, and the amount of heavy metals by more than 70%. The proposed process was developed on the basis of solvent deasphalting technology using light hydrocarbon solvents and comprising the steps of extraction with isolation of the insoluble fraction of asphaltenes, in which a significant portion of initial heavy metals and sulfur is concentrated, and solvent recovery from the DAO solution by evaporation or rectification. The main feature of this technology is the so-called sonic reactor, which uses low-frequency sonic energy of large amplitudes, significantly improving the efficiency of mass transfer at the SDA step and thereby reducing the required extraction time from 6–10 h to 2 min. The enhancement of mass transfer processes by intense energy supply greatly simplifies the design of the deasphalting unit [121].

Gomez [122] patented a process for treatment of crude oils with acid or alkali to remove sulfur and metals using microwave heating. The experiments were carried out in a 3-L autoclave using sulfuric acid in a nitrogen atmosphere at a pressure of 8 bar. The autoclave was fitted with a 1.2-kW microwave generator at a frequency of 2450 MHz. Microwave radiation was applied through a quartz window at the bottom of the autoclave. By this arrangement of the process, it is possible to recover more than 86% of S, Ni, and V from the starting petroleum feedstock. Chamorro and Romano [123] patented a similar process for simultaneous desulfurization and demetallization of carbonaceous materials using microwave energy and an acidic aqueous phase. In the extraction of metals and

sulfur from petroleum coke into a medium of concentrated sulfuric and nitric acids at a pressure of about 7 bar (extraction time 15 min), the recovery of S, Ni, and V was more than 40%.

Thus, physical treatment methods including exposure to radiation of different types and frequencies and plasma treatment hold promise for upgrading heavy petroleum feedstock and isolating and/or concentrating metals from it, particularly in conjunction with mass transfer and catalytic processes. However, despite the possibility of supplying energy directly to the system and overcoming the drawbacks of the conventional thermal processes associated with long heating times, temperature gradients, heat losses, and harmful emissions into the environment, the physical methods have not received widespread use. In the case of microwave radiation, this is mainly due to the lack of available industrial equipment that could provide scaling the technology [124].

CONCLUSIONS

Demetallization of heavy petroleum feedstock is generally considered in terms of the common approaches to conditioning (upgrading) and refining of heavy oils, which are used to improve the quality and/or effective utilization of the organic portion of petroleum feedstock. In this connection, the concentration of metals from HPF to various degrees can be achieved as a result of both destructive thermal or catalytic thermal conversion processes and nondestructive mass transfer processes.

The main advantages of the thermal processes of refining heavy oil residues include smaller capital investment and operating costs compared with the catalytic processes, as well as their indifference to the kind of feed, especially concerning the coking tendency and the metal content of the feedstock. Their main disadvantage is the poor quality of the liquid products.

Delayed coking is one of the most widespread thermal processes for upgrading of heavy oil residues with a high metal content. The degree of demetallization in this process reaches 95–98%, however, the main obstacle to widespread implementation of the coking process is the high yield of low-grade coke having high sulfur and ash contents. Although flexicoking holds promise for concentration of metals, the process has found limited application because of the high capital costs associated primarily with the need to add a coke gasification reactor.

A significantly higher yield and better quality of distillate products are obtained in catalytic and hydrocatalytic processes. Resulting in demetallization, removal of hetero compounds, and hydrogen saturation, catalytic hydrogenation/hydrogenolysis processes make it possible to upgrade heavy petroleum feedstock and simultaneously produce commercial motor fuel or high-quality feedstock for further pro-

cessing. However, these processes inherently require significant capital and operating costs associated with high catalyst and hydrogen consumption.

Today, the general trend in the development of the most promising processes and technologies for demetallization of crude oils and concentration of valuable metals is, on one hand, the creation of processes for their isolation from the hydrocarbon feedstock at the earlier stages of refining and, on the other hand, a significant reduction in the yield of metal-containing residues by implementing the slurry hydroconversion, fluid coking or flexicoking, and supercritical fluid extraction processes.

If the described HPF demetallization technologies are implemented, not only significant improvement in the quality of commercial oil and feedstock for manufacturing the most valuable petroleum products, but also the associated production of concentrates of rare metals will be possible.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation in applied research “Study of the potential of bitumen and heavy crude oils from different deposits of the Russian Federation for use as a raw material in the manufacture of metals (including rare and rare earth metals)”, grant agreement no. 14.576. 21.0043 of July 8, 2014, RFMEFI57614X0043) in the framework of the 2014–2020 Federal Target Program “Research and development on priority directions of scientific-technological complex.”

