

**Abstract**  
**Process Economics Program Report 214A**  
**HEAVY OIL HYDROTREATING**  
**(December 2007)**

Worldwide, the importance of hydrotreating heavy oils is growing in order to meet the demand for low sulfur, improved quality heavy fuel oils and feedstocks for fluid catalytic cracking (FCC), resid FCC and, lately, hydrocracking and coking. Increasing production of higher sulfur and gravity crude oils, increasingly stringent sulfur and other environmental regulations and increasing global demand for transportation fuels are factors driving the growth. Furthermore the production and refining of bitumens and other heavy alternate crude oils (syncrudes) is forecast to increase significantly in North America.

Heavy petroleum oils are characterized as boiling above about 650°F (343°C) and having relatively high specific gravity, low hydrogen-to-carbon ratios, and high carbon residue. They contain large amounts of asphaltenes, sulfur, nitrogen and metals, which increase hydrotreating difficulty. Feed properties are important in setting the process design and operating conditions.

Hydrotreating of heavy oils reacts them with hydrogen over a selective catalyst under high pressure and temperature to cleave sulfur, nitrogen and metals from the oil and to partially saturate polynuclear aromatic rings in order to reduce the carbon residue. Sulfur and nitrogen leave as H<sub>2</sub>S and NH<sub>3</sub>. As metals and coke accumulate on the catalyst, the reactor temperature is increased to compensate for reduced activity until the maximum operating temperature is reached.

Advances in heavy oil hydrotreating are a combination of catalyst development and reactor development. Heavy oil hydrotreating is performed in a series of reactors, each containing catalyst optimized for a different purpose. The reactors in the hydrotreating unit may be fixed bed, moving bed, ebullated bed or a combination. A guard bed protects downstream catalyst from metals and contributes to sulfur removal.

This PEP Report provides an overview of heavy oil hydrotreating developments in chemistry, catalysts, process and hardware technology since PEP Report 214, *Hydrotreating*, issued in 1996. The report then develops the process economics for hydrotreating two heavy oil feedstocks: vacuum gas oil (VGO) and the heavier atmospheric residue (AR), each by a generic, conventional hydrotreating process. Additionally, the economics of hydrotreating VGO by our concept of the new IsoTherming™ type process is evaluated.

Report No. 214A

## HEAVY OIL HYDROTREATING

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## 1 INTRODUCTION

Worldwide, the importance of hydrotreating heavy oils is growing in order to meet the demand for low sulfur, improved quality heavy fuel oils and feedstocks for fluid catalytic cracking (FCC), resid FCC and, lately, hydrocracking and coking. Increasing production of higher sulfur and gravity crude oils, increasingly stringent sulfur and other environmental regulations and increasing global demand for transportation fuels are factors driving the growth. Furthermore the production and refining of bitumens and other heavy alternate crude oils (syncrudes) is forecast to increase significantly in North America.

Heavy petroleum oils are characterized as boiling above about 650°F (343°C) and having relatively high specific gravity (often less than 20 API), low hydrogen-to-carbon ratios, and high carbon residue. They contain large amounts of asphaltenes, sulfur, nitrogen and metals, compared to the next lower boiling crude oil fractions, the middle distillates.

During hydrotreating heavy oils are reacted with hydrogen over a selective catalyst usually having molybdenum with either nickel or cobalt and more frequently additional promoters on an alumina support. The reactions to cleave sulfur, nitrogen and metals from the oil and to partially saturate polynuclear aromatic rings in order to reduce the carbon residue occur under high pressure and temperature. These characteristics increase the complexity of the simultaneous networks for hydrodemetallization, hydrodenitrogenation, hydrodeasphalting and aromatic saturation reactions and cause hydrotreating difficulty through catalyst deactivation. As metals and coke accumulate on the catalyst, the reactor temperature is increased to compensate for reduced activity until the maximum operating temperature is reached.

