ENERGY&FUELS
AN AMERICAN CHEMICAL SOCIETY JOURNAL
VOLUME 21, NUMBER 6 NOVEMBER/DECEMBER 2007

©Copyright 2007 by the American Chemical Society

Reviews

A Review of Slurry-Phase Hydrocracking Heavy Oil Technology

Shuyi Zhang,* Dong Liu, Wenan Deng, and Guohe Que

*State Key Laboratory of Heavy Oil Processing, University of Petroleum China, Dongying,
Shandong, China 257061*

Received May 18, 2007. Revised Manuscript Received July 26, 2007

The technologies of slurry-phase hydrocracking of heavy oil and the latest development of dispersed catalysts were reviewed. Catalysts for slurry-phase hydrocracking of heavy oil have undergone two development phases, that is, heterogeneous solid powder catalysts and homogeneous dispersed catalysts. The homogeneous dispersed catalysts are divided into water-soluble dispersed catalysts and oil-soluble dispersed catalysts. Solid powder catalysts have low catalytic activity, which will produce a large number of solid particles in bottom oil; thus it is difficult to dispose and utilize. Dispersed catalysts are highly dispersed and have greater surface area to volume ratio. Therefore, they show high catalytic activity and good performance. They are desirable catalysts for slurry-phase hydrocracking of heavy oil.

1. Introduction

The hydroconversion process of heavy oil and residue is one of the main processes for converting a heavy carbonaceous feedstock to lower-boiling products. Generally heterogeneous catalysts, such as sulfide of cobalt, molybdenum, or nickel supported by alumina or silica–alumina, are used in the process. The constituents having higher molecular weight in heavy oil and residue deposit on the surface of the catalyst, block the pores of the catalyst, and then result in rapid decline of the hydrogenation activity.[1] Eventually, coke and metal impurities removed from heavy oil and residue deposit on the surface of the catalyst and result in deactivation of the catalyst. Moreover, the rapid increase in pressure drop of the bed layer makes it difficult to maintain normal operations, which becomes more serious when the feedstock contains higher metal and carbon residue. Thereby, the catalysts display short service life and bad operation stability, and therefore shut-down is more frequent.

In order to solve these problems, slurry-phase hydrocracking processes, which adopt unsupported dispersed catalysts, have been developed. The technology has the same processing as thermocracking, and the difference was in mixing the feed oil, hydrogen, and dispersed unsupported catalysts together going through the reactor. The reaction was mainly about thermal cracking; the purpose of catalyst and hydrogen was inhibition of coke formation by hydrogenating the coke precursor and removing heteroatoms. On the other hand, the catalyst acts as a supporter of coke and, hence, reduces coking of the reactor wall.[2] Accordingly slurry-phase hydrocracking adopted single-use catalysts and did not care whether it was deactivated; thus, it could process inferior residues, containing sulfurous compounds in exceedingly large quantities, nitrogenous compounds, and high molecular weight organmetallic complexes.

2. The Main Technologies of Slurry-Phase Hydrocracking Heavy Oil

Slurry-phase hydrocracking of heavy oil was first used in Germany as early as 1929 for hydrogenation of coal, and two units were successfully working during World War II, which were switched to vacuum residue (VR) feed and operated until 1964.[3] In today's world, research on slurry-phase hydrocracking processes is very active. There are now more than 10 such

---

(1) Speight, J. G. New approaches to hydroprocessing. *Catal. Today.* **2004**, *98* (1), 55–60.

(2) Liang, W. *Heavy Oil Chemistry [M]*; Petroleum University Press: Shandong, 2000; pp 318–331.

(3) Rana, M. S.; Sámano, V.; Ancheyta, J.; Diaz, J. A. I. A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel* **2007**, *86* (9), 1216–1231.

10.1021/ef700253f CCC: $37.00 © 2007 American Chemical Society
Published on Web 09/15/2007

technologies that are in pilot stage. Some of them have already had industrialized application.

One is the VEBA-combi-cracking (VCC) process[4–6] developed in Germany. This process adopts red mud, that is, a kind of solid material with iron content, and the fine coke powder of Bovey coal as a catalyst. In this technology, not only is the reaction pressure (15–27 MPa) relatively high, but also a relatively large amount of catalyst, such as about 5 wt % raw materials, must be used.