REFERENCES

- I. G. Yashchenko, *Gorn. Vedom.*, No. 7, 26 (2011).
- E. Danilova, *Chem. J.*, December, 34 (2008).
- D. K. Banerjee, *Oil Sands, Heavy Oil & Bitumen: From Recovery to Refinery* (Penn Well, Tulsa, 2012).
- J. Ancheyta, *Modeling of Processes and Reactors for Upgrading of Heavy Petroleum* (CRC Press, Boca Raton, 2013).
- A. F. Akhmetov and Yu. V. Krasil'nikova, *Bashkir. Khim. Zh.* **18**, 93 (2011).
- N. K. Nadirov, A. V. Kotova, and V. F. Kam'yanov, *New Kazakhstan Oils and Their Use: Metals in Crude Oils* (Nauka, Alma-Ata, 1984) [in Russian].
- M. Ya. Shpirt, D. N. Nukenov, S. A. Punanova, and M. Ya. Visaliev, *Solid Fuel Chem.* **47**, 71 (2013).
- A. A. Sukhanov and Yu. E. Petrova, *Neftegaz. Geol., Teor. Prakt.* **3** (2), 11 (2008).
- R. R. Moskalyk and A. M. Alfantazi, *Minerals Eng.* **16**, 793 (2003).
- A. A. Sukhanov and Yu. E. Petrova, *Neftegaz. Geol., Teor. Prakt.* **4** (1), 13 (2009).
- P. A. Vasilenko, D. N. Nukenov, S. A. Punanova, and K. I. Yakubson, *Geol. Geofiz. Razrab. Neft. Gaz. Mestorozhd.*, No. 5, 41 (2002).
- E. P. Kalinin, *Vestnik*, No. 1, 6 (2009).
- A. A. Sukhanov, V. P. Yakutseni, and Yu. E. Petrova, *Neftegaz. Geol., Teor. Prakt.* **7** (4), 23 (2012).
- B. V. Raja, *Steelworld* **13** (2), 19 (2007).
- A. R. Garushev, M. Yu. Malikova, and Yu. I. Stashok, *Neft. Khoz.*, No. 11, 70 (2007).
- S. A. Akhmetov, *Technology of High-Conversion Processing of Oil and Gas: A Textbook* (Gilem, Ufa, 2002) [in Russian].
- R. Kh. Muslimov, G. V. Romanov, and G. P. Kayukova, *Integrated Development of Heavy Oils and Natural Bitumens of the Permian Play of the Republic of Tatarstan* (Fen, Kazan, 2012) [in Russian].
- S. N. Khadzhiev and M. Ya. Shpirt, *Trace Elements in Crude Oils and Their Refinery Products* (Nauka, Moscow, 2012) [in Russian].
- A. K. Manovyan, *Technology of Primary Processing of Oil and Gas: A Textbook* (Khimiya, Moscow, 2001), 2nd Ed. [in Russian].
- Integrated Program of Development of Heavy Oil and Natural Bitumen Deposits of the Republic of Tatarstan up to 2020* (AN RT, Kazan, 2010) [in Russian].
- Technoeconomic Assay of Development Extraheavy Oil Fields in Tatneft' Licensed Areas* (TatNIPIneft', Al'met'evsk, 2008) [in Russian].
- S. N. Sudykin, R. Z. Sakhabutdinov, F. R. Gubaidullin, et al., *Neft. Khoz.*, No. 7, 61 (2010).
- http://npckvadra.ru/wp-content/uploads/2013/04/tehn_cvst_met.pdf
- JP Patent Appl. No. 53-8315 (1984).
- S. V. Obratsov, G. Ya. Mikhailova, and A. A. Kaplin, RU Patent No. 1608562 (1990).
- Yu. A. Tsibul'nikova, S. V. Ryabova, S. V. Obratsov, and A. N. Didenko, RU Patent No. 1475170 (1991).
- C. Savastano, RU Patent No. 2014344 (1994).
- S. V. Obratsov and A. A. Orlov, RU Patent No. 2462501 (2012).
- L. N. Kremer, T. M. Nguyen, and J. J. Weers, RU Patent No. 2346024 (2006).
- N. L. Egin, *Recovery of Metals from Crude Oils* [in Russian]. <http://nlegin.ru/izobreteniya/metall.html>.
- B. Wu, J. Zhu, J. Wang, and C. Jiang, *Energy Fuels* **20**, 1345 (2006).
- B. M. Nuranbaeva, T. K. Akhmedzhanov, and L. T. Ismagilova, *Sovrem. Nauk. Tekhnol.*, No. 4, 49 (2013).
- T. K. Akhmedzhanov, *Nauchn.-Tekh. Obespech. Gorn. Proizv.*, Tr. **80**, 185 (2011).
- F. I. Samedova, S. Yu. Rashidova, A. M. Kasumova, and N. A. Kuliev, *Sverkhkrit. Flyuidy, Teor. Prakt.* **3** (2), 52 (2008).
- F. I. Samedova, A. M. Kasumova, S. Yu. Rashidova, and G. R. Bakhshesh, *Sverkhkrit. Flyuidy, Teor. Prakt.* **6** (1), 13 (2011).
- F. I. Samedova, S. Yu. Rashidova, A. M. Kasumova, and N. A. Kuliev, *Sverkhkrit. Flyuidy, Teor. Prakt.* **8** (4), 53 (2013).
- A. V. Soyn, Extended Abstract of Candidate's Dissertation in Chemistry (Moscow, 2010).
- N. S. Musina, Extended Abstract of Candidate's Dissertation in Chemistry (Moscow, 2014).