Advances in heavy oil hydrotreating are a combination of catalyst development and reactor development. The method of feed introduction, the arrangement of the catalyst beds and the design and manner of operation of the reactors are important factors in residue hydrotreating. Heavy oil hydrotreating is performed in a series of reactors, each containing catalyst optimized for a different purpose. Depending upon the oil properties, the reactors in the hydrotreating unit may be fixed bed, moving bed, ebullated bed or a combination. A guard reactor protects downstream reactors from metals and contributes to sulfur removal.

This report reviews the heavy oil hydrotreating process with emphasis on developments since PEP Report 214, *Hydrotreating*, issued in 1996. Market related information on heavy oil supply, product regulations and catalytic metal price history is presented in Section 4, Industry Status. Section 5 reviews developments in the fundamental chemistry of the process, oil properties and catalysts. Processes and hardware technologies are reviewed in Section 6.

The report then develops process economics for hydrotreating two heavy oil feedstocks: vacuum gas oil (VGO), main feedstock to FCC units, and the heavier atmospheric residue (AR), resid FCC (RFCC) feedstock. Each feedstock is hydrotreated by a generic, conventional process. Additionally, the economics of hydrotreating VGO by our concept of the new IsoTherming™ type process is evaluated. Section 7 discusses VGO hydrotreating economics; Section 8, the AR hydrotreating economics.



## 2 CONCLUSIONS

From our technical and economic analysis, combined with our review of the literature and patents, we conclude:

1. Hydrotreating of heavy oils will grow due to the refining of heavier, high sulfur crude oils including bitumen, combined with increasing global demand for transportation fuels (especially those of low SO<sub>x</sub> and NO<sub>x</sub> emissions) and the imposition of new, low sulfur specifications for residual fuel oils and marine fuels that are expected by 2015.
2. Worldwide demand for heavy fuel oil is projected to continue to be relatively constant. However, demand for the heaviest grade, bunker fuel, which comprised about 33% of the market in 2005, could increase by 33% by 2015 due to growth in world trade.
3. Without new residue desulfurization investments, by 2015 a global shortage of 1 million B/D of low sulfur fuel oil could develop while at the same time a surplus exists of about 2 million B/D of high sulfur fuel oil. The key issue is: will the price spread between high and low sulfur oils be able to support the investment?
4. The price of the catalytic metals used in hydrotreating catalysts will continue to be cyclic and volatile since molybdenum and cobalt are by-products of other metals.
5. Hydrotreating heavy oils is a more complex process than hydrotreating middle distillates because of the asphaltenes and metal compounds not found in lighter oils.
6. The presence of asphaltenes and the associated metals deposition during residue oil hydrotreating make the catalyst pore diameter an important property.
7. On the basis of new analytical techniques, asphaltene molecular weight in the range of 1,000 to 20,000 measured by either gel permeation chromatography or by vapor phase osmometry is now believed to be high due to agglomeration during those procedures.
8. Heavy fuel oils may become unstable (breakdown) through heating-cooling cycles, contact with air and water during shipment and storage as well as through improper handling or the addition of improper additives.
9. Reaction mechanisms of hydrodesulfurization and hydrodenitrogenation are complex.
10. Our economic evaluation showed the battery limits investment cost estimated for a generic, conventional atmospheric hydrotreater to be 203 \$ million compared to 58 \$ million for a generic, conventional vacuum gas oil hydrotreater.
11. Our estimated before tax return on investment (ROI) of 63% and 85% for the conventional and IsoTherming™ vacuum gas oil processes shows excellent profitability. The atmospheric residue hydrotreating process earned a respectable 26.5% return.
12. Our concept of an IsoTherming type process was both 22% less capital intensive (BLI of 44.4 versus 57.7 \$million) and more profitable (ROI of 85% compared to a very good 63% ROI) than our version of a generic conventional process. The spread between the value of the feedstock and product was the greatest factor affecting ROI.