A second is the M-coke technology[7–9] developed by Exxon Mobil. In this technology, phosphomolybdic acid and molybdenum naphthenate were used as catalyst. Its reaction pressure was about 17 MPa, and reaction temperature was 440 °C, and its residue conversion reached 90%. Although the dispersion rate and activity of the catalyst are high, this technology remains until now in an experimental scale (1 drum/day). A reason may be that the cost of catalyst is relatively high with low economic profit.

A third is the HDH technology[10,11] developed by the Venezuelan INTEVEP Company. This technology uses a kind of inexpensive natural ore, which is a special local product currently in Venezuela, after it is crushed and fined as a catalyst. Although the catalyst is inexpensive, it must be used in a very large amount. The required separation system for solid matter of catalyst and nonconverted bottom oil is relatively complex. Furthermore, the mineral ore is produced specially only in Venezuela.

Still another is the Canadian CANMET process.[12–14] The catalyst used in this process is $FeSO_4$ with a relatively high dosage (1–5%). The desulfuration and denitrogenation rate of this process is not high, although it does appear to achieve the expected quality of products. There also exist some problems in the separation of catalyst and nonconverted bottom oil.

A fifth is the SOC technology[15,16] developed by a Japanese company, Ashi Kasei Industrial Co. In this technology, the catalyst, consisting of highly dispersed superfine powder and transition metallic compound, is used with high reaction activity and good anticoking effects. But, this process requires a high reaction pressure (20–22 MPa) and a relatively high investment cost in the facility.

KOBE STEEL LTD discovered a method for hydrocracking residue with raw material limonite ore as catalyst.[17–19] Limonite ore catalyst was pulverized into a powder and particle size of not more than 2 μm in order to have high catalytic activity. The active iron catalyst might be an economic alternative for cracking heavy crude.

There are other technologies currently available around the world, such as the Aurabon technology[20] developed by the American UOP Company and the hydrocracking technology[21] developed by IFP (Institut Francais du Petrole).The catalysts used in this process are molybdenum and cobalt as naphthenates. EST[22–24] technology developed by ENI adopted dispersed molybdenum as catalyst. This oil-soluble catalyst decomposes microcatalyst particles online; it can easily mix with raw material and the hydrogen, having very high activity in promoting thehydrogenation reaction. But this catalyst has no activity in promoting the thermal cracking reaction; the free radicals cracked by C–C and C–heteroatoms will saturate quickly and inhibit the aromatic coalescence reaction. Experiment proved that Mo has higher catalytic activity than Ni, V, Co, Fe, etc. The ENI slurry technology (EST) process is moving towards the commercial proof at one of the Agip's refinery in Italy. The important modifications have been claimed by ENI for slurry processes (EST); the modifications mainly concern the possibility of obtaining high conversions while maintaining the stability of the residues.

$(HC)_3$ technology[25,26] developed by Alberta Research Co., Canada, adopts an oil-soluble, metal-containing compound additive (such as iron pentacarbonyl or molybdenum 2-ethyl hexanoate) as catalyst. The additive is operative to impede coalescence of coke precursors. Recently, Headwaters Technology Innovation Group (HTIG) proposed a homogeneous catalyst[27,28] based hydrocracking technology [$(HC)_3$ technology], which has been developed for upgrading of indigenous heavy

---

(4) Graeser, U.; Eschet, G.; Holighnaus, R. Veba-Combi-Cracking, A proven technology for high conversion of heavy bottoms. *1986 Proceedings of the Refining Department*; American Petrolium Institute: San Diego, 1986; pp 169–199.

(5) Dohler, W.; Kretschmar, K.; Merz, L. Veba-Combi-Cracking—A technology for upgrading of heavy oils and bitumen. *Div. Petrol. Chem., ACS* **1987**, *32* (2), 484–489.

(6) Wenzel, F.; Kretschmar, K. *Veba-Combi-Cracking process-status and future trends*. Oil Sands-Our Petroleum Future; Alberta Research Council: Edmonton, Alberta, Canada, 1993; pp 268–253.

(7) Schuetze, B.; Hofmann, H. How to upgrade heavy feeds. *Hydrocarbon Process.* **1984**, *62* (2), 75–78.

(8) Bearden, R., Jr. Hydroconversion of heavy hydrocarbons. U.S. Patent 4,134,825, 1979.

(9) Bearden, R., Jr. Catalyst for the hydroconversion of heavy hydrocarbons. U.S. Patent 4,226,742, 1980.

(10) Drago, G.; Gultian, J.; Krasuk, J. The development of HDH process, a refiners tool for redidual upgrading. *Div. Petrol. Chem., ACS* **1990**, *35* (4), 584–592.