39. A. A. Shchepalov, *Heavy Oils, Gas Hydrates, and Other Promising Sources of Hydrocarbon Feedstock: A Tutorial* (Nizhegorodsk. Gos. Univ., Nizhni Novgorod, 2012) [in Russian].
40. V. G. Kozin, N. L. Solodova, N. Yu. Bashkirtseva, and A. I. Abdullin, *Modern Technologies for Manufacture of Motor Fuel Components* (Kazansk. Gos. Tekhnol. Univ., Kazan, 2008) [in Russian].
41. S. A. Akhmetov, *Oil and Gas Processing Technology and Equipment: A Textbook* (Nedra, St. Petersburg, 2006) [in Russian].
42. L. C. Castañeda, J. A. D. Muñoz, and J. Ancheyta, *Fuel* **100**, 110 (2012).
43. D. A. Khalikova, S. M. Petrov, and N. Yu. Bashkirtseva, *Vestn. Kazansk. Technol. Univ.* **16**, 217 (2013).
44. R. Z. Magaril, *Theoretical Principles of Chemical Processes in Oil Refining: A Textbook* (Khimiya, Leningrad, 1985) [in Russian].
45. W. L. Leffler, *Petroleum Refining in Nontechnical Language* (PennWell, Tulsa, 2008).
46. V. M. Kapustin and A. A. Gureev, *Oil Refining Technologies, part 2: Destructive Processes* (KolosS, Moscow, 2007) [in Russian].
47. N. I. Chernozhukov, *Oil and Gas Processing Technologies, part 3: Purification and Separation of Petroleum Feedstock, Manufacture of Commercial Petroleum Products*, Ed. by A. A. Gureev and B. I. Bondarenko (Khimiya, Moscow, 1978), 6th Ed. [in Russian].
48. E. G. Telyashev, in *Proceedings of XV Annual Roundtable "Refining and Petrochemicals in Russia and the CIS Countries"* (Geneva, 2012).
49. J. G. Speight, *The Chemistry and Technology of Petroleum* (CRC, Boca Raton, 2006), 4th Ed.
50. J. M. Lee, S. Shin, S. Ahn, et al., *Fuel Process. Technol.* **119**, 204 (2014).
51. M. Al-Sabawi, D. Seth, and T. de Bruijn, *Fuel Process. Technol.* **92**, 1929 (2011).
52. D. G. Filenko, K. A. Shchekoldin, Z. M. Radzhabov, et al., *Oboron. Kompl. Nauchno-Tekh. Progr. Ross.*, No. 1, 34 (2012).
53. F. D. Gumerov, A. N. Sabirzyanov, G. I. Gumerova, et al., *Butlerov. Soobshch.* **5** (1), 9 (2004).
54. J. Speight, *The Desulfurization of Heavy Oils and Residua* (CRC, Boca Raton, 1999), 2nd Ed.
55. <http://www.kbr.com/Technologies/Process-Technologies/Residuum-Oil-Supercritical-Extraction/>
56. <http://www.axens.net/our-offer/by-market/oil-refining/bottom-of-the-barrel.html>
57. <http://www.uop.com/processing-solutions/refining/residue-upgrading/>
58. K. H. Chung, Z. Xu, X. Sun, et al., *Pet. Technol. Quart.*, No. Q4, 99 (2006).
59. P. C. Mandal, S. M. Wahyudiono, and M. Goto, *J. Hazard. Mater.* **187**, 600 (2011).
60. P. C. Mandal, S. M. Wahyudiono, and M. Goto, *Fuel* **92**, 288 (2012).
61. D. Severin and H. Siese, *Proceedings of the 3rd International Symposium on Supercritical Fluids*, Ed. by G. Brunner and M. Perrut (Strasbourg, 1994), vol. 1.