### 3 SUMMARY

Worldwide, the importance of hydrotreating heavy oils is growing in order to produce low sulfur, improved quality feedstocks for fluid catalytic cracking (FCC), resid FCC (RFCC) and, lately, hydrocracking and coking feedstocks. The traditional role of improving the quality of fuel oils is also growing due to crude oil supply and environmental factors. This PEP Report provides an overview of heavy oil hydrotreating developments in chemistry, catalysts, process and hardware technology since PEP Report 214A, *Hydrotreating*, issued in 1996. The report then develops process economics for hydrotreating two heavy oil feedstocks: vacuum gas oil (VGO) and the heavier atmospheric residue (AR). The economics of generic, conventional VGO and AR processes are determined plus the economics for our concept of the new IsoTherming™ type process. A 55,000 B/D FCC feedstock IsoTherming VGO unit is under contract following several commercialized units operating for diesel fuel. Below we briefly summarize the most significant developments in heavy oil hydrotreating.

#### COMMERCIAL ASPECTS

Worldwide, the importance of hydrotreating heavy oils for FCC feedstocks and fuel oil is increasing due to:

- More heavy crude oils and oil sands bitumen are being refined,
- Increasing demand for near zero sulfur vehicle fuels,
- Growing regulatory requirements for low sulfur marine and stationary boiler fuels,
- Increasing recognition of the benefits of removing catalyst poisons of downstream processes, which is required for optimum performance.

Hydrotreating is a preferred process for removing the high levels of sulfur, nitrogen and oxygen found in heavy crude oils. These heteroatoms concentrate in the heavier distillation fractions. Hydrotreated heavy oils are primarily intermediate refinery streams as feedstocks mainly for FCC and RFCC units but some applications are developing such as removing metals and nitrogen to extend the catalyst life of hydrocrackers.

Of the world's 656 refineries, 22% appear to have heavy oil hydrotreating capacity and 24 or 3.7% have a residue oil hydrotreater. These units are predominately located in the Asia-Pacific region. Only 36% of capacity is in North American refineries. Worldwide heavy oil capacity totals 17,308,000 B/cD or 20.4 vol% of the world's 84,984,000 B/cD crude oil capacity.

The global residual fuel oil market through 2015 is likely to be characterized by:

1. Continuing fuel oil contamination problems
2. Declining inland fuel oil demand due to competition from natural gas and further reduction in sulfur specifications
3. A growing international bunker fuel market with a trend towards lower sulfur specifications and widening price differentials between low and high sulfur fuel oils

In 2005, about one-third of the 10 million B/D fuel oil market was the heaviest grade, bunker fuel oil. Worldwide overall demand for heavy fuel oil is projected to remain relatively constant. The inland demand for fuel oil is projected to continue to decline. But due to continued growth in world trade, especially driven by economic growth in China, the demand for bunker fuel could increase by about one-third between 2005 and 2015.

Without new residue desulfurization investments (or development of on-board exhaust gas scrubbing), by 2015 there could be as much as a 1 million B/D global shortage of low sulfur fuel oil concurrent with a surplus of about 2 million B/D of high sulfur fuel oil. The low sulfur fuel oil shortage will be greater in some areas such as the U.S. and parts of Asia and less in other areas such as some regions of Europe. U.S. residual fuel oil consumption is projected by the Energy Information Administration to most likely decrease from 0.92 million B/D in 2005 to 0.82 million B/D in 2020 but to increase slightly to 0.83 million B/D in 2030. It is well known that the trend in crude oil supply continues to heavier, higher sulfur oils. Oil sands bitumen production is projected to grow very rapidly.

The emission regulations protocol adopted by the International Maritime Organization, MARPOL, became effective in 2005. Amendments that must be adopted by 2008 will result in the shipping industry moving away from high sulfur fuel oil to low sulfur fuel oil. These amendments include lower SO<sub>x</sub> emissions, lowering the sulfur cap in sulfur control areas to 1% or even 0.5%, lower NO<sub>x</sub> emissions limits on existing engines as well as new and new NO<sub>x</sub> control areas. This would take away a major outlet for heavy, high sulfur fuel oils.