(11) Solari, R. B. HDH hydrocracking as an alternative for high conversion of the bottom of the barrel. Presented at the 1990 NPRA Annal Meeting, San Antonio, March 25, 1990.

(12) Khulbe, C. P.; Ranganathan, R.; Pruden, B. B. Hydrocracking of heavy oils/fly ash slurries. U.S. Patent 4,299,685, 1981.

(13) Silva, A. E.; Rohrig, H. K.; Dufresne, A. R. CANMET process going into Montrel refinery. *Oil Gas J.* **1984**, (March 26), 81–88.

(14) Pruden, B., Muir, G., Skipek, M. *The CANMET hydrocracking process: recent developments*; Oil Sands-Our Petroleum Future, Alberta Research Council: Edmonton, Alberta, Canada, 1993; p 277.

(15) Seko, M.; Kato, K.; Shohji, Y. Super oil cracking (SOC) processing for upgrading vaccum residues. Presented at the NPRA Annal Meeting, 1988; AM-86-61.

(16) Seko, M; Ohtake, N. Super oil cracking (SOC) process. *AIChE Symp. Ser.* **1989**, *273*, 5.

(17) Yasumuro, M.; Okui, T.; Okuyama, N.; Tamura, M.; Shigehisa T Method for hydrocracking petroleum heavy oil. Canadian Patent CA 2426374, 2003.

(18) Matsumura, A.; Kondo, T.; Sato, S.; Saito, I.; de Souza, W. F. Hydrocracking Brazilian Marlim vacuum residue with natural limonite. Part 1: catalytic activity of natural limonite. *Fuel* **2005**, *84* (4), 411–416.

(19) Matsumura, A.; Sato, S.; Kondo, T.; Saito, I.; de Souza, W. F. Hydrocracking Marlim vacuum residue with natural limonite. Part 2: experimental cracking in a slurry-type continuous reactor. *Fuel* **2005**, *84*, 417–421.

(20) *The Institute of Heavy Oil Processing, Heavy Oil Processing Handbook*, The Chemical Daily Co: Tokyo, 1982; 54.

(21) Yves, J.; Davidson, M.; Le Page, J. F. Process for Hydrotreating Heavy Hydrocarbons in Liquid Phase in the presence of a Dispersed Catalyst. U.S. Patent 4,285,804, 1981.

(22) Montanari, R.; Marchionna, M.; Panariti, N. Process for the conversion of heavy feedstocks such as heavy crude oils and distillation residues. World Patent WO2004056946, 2004.

(23) Marchionna, M.; Delbianco, A.; Panariti, N. Process for the conversion of heavy charges such as heavy crude oils and distillation residues. U.S. Patent application 20030089636, 2003.

(24) Romolo, M.; Sergio, R. Presented at the European Refining Technology Conference, Paris, 2002.

(25) Cyr, T.; Lewkowicz, L.; Ozum, B.; Lott, R. K.; Lee, L.-K. Hydrocracking process involving colloidal catalyst formed in situ. U.S.Patent 5,578,197, 1996.

(26) Lott, R. K. $(HC)_3$ process-A slurry hydrocracking technology designed to convert bottoms and heavy oils. Proceeding of 7th UNITAR International Conference on Heavy Crude and Tar Sand, Beijing, Petroleum Industry Press: Beijing, 1998.

(27) Lott, R. K.; Lee, L.-K. Ebullated bed hydroprocessing methods and systems and methods of upgrading an existing ebullated bed system. U.S. Patent Application 20050241991, 2005.

(28) Lott, R. K.; Lee, L.-K. Hydroprocessing method and system for upgrading heavy oil using a colloidal or molecular catalyst. U.S. Patent Application 20050241993, 2005.

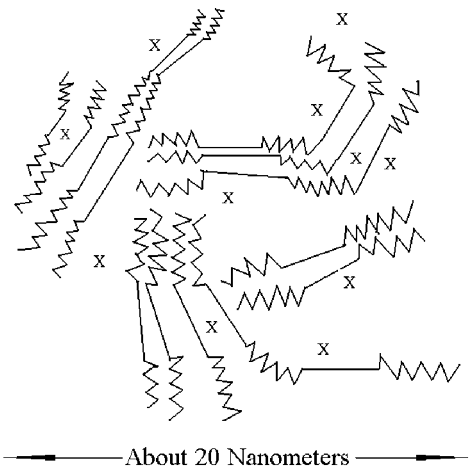

Figure 1. Catalyst molecules or particles (X) dispersed and intimately associated with large asphaltene molecules.