62. C. Kersch, S. P. Ortiz, G. F. Woerlee, and G. J. Witkamp, *Hydrometallurgy* **72**, 119 (2004).
63. C. Kersch, M. Van der Kraan, G. F. Woerlee, and G. J. Witkamp, *J. Chem. Technol. Biotechnol.* **77**, 256 (2002).
64. M. F. Ali and S. Abbas, *Fuel Process. Technol.* **87**, 573 (2006).
65. <http://www.fwc.com/What-We-Do/Refining/FW-Residue-Upgrading-Technologies.aspx>
66. <http://www.cbi.com/technologies/refining-technology>
67. N. I. Iskritskaya, *Neftegaz. Geol., Teor. Prakt.* **1**, 12 (2006).
68. D. N. Nukenov, S. A. Punanova, and Z. G. Agafonova, *Metals in Crude Oils, Their Concentration and Recovery Methods* (GEOS, Moscow, 2001) [in Russian].
69. E. Furimsky, *Fuel Process. Technol.* **67**, 205 (2000).
70. E. Koshka, J. Kuhach, and E. Veith, *World Heavy Oil Congress: Edmonton, Alberta* **329**, 285 (2008).
71. M. A. Silverman, S. K. Pavel, and M. D. Hillerman, *World Heavy Oil Congress: Edmonton, Alberta* **419**, 7 (2011).
72. <http://www.ellycrack.no/bilder/ELLYCRACK%2016%2010%2009.pdf>
73. W. A. Brown and G. Monaghan. http://www.etxsystems.com/Publications/Presentations/ETX_WHOC11.pdf
74. A. A. Ryumin, RU Patent No. 2033449 (1995).
75. G. K. Tarabrin, I. M. Tartakovskii, E. M. Rabinovich, et al., RU Patent No. 2118389 (1998).
76. D. M. Soskind, V. V. Gribkov, N. P. Slatvinskii-Sidak, et al., *Khim. Tekhnol. Topl. Masel*, No. 4, 7 (1988).
77. L. Bressan. <http://www.ati2000.it/index.php?page=download&t=pubblicazioni&id=31960>
78. G. J. Stiegel. <http://www.canadiancleanpowercoalition.com/pdf/GP6%20-%20stiegel060905.pdf>
79. O. Holopainen, *Bioresource Technol.* **46**, 125 (1993).
80. V. G. Sister, E. M. Ivannikova, A. I. Yamchuk, et al., *Gaz. Prom-st.*, No. 12, 60 (2013).
81. S. N. Khadzhiev, *Cracking of Petroleum Fractions on Zeolite Catalysts* (Khimiya, Moscow, 1982) [in Russian].
82. N. L. Solodova and N. A. Terent'eva, *Vestn. Kazansk. Tekhnol. Univ.*, No. 1, 141 (2012).
83. S. Lars, T. Andersson, S. T. Lundin, et al., *Appl. Catal.* **9**, 317 (1984).
84. R. L. Jones, *J. Catal.* **129**, 269 (1991).
85. P. O'Connor, J. P. J. Verlaan, and S. J. Yanik, *Catal. Today* **43**, 305 (1998).
86. S.-I. Andersson and T. Myrstad, *Appl. Catal A: Gen.* **170**, 59 (1998).
87. 25 Years of RFCC Innovation. <http://www.uop.com/?document=uop-25-years-of-rfcc-innovation-tech-paper&download=1>
88. M. Ya. Visaliev, M. Ya. Shpirt, Kh. M. Kadiev, et al., *Solid Fuel Chem.* **46**, 100 (2012).
89. G. A. Berg and S. G. Khabibullin, *Catalytic Hydrofining of Oil Residues* (Khimiya, Leningrad, 1986) [in Russian].