The main catalytic metals in hydrotreating catalysts are molybdenum, nickel and cobalt. Catalysts account for about 11% of the cobalt market. Just about 7% of U.S. molybdenum consumption in 2004 and 2005 is estimated to have been used for catalysts. Molybdenum is primarily produced as a byproduct of copper refining while cobalt is a byproduct of nickel refining. Since the costs of producing these metals from primary mines are much greater than the by-product production costs, the prices of these metals historically have been cyclic and volatile. Since about 2004, the prices of molybdenum and nickel have risen rapidly while cobalt decline through 2005.

## **TECHNICAL ASPECTS**

The performance of a hydrotreating process depends upon the nature and concentration of the heteroatoms (sulfur, nitrogen, oxygen and metals) present in the feedstock, the product specifications, the catalyst properties (activity, selectivity and rate of deactivation), reactor design and operating conditions.

We review the properties of two major heavy oil feedstocks for hydrotreaters: FCC gas oil feedstock and oil sands bitumen with emphasis on bitumen derived gas oils since properties of residual oils and their catalytic cracking are reviewed in PEP Report 228. Heavy oils can be envisioned as composed of three major components: oil, resins and asphaltenes, which also contain heteroatoms (sulfur, nitrogen, oxygen and metals). A 20 year debate on the order of magnitude of asphaltene molecular weight now appears to be resolved by new analytical techniques and studies. The molecular weight range of 1000 to about 20,000 (by gel permeation chromatography and vapor pressure osmometry) is now believed to be high due to agglomeration during preparation or measurement.

Organosulfur compounds are usually present in all distillation fractions of crude oil; the concentration usually increases with boiling point. The low boiling fraction contains mainly mercaptans, sulfides and disulfides, which are very reactive in hydrotreating and are easily completely removed. For medium distillates, thiophenes, benzothiophenes and their alkylated derivatives predominate. These are more difficult to desulfurize than the mercaptans and

sulfides, but not as difficult as sulfur compounds found in the heavier distillate fractions or in the residue oil fractions. The heavy distillates contain mainly alkylated benzothiophenes, dibenzothiophenes and alkylated dibenzothiophenes plus some polynuclear aromatic sulfur compounds.

Most of the nitrogen present in heavy crude oils resides in heterocyclic organonitrogen compounds of either basic or nonbasic ring structures. The nonbasic nitrogen compounds are more difficult to remove with conventional sulfided NiMo catalysts than the basic compounds. The reaction mechanisms of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are complex and derived largely from model compound studies. For example, it is well known that nitrogen-containing compounds inhibit HDS. However, the presence of H<sub>2</sub>S significantly increases the HDN reaction rate of heavy gas oil.

The surface of HDS catalysts is generally believed to contain two types of adsorption sites: one site competitively adsorbs the sulfur molecule such as dibenzothiophene and its products; the other site adsorbs H<sub>2</sub>. Adsorbed hydrogen is dissociated into hydrogen atoms. The hydrogen atoms migrate (spillover) to the adsorbed sulfur molecule (the catalyst's MoS<sub>2</sub> phase) where hydrogenation occurs on weakly reduced sites or hydrogenolysis occurs on strongly reduced site. Research has identified a number of elements in addition to cobalt and nickel that can be used as additives for CoMo and NiMo catalysts.

The nature of the support strongly influences the sulfided molybdenum active phases through differences in interactions between the support and catalytic metals. Hydrotreating catalysts are made in various average pore sizes, in several pellet shapes and with active metal combinations of primary, secondary and even tertiary elements. Pore diameter is an important property for residue hydrotreating due to the large asphaltene molecules and associated metals deposition and diffusion considerations. Large pore demetallization catalyst is used in the first bed while smaller pore, more active HDS/HDN catalyst is used in the following bed or beds.