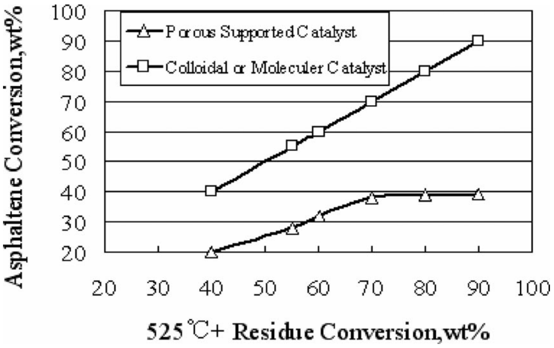

Figure 2. Conversion performance between colloidal or moleculer catalyst and porous catalyst.

crude or bitumen. In this process, the catalyst is homogeneously dispersed as a colloid with particles similar in size to the asphaltene molecule. The colloidal or molecular catalyst is preferentially associated with asphaltenes within the heavy oil feedstock (Figure 1). A heavy oil feedstock comprising Cold Lake bitumen atmospheric residue and 300 ppm of a molybdenum disulfide catalyst in colloidal or molecular form was introduced into a pilot slurry-phase hydroprocessing reactor system and operated at various percent residue conversion levels. The conversion of the asphaltenes versus the overall conversion level for the residue material is plotted in the chart shown in Figure 2.

According to the chart of Figure 2, the comparative study showed that the percent conversion of asphaltenes using the colloidal or molecular catalyst was the same as the percent conversion of the residue material as a whole. That means the asphaltenes were converted into lower boiling materials at the same conversion level as the residue material as a whole, demonstrating that the colloidal or molecular catalyst was as active in converting asphaltenes as other residue hydrocarbon molecules. In contrast, the percent conversion of asphaltenes using the porous supported catalyst was half or less of the percent conversion of the residue fraction as a whole. That means the porous supported catalyst was substantially less effective in converting asphaltenes than other hydrocarbons in the residue material, most likely because the larger asphaltenes are not able to diffuse into the pores of catalyst as readily as other smaller molecules in the residue material. Therefore using the colloidal or molecular catalyst can reduce equipment fouling and increase conversion level more efficiently than use of the supported catalyst.

As we known, Chinese crude is relatively heavy as can be visualized from the contents of >500 °C residue by assay of true boiling point distillation (TBP) of main domestic crudes, Table 1.[29]

Therefore investigate the hydrogenation process of domestic heavy oil is very important. Fushun Research Institute of Petroleum and Petrochemicals (FRIPP) developed a suspension bed hydrocracking process[30] comprising mixing a heavy oil and residuum feedstock with a catalyst, heating the resulting mixture, introducing it into a suspension bed reactor, and performing the hydrocracking reaction at a temperature of 380–460 °C under a hydrogen pressure of 10–15 MPa; wherein said catalyst is a dispersing-type, nonsupported catalyst in the form of an aqueous solution, comprising 2–15 wt % Mo, 0.1–2 wt % Ni, and 0.1–3 wt % P, and is added in an amount to provide 150–1500 ppm active metals. This is accomplished by introducing nickel and then adjusting the composition of water-soluble catalyst. Increasing the contents of active metals in the catalyst would lower the cost of equipment and operation and reduce the quantity of waste.

PetroChina Company Limited and University of Petroleum China[31] developed a new and improved heavy oil hydrocracking process using a multimetallic liquid catalyst in a slurry-bed reactor. A fixed-bed hydrotreating reactor is also used online to enhance lightweight oil yield from heavy oil under normal pressure. The process is especially effective to process at normal pressures residual oil having a relatively high content of nitrogen and/or metal, a relatively high viscosity, a high acid number, or a high residual coke content. Karamay atmospheric residue was carried out in this hydrocracking process. The reaction temperature was 400–480 °C. The hydrogen partial pressure was 4–12 MPa. Multimetallic liquid catalyst type UPC-21 was used. The concrete data for this process is as follows.

As Table 2 shows, bottom oil circulation is adopted as a feature of this invention, which increases the flexibility of the operation of the facility. The process is preferably applied to mainly produce naphtha and diesel oil. It is especially effective in processing petroleum residual oil with high nitrogen content, high metal content, and high viscosity, having a high acid number and having high residual coke, still realizing conversion rates of more than 80–95%.