90. H. Toulhoat, R. Szymanski, and J. C. Plumail, *Catal. Today* **7**, 531 (1990).
91. R. J. Quann, R. A. Ware, C. H. Hung, and J. Wei, *Adv. Chem. Eng.* **14**, 95 (1988).
92. M. S. Rana, J. Ancheyta, P. Rayo, and S. K. Maity, *Catal. Today* **98**, 151 (2004).
93. M. S. Rana, J. Ancheyta, S. K. Maity, and P. Rayo, *Catal. Today* **104**, 86 (2005).
94. J. Ancheyta, M. S. Rana, and E. Furimsky, *Catal. Today* **109**, 3 (2005).
95. E. Furimsky, *Catal. Today* **30**, 223 (1996).
96. E. Furimsky, *Appl. Catal.*, A **171**, 177 (1998).
97. S. Kressmann, F. Morel, V. Harle, and S. Kasztelan, *Catal. Today* **43**, 203 (1998).
98. J. K. Minderhoud, J. A. R. van Veen, and A. P. Hagan, *Stud. Surf. Sci. Catal.* **127**, 3 (1999).
99. W. C. van Zijll Langhout, C. Ouwerker, and K. M. A. Pronk, *Oil Gas J.*, December, 120 (1980).
100. E. Furimsky and F. E. Massoth, *Catal. Today* **52**, 381 (1999).
101. http://www.chevrontechnologymarketing.com/CLGtech/Resid_Hydroprocessing.aspx
102. B. Scheffer, M. A. van Koten, K. W. Robschlager, and F. C. de Boks, *Catal. Today* **43**, 217 (1998).
103. F. Morel, S. Kressmann, V. Harle, and S. Kasztelan, *Stud. Surf. Sci. Catal.* **106**, 1 (1997).
104. R. M. Eccles, *Process. Fuel Technol.* **35**, 21 (1993).
105. S. Zhang, D. Liu, W. Deng, and G. Que, *Energy Fuel* **21**, 3057 (2007).
106. G. Bellussi, G. Rispoli, A. Landoni, et al., *J. Catal.* **308**, 189 (2013).
107. S. N. Khadzhiev, *Pet. Chem.* **51**, 1 (2011).
108. S. N. Khadzhiev and Kh. M. Kadiev, RU Patent No. 2412230 (2011).
109. Kh. M. Kadiev and S. N. Khadzhiev, RU Patent No. 2400525 (2010).
110. S. N. Khadzhiev, V. N. Kapustin, A. L. Maksimov, et al., *Neftepererab. Neftekhim.*, No. 9, 26 (2014).
111. N. Panariti, A. Del Bianco, G. Del Piero, and M. Marchionna, *Appl. Catal. A* **204**, 203 (2000).
112. N. Panariti, A. Del Bianco, G. Del Piero, M. Marchionna, P. Carniti, *Appl. Catal. A* **204**, 215 (2000).
113. A. G. Okunev, E. V. Parkhomchuk, A. I. Lysikov, et al., *Usp. Khim.* (2015) (in press).
114. A. E. Silva, H. K. Rohrig, and A. R. Dufresne, *Oil Gas J.*, March, **81** (1984).
115. D. Gillis, <http://www.uop.com/?document=uopuniflexslurrytreatmentalternativepaper&download=1>
116. Slurry Phase Hydrocracking: Bottoms Upgrading for Today's Market [Electronic resource]. *Chemical Engineering World*. March 2014. P.52. Mode of access: <http://kbr.com/Newsroom/Publications/Articles/Slurry-Phase-Hydrocracking-Bottoms-Upgrading.pdf>
117. Yu. A. Trutnev, R. Sh. Mufazalov, N. Ya. Mukhortov, et al., RU Patent No. 2133766 (1999).
118. V. M. Giniyatullin, Extended Abstract of Candidate's Dissertation in Engineering (Ufa, 1998).
119. G. G. Garifzyanova and G. G. Garifzyanov, *Khim. Tekhnol. Topl. Masel*, No. 3, 15 (2006).
120. G. G. Garifzyanova, <http://chem.kz/50407388.pdf>
121. Petrosonic Energy Inc. official website [Electronic resource]. Mode of access: <http://www.petrosonic.net/s/Sonoprocess.asp>
122. R. A. M. Gomez, US Patent No. 6955753 (2005).
123. D. L. M. De Chamorro and Maria M. C. Romano, US Patent No. 6068737 (2000).
124. S. Mutyala, C. Fairbridge, J. R. J. Pareet al., *Fuel Process. Technol.* **91**, 127 (2010).

Translated by S. Zatonsky