Rapid catalyst deactivation is a major operational and economic problem in hydrotreating of heavy oils. Under favorable reaction conditions coking occurs at relatively low overall rates. The main mechanisms for catalyst deactivation of hydrotreating catalysts are the formation of coke and metal deposits on the catalyst. Deactivation by poisoning, fouling, aging or sintering can occur but are relatively infrequent.

Advances in residue hydrotreating are a combination of catalyst development and reactor development. The method of feed introduction, the arrangement of the catalyst beds and the design and manner of operation of the reactors are important factors in residue hydrotreating. Hydrotreating is performed with a series of reactors, each with catalyst optimized for a different purpose. Depending upon the residue properties, the reactors in a hydrotreating unit may be fixed bed, moving bed, ebullated bed or a combination. A guard reactor protects downstream reactors from metals and contributes to sulfur removal.

Hydrotreating processes for heavy oils are surveyed. One newly commercialized process is IsoTherming™. This is a hydrotreating process developed and commercialized in a 2003 startup by Process Dynamics, Inc. and recently acquired by DuPont. A contract was awarded in November, 2006 to revamp a 55,000 B/D gas oil hydrotreater to produce 800 ppm sulfur catalytic cracking feedstock. The process is differentiated from other processes by dissolving the hydrogen into the feed oil prior to the reactor rather than supplying the hydrogen to the reactor in a gas phase. The reactors are fixed beds operated liquid full. Dissolving the hydrogen into the oil allows higher reactor space velocities and hence smaller reactors than conventional reactors. Hydrogen recycle is eliminated. A portion of the reactor effluent is recycled to return hydrogen to the reactor. The oil recycle is a means of removing heat causing the reactor to operate more isothermally, which improves yields with less light ends made.

Feed properties are important in setting the operating conditions. The main operating variables for hydrotreating reactors are: hydrogen partial pressure, reactor temperature, liquid hourly space velocity. Important secondary variables include hydrogen purity and recycle ratio and H<sub>2</sub>S partial pressure. The catalyst ages due to accumulation of metals and coke. Reactor temperature is raised over time to compensate for the loss in catalytic activity. For a grassroots unit, the design pressure and catalyst type are two important decisions. A higher pressure reduces reactor volume, reducing catalyst costs. Higher pressure also favors hydrogenation that improves HDS activity, aromatics saturation and conversion, which increases hydrogen consumption. The rate of catalyst deactivation is reduced. However, the operating pressure is limited due saturation of the catalyst and capital costs.

FCC feed hydrotreating is performed mainly to remove sulfur, metals and carbon residue to improve the FCCU performance. The reduction in nitrogen, which is a temporary FCC catalyst poison, is usually a secondary benefit. Ultra low sulfur gasoline and near zero sulfur diesel fuel requirements have increased the benefits of severe feed hydrotreating. With sufficient hydrotreating, the FCCU remains the primary conversion process capable of producing ultra low sulfur gasoline and LCO that is easier to hydrotreat for blending to make near zero sulfur diesel fuel.

## **ECONOMIC ASPECTS**

In this report, we develop the process economics for hydrotreating two heavy oil feedstocks, vacuum gas oil and atmospheric residue. VGO is the main feedstock to FCC units while atmospheric residue (AR) is a common feedstock to resid FCC (RFCC) units. The AR feedstock is much more difficult to hydrotreat than the VGO feedstock due to higher metals content, higher and harder to reach sulfur and nitrogen (a catalyst poison) in the asphaltenes fraction and high carbon residue. Reduction in these properties is the main purpose of hydrotreating and creates the value of the process. Economics for two VGO hydrotreating process are presented: a generic, conventional VGO process and a process design based on the new IsoTherming™ process. For the AR, economics of a generic, conventional process design is developed. Unit feedstock capacity of each plant is 30,000 BPSD equal to 28,500 BPCD at 0.95 operating factor. Table 3.1 summarizes the economic results for each process.