3. Catalysts and Catalyst Development

Slurry-phase hydrocracking technology is a very new technology, but some of these technologies are only being tested on an experimental scale, some adopt a solid catalyst, and some use expensive catalysts or require high reaction pressures. However, the effectiveness of the slurry-phase hydrocracking technology is highly dependent upon catalyst. Catalyst with poor activity will result in coke formation and incompatible product. Catalysts for slurry-phase hydrocracking of heavy oil have undergone two development phases, that is, heterogeneous solid powder catalysts and homogeneous dispersed catalysts. The homogeneous dispersed catalysts are divided into water-soluble dispersed catalysts and oil-soluble dispersed catalysts. Solid powder catalysts have low catalytic activity; it was overtaken

---

(29) Yang, G. *Some Fundamental Aspects of Heavy Oil and Residuum Processing*; Petroleum University Press: Shandong, 1997.

(30) Li, Y.; Wang, J.; Jiang, L.; Zhang, Z.; Liu, J.; Ren, S.; Zhao, B.; Jia, Y. Hydrocracking of heavy oil and residuum with a dispersing-type catalyst. U.S. Patent 6,004,454, 1999.

(31) Que, G.; Men, C.; Meng C.; Ma, A.; Zhou, J.; Deng, W.; Wang, Z.; Mu, B.; Liu, C.; Liu, D.; Liang, S.; Shi, B. Heavy oil hydrocracking process with multimetallic liquid catalyst in slurry bed. U.S. Patent 6,660,157, 2003.

Table 1. TBP of Main Domestic Crude

crude	Daqing	Shengli	Gudao	Liaohe	Northchina	Zhongyuan	Xinjiang
<200 °C	11.5	7.6	6.1	9.4	6.1	19.4	15.4
<350 °C	31.2	25.1	21.0	30.9	26.0	44.5	41.4
>500 °C	57.2	52.6	48.2	60.1	60.9	67.7	70.3

Table 2. Product Distribution under Different Reaction Temperatures

reaction temperature, °C	440	440	445	445
hydrogen partial pressure, MPa	10	10	10	10
hydrogen–oil ratio,N m^3/m^3	757/1	800/1	737/1	800/1
recycling ratio (fresh raw material/bottom oil)	100/0	66/34	100/0	70/30
total volume hourly space velocity, h^{-1}	1.10	1.14	1.13	1.14
volume hourly space velocity of fresh raw material, h^{-1}	1.10	0.75	1.13	0.80
product distribution, m %				
C1–C4 (gas) yield	4.76	5.50	4.96	7.40
C5–180 °C (naphtha fraction) yield	9.27	9.60	10.28	13.80
180–350 °C (diesel oil fraction) yield	24.08	27.30	27.41	29.60
350–524 °C (vacuum gas oil fraction) yield	37.50	53.10	37.62	45.40
<524 °C yield	75.61	96.30	80.27	96.20
>524 °C (bottom oil) yield	25.39	4.60	20.90	5.00
hydrogen loss °C m %	1.13	0.92	1.18	1.18
total yield[a]	101.0	100.92	101.18	101.18

[a] Total yield = total production yield/feed oil.

by the slurry-phase hydrocracking technologies in early stage, such as VEBA-Combi-Cracking (VCC) process, Canadian CANMET process, HDH technology as catalyst. These catalysts will produce a large number of solid particles in bottom oil; thus it is difficult to dispose and utilize them. Dispersed catalysts are highly dispersed and have greater surface area to volume ratio. Therefore, they have high catalytic activity and good performance. They are desirable catalysts for slurry-phase hydrocracking of heavy oil.

Oil-soluble catalysts are produced by the combination of an oxide, a sulfide, or a salt of metal selected from group IV through group VIII including transition metal-based catalysts derived from the organic acid salt or metal–organic compounds of vanadium, tungsten, chromium, iron, etc.

UOP Company took a vanadium catalyst precursor, V_2O_5, contacting with ammonium sulfide to form an ammonium salt of the vanadium sulfide.[32] The vanadium sulfide catalyst is a colloidal dispersion with a hydrocarbon feedstock preferably containing asphaltenes and organometallic compounds and has the effect of inhibiting coke formation, deasphaltene, and demetal in hydrocracking conditions.

Exxon Co. takes molybdenum alicyclic aliphatic carboxylic acids and molybdenum naphthenate oil-soluble metal compound as catalysts. Oil-soluble catalyst is converted to a solid, noncolloidal catalyst in the presence of a hydrogen-containing gas under hydroconversion conditions.[33,34] By contrast Alberta Research Co. takes oil-soluble molybdenum colloidal or molecular catalysts.

Strausz[35,36] took molybdenum naphthenate and nickel di-2-ethylhexanoate as the metal precursor for hydrocracking heavy oil. The precursor will chemically react with the micellarly dispersed asphaltene in bitumen. The reaction appears to involve ligand exchange and molecular complexation mechanisms binding the metal to the asphaltene micelle. It is believed that the product takes the form of a micelle–metal complex and it is the decomposition of this complex at hydrocracking conditions that yields the metal oxide/sulfide particles that are catalytic. It was reasoned that the strong chemical affinity between the metal and asphaltene might survive the hydrocracking step. If so, the possibility that the metal might remain bonded to the asphaltenes or to the coke formed from it raised through hydrocracking.

Cyr[37] takes an oil-soluble, metal-containing compound additive, such as iron pentacarbonyl or molybdenum 2-ethyl hexanoate, and additive mixing in the reactor with stripping, combining to yield well dispersed colloidal catalytic particles, which function to impede coke evolution and provide high conversion of the high boiling (504 °C) fraction of the feedstock. It was postulated that a well dispersed, oil-soluble, metal compound might be used to react in situ with sulfur moieties of the bitumen VTB to produce colloidal, catalytic particles having wetting characteristics that would enable the colloidal particles to collect at the surfaces of the precursor spheroids and inhibit the spheroids from coalescing. Chemical analysis of the coke sample indicated that metal sulfide additive was associated therewith in a significant amount and that most of the metal sulfides were colloidal, typically being less than 0.1 nm in dimension.

Shen et al.[38] reported hydrocracking of Liaohe vacuum residue in the presence of oil-soluble catalysts, molybdenum dithiocarboxylate, nickle naphthenate and iron naphthenate, as well as their mixtures, conducted in an autoclave. The test results indicated that a slight synergism occurred when the bimetallic oil-soluble catalysts were used. The active forms of the catalysts generated from the oil-soluble catalyst precursors were nonstoichiometric sulfides. Complex sulfides could be produced in the presence of multicomponent catalysts.

Dong[39] used oil-soluble catalysts, developed by Fushun Research Institute of Petroleum and Petrochemicals (FRIPP) for hydrocracking of residue in a suspension bed, which was described in the article. Total distillate (<538 °C) yield of over 70% was obtained when hydrocracking Gudao vacuum residue in an autoclave using the oil-soluble catalysts. The catalysts exhibited high activity and capability for inhibiting coke formation.

The oil-soluble catalysts have highly active forms and easy dispersion; however, their high costs greatly restrict their development in slurry-bed hydrocracking. Thus water-soluble, cheap inorganic compounds as catalysts became popular.

UOP[40,41] added a metal compound, a heteropoly acid, and water to an asphaltene-containing oil charge stock, and when

---

(32) Gatsis, J. G. Hydrocarbon hydrorefining process utilizing a nonstoichiometric vanadium sulfide catalyst. U.S. Patent 4,194,967, 1980.

(33) Bearden, R., Jr.; Aldridge, C. L. Hydroconversion of heavy hydrocarbons. U.S. Patent 4,134,825, 1979.

(34) Bearden, R., Jr.; Aldridge, C. L. Catalyst for the hydroconversion of heavy hydrocarbons. U.S. Patent 4,226,742, 1980.

(35) Strausz, O. P. Process for hydrocracking heavy oil. U.S. Patent 6,068,758, 2000.

(36) Strausz, O. P. Oil-soluble catalysts for the hydrocracking of Athabasca bitumen. *Fuel Energy Abstr.* **1996**, *37* (3), 176.

(37) Cyr, T.; Lewkowicz, L.; Ozum, B.; et al. Hydrocracking process involving colloidal catalyst formed in situ. U.S. Patent 5,578,197, 1996.

(38) Shen, R.; Zhao, H.; Liu, C.; Que, G. Hydrocracking of Liaohe vacuum residue on bimetallic oil-soluble catalysts. *Pet. Process. Petrochem.* **1998**, *29* (11), 10–12.

(39) Dong, Z.-x. Hydrocracking of Gudao vacuum residue using oil-soluble catalysts. *Ind. Catal.* **2003**, *11* (4), 27–29.

(40) Gatsis, J. G. Catalyst for the hydroconversion of asphaltene-containing hydrocarbonaceous charge stocks. U.S. Patent 5,474,977, 1995.