The battery limit investment of 58 \$ million or 1,933 \$/BPSD for the VGO conventional base case 30,000 BPSD unit compares favorably with a published 55 \$ million inside battery limits cost estimate for a hydrotreater of the same capacity. Our 44 \$ million BLI cost estimate for our concept of a IsoTherming type process, showed a significant 22% reduction but not a 50% reduction in cost compared to the conventional process of a proprietary analysis, possibly due to differences in scope and design. Our designs are not optimized and may include more items such as the amine absorber-regenerator. The reduction in capital arises from the use of smaller liquid full fixed bed reactors instead of trickle bed reactors, the elimination of the recycle hydrogen compressors, a considerably smaller amine unit and fewer separators and associated equipment with only the addition of static mixers and a recycle oil pump.

The 146 \$ million or 4,875 \$/BPSD BLI estimate for the AR unit coincidentally equaled a published estimate when scaled for capacity and adjusted for inflation.

**Table 3.1**  
**SUMMARY OF COST ESTIMATES FOR HYDROTREATING VGO AND AR**

<b><u>Type Process</u></b>	<b><u>VGO Hydrotreater Conventional</u></b>	<b><u>IsoTherming™</u></b>	<b><u>AR Hydrotreater Conventional</u></b>
Feedstock	VGO blend	VGO blend	Arabian Heavy AR
Capacity <sup>a</sup> , BPSD	30,000	30,000	30,000
Nominal Reactor Pressure, psig	1,500	1,500	2,200
Capital Investment, \$ millions			
Battery Limits Investment (BLI)	57.7	44.4	146.2
Off-sites	30.3	26.3	56.7
Total Fixed Capital (TFC) <sup>b</sup>	88.0	70.7	202.9
Production Costs, ¢/lb FCC feed			
Raw Materials	16.53	16.44	13.37
Product Credits	-0.18	-0.13	-0.81
Utilities	0.18	0.18	0.24
Total Labor <sup>c</sup>	0.10	0.09	0.18
TOTAL DIRECT OPERATING COSTS, ¢/lb	16.68	16.62	13.11
Indirect Costs <sup>d</sup>	0.49	0.41	0.93
NET PRODUCTION COST, ¢/lb	17.17	17.03	14.04
Pretax ROI, %/yr	63%	85	26.8
FCC Feedstock Product Value, ¢/lb	18.84	18.84	15.63
Value of FCC Feed required for 25%/yr ROI, ¢/lb	17.83	17.56	15.52

<sup>a</sup> At 0.95 on stream factor.

<sup>b</sup> Total Fixed Capital includes a 15% contingency, utilities and tankage investments and allowances for general services facilities and for general waste treatment.

<sup>c</sup> Includes operating labor, control laboratory workers and maintenance labor. The number of operators is 4 per shift in all cases.

<sup>d</sup> Includes plant overhead, taxes and insurance, depreciation at 10%/y of TFC, general & administrative, sales and research expenses.

The product value of each process depends highly upon the spread between the feedstock and product value. By-products are small by design to maximize the main product. Raw material costs are by far the largest cost area. Comparing the production costs of the three processes, the VGO processes have a higher net production cost than the AR process because of the higher feedstock value. The IsoTherming type process shows a reduction in raw material cost since hydrogen is used more efficiently and less hydrogen is purged.

The ROI of the IsoTherming type process (85%) was significantly greater than the ROI of the conventional process (63%). Both these ROI's are historically high due to the state of the refining markets in mid 2006. The higher ROI of the VGO processes compared to the AR process (a profitable 26.5%, just above the 25% ROI used as one investment screening guide) is in part a result of the price spreads between feedstock and product.

## 4 INDUSTRY STATUS

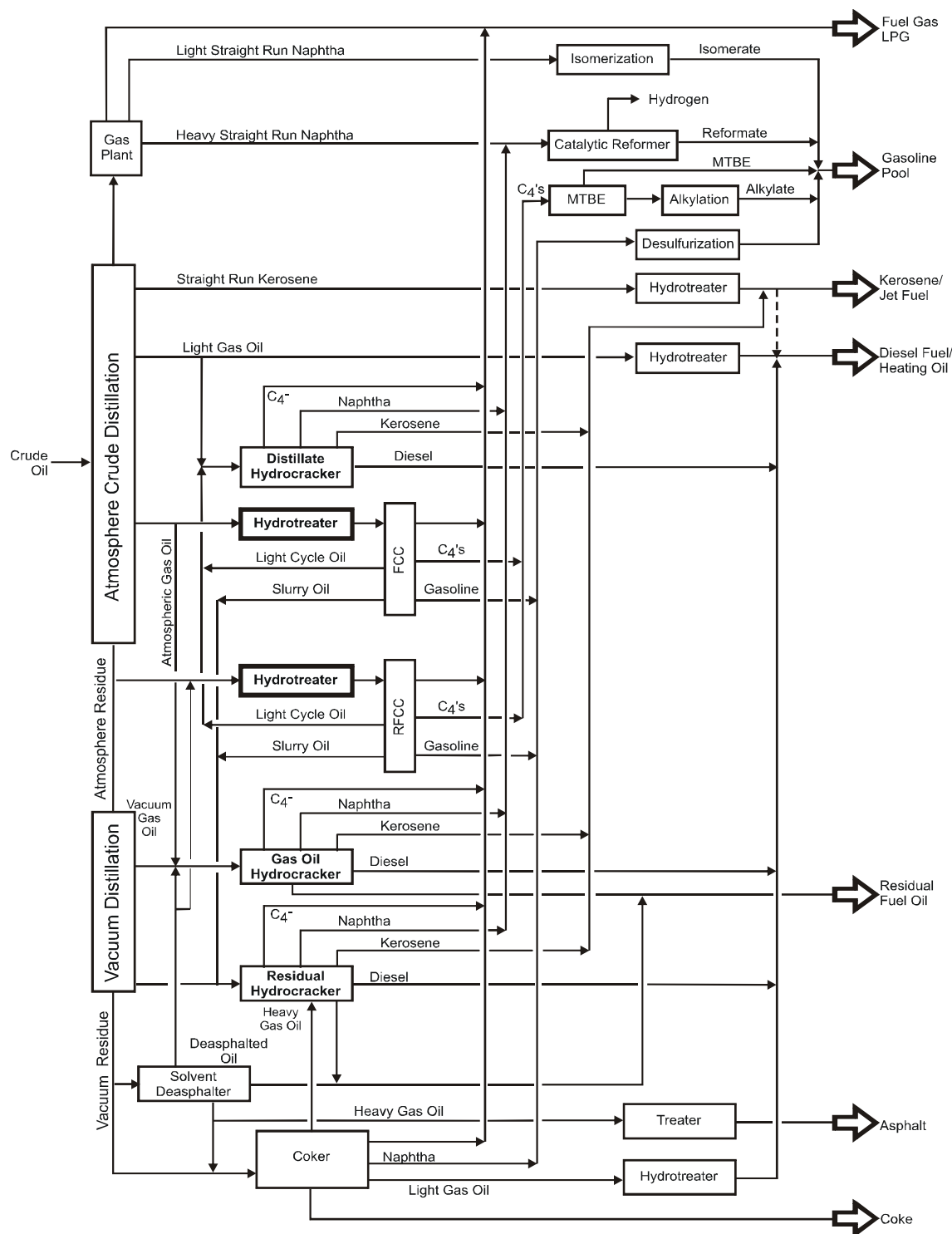
World crude oil demand is forecast to grow about 1.5%/yr and to supply an increasing percentage of transportation fuels. In the United States, crude oil demand growth is projected to increase about 1.1%/yr through 2030. U.S. refiners are refining increasingly