(41) Gatsis, J. G. Catalyst for the hydroconversion of asphaltene-containing hydrocarbonaceous charge stocks. U.S. Patent 5,288,681, 1994.

the metal compound is added to the heavy asphaltene-containing hydrocarbonaceous oil in the presence of water, the metal compound is converted to an organometallic compound under hydroconversion conditions. When a heteropoly acid is present, there is a synergistic effect on the catalytic properties of the slurry catalyst produced.

Exxon Research and Engineering Company[42–47] utilized a catalyst for hydrocracking heavy oil, coal, or mixtures thereof. Catalyst was prepared by first forming an aqueous solution of phosphomolybdic acid and phosphoric acid at a specified ratio of atoms of P/Mo and subsequently adding this solution to a hydrocarbon material, followed by heating in the presence of H_2S to form a solid molybdenum and phosphorus-containing catalyst.

Chevron[48–52] dissolved a molybdenum compound, such as MoO_3, in aqueous ammonia to form ammonium molybdates (the ammonium molybdates are soluble in the aqueous medium) and then injected hydrogen sulfide to the dissolving stage. The addition of hydrogen sulfide causes some dissolved molybdenum to separate as ammonium molybdenum oxysulfide solids. They had discovered that a significant improvement in the catalyst's activity is achieved by performing a significant portion of the multistage sulfiding of the precursor ammonium salt in an aqueous phase.

The ammonia removal step has a favorable effect upon catalyst activity, because ammonia may be a depressant to the activity of a hydrogenation catalyst. Ammonia removal is beneficial to catalyst activity because excess ammonia will tend to neutralize the relatively small amount of acid sites of the catalyst–hydrogen sulfide system and remove any small amount of cracking and denitrogenation activity that may be present. But primarily, the ammonia will be adsorbed at metal sites and constitute a catalyst poison.

A highly dispersed iron-based ionic liquid or liquid-gel catalyst,[53] which may be anion-modified and metal-promoted, has high catalytic activity and is useful for hydrocracking reactions for carbonaceous feed materials. The catalyst is produced by aqueous precipitation from saturated iron salt solutions such as ferric sulfate and ferric alum and may be modified during preparation with anionic sulfate and promoted with small percentages of at least one active metal such as cobalt, molybdenum, palladium, platinum, nickel, or tungsten or mixtures thereof. The resulting catalyst may be used in a preferred ionic liquid form or in a liquid-gel form, and either fluidic form can be easily mixed and reacted with carbonaceous feed materials such as coal, heavy petroleum fractions, mixed plastic waste, or mixtures thereof.

The water-soluble bimetallic and multimetallic catalysts developed by Fushun Research Institute of Petroleum and Petrochemicals[54] are characterized by high activity and no coking (benzene insoluble, <1 %). When the bimetallic Mo–Ni catalyst is used to treat atmospheric residue and vacuum residue, the yields of the distillates (<500 °C) reach over 70% and 60%, respectively. While with use of the multimetallic catalyst to Liaohe atmospheric residue and vacuum residue from Saudi Arabian light and middle crude, the yields of the distillates (<500 °C) reach 75% and 70%, respectively.

Sodium molybdate, nickel nitrate, and iron nitrate were used as precursors to prepare water-soluble multimetal composite catalysts for residue suspended bed hydrocracking.[55] Results showed that the coke inhibiting behavior of the catalyst, in terms of *R* (conversion–coke inhibiting–cracking inhibiting index), was arranged in sequence of Mo–Ni–Fe > Mo–Fe > Ni–Fe > Mo > Fe from the higher level to the lower level. Results of X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) and X-ray photoelectron spectra (XPS) analyses indicated that with the increase of medium viscosity, improved dispersion of the catalyst in the medium was observed, the particle size of the catalyst decreased, and the surface area of the catalyst increased. The analyses also indicated that with the increase of sulfurization temperature, the degree of activation (the extent to turn into sulfides) increased, the crystallinity of the sulfides (the activated phase in the catalyst) increased, and the catalyst particle size increased, while the surface area decreased and the degree of catalyst dispersion in the medium decreased.

The vacuum residue of Gudao crude oil was hydrocracked in a batch autoclave in the presence of the dispersed-phase catalysts.[56] Five oil-soluble organometallic catalysts and eight water-soluble inorganic catalysts were evaluated. The experimental results indicated that the water-soluble catalysts added to autoclave using the high-dispersive method were effective for the residue hydrocracking. Among the catalysts tested, oil-soluble molybdenum lithiocarboxylate (MoDTC) and molybdenum lithiophosphate (MoDTP) and water-soluble ammonium heptamolybdate (AHM), ammonium phosphor-molybdate (APM), and ammonium tetrathiomolybdate (ATM) were more effective.

Atmospheric residue of Karamay was hydrocracked in the presence of multimetal dispersed catalyst in slurry bed[57] keeping the total volume space hourly velocity constant. The hydrocracked tail oil was pumped back and mixed with the fresh feed for recycling. Three optional models of recycling were used: atmospheric bottom residue recycling, vacuum bottom residue recycling, and partial vacuum bottom residue mixed with vacuum gas oil recycling. The results showed that the recycling of bottom oil raised the total conversion. The catalyst fines

---

(42) Bearden, R., Jr. Hydrocracking with phosphomolybdic acid and phosphoric acid. U.S. Patent 4637870, 1987.

(43) Bearden, R., Jr.; Aldridge, C. L. Hydrocracking with aqueous phosphomolybdic acid. U.S. Patent 4637871, 1987.

(44) Bearden, R., Jr. Hydroconversion process using a sulfided molybdenum catalyst concentrates. U.S. Patent 4,740,295, 1988.

(45) Bearden, R., Jr. Method of preparing a hydroconversion sulfided molybdenum catalyst concentrates.U.S. Patent 4,740,489, 1988.

(46) Bearden, R., Jr. Hydroconversion process using a sulfided molybdenum catalyst concentrates. U.S. Patent 5,039,392, 1991.

(47) Hou, Z.; Bearden, R., Jr.; Thomas D. F.; et al. Slurry hydroprocessing using bulk multimetallic catalysts. U.S. Patent 6,712,955, 2004.

(48) Lopez, J.; McKinney, J. D.; Pasek, E. A. Heavy Oil Processing. U.S. Patent 4,557,821, 1985.

(49) Lopez, J.; Pasek, E. A. Process for preparing heavy oil hydroprocessing slurry catalyst. U.S. Patent 4,710,486, 1987.

(50) Lopez, J.; Pasek, E. A.; Cugini, A. V. Heavy oil hydroprocess including recovery of molybdenum catalyst. U.S. Patent 4,762,812, 1988.

(51) Lopez, J.; Pasek, E. A. Dispersed group VIB metal sulfide catalyst promoted with Group VIII metal. U.S. Patent 4,824,821, 1989.

(52) Lopez, J.; Pasek, E. A. Heavy oil hydroprocessing with Group VI metal slurry catalyst. U.S. Patent 4,857,496, 1989.

(53) Pelrine, B. P.; Comolli, A. G.; Lee, L.-K. Iron-based ionic liquid catalysts for hydroprocessing carbonaceous feeds. U.S. Patent 6,139,723, 2000.

(54) Wang, X.; Li, Y.; Zhang, Z. Study on homogeneneous catalyst and process for residue suspended bed hydrocracking. *Pet. Refinery Eng.* **2000**, *30* (4), 50–52.

(55) Guan, C.; Wang, Z.; Guo, A.; Que, G. Sulfurization of water-soluble catalyst for suspended bed hydrocracking of residue. *Acta Pet. Sin. (Pet. Process. Sect.)* **2004**, *20* (2), 75–80.

(56) Liu, C.; Que, G.; Liang, W.; Zhu, Y. Hydrocracking of Gudao residue by using dispersed-phase catalysts I. Preliminary evalution of catalysts. *Pet. Refining* **1993**, *24* (3), 57–62.

(57) Zhou, J.; Deng, W.; Liu, D.; Liang, S.; Que, G. Effect of vacuum bottom residue recycling on slurry bed hydrocracking of residue. *Acta Pet. Sin. (Pet. Process. Sect.)* **2001**, *17* (4), 82–85.

dispersed in the bottom oil still remained active. It can inhibit the formation of insoluble toluene.

4. Future Prospectives

As we known, the increasing demand for distillate fuels for transportation and the severity of environmental regulation make the hydrogenation process of vacuum residue a necessity for almost all modern refinery schemas. Slurry-bed hydrocracking residua technology as a new technology has already attracted attention by the world. We can predict that slurry-bed hydrocracking residua technology by right of its only advantages will occupy an important position by lowering production rate of the bottom oil, higher production rate of the light quality oil, and solving the self-contradiction aspect of the petroleum product supply and demand.

EF700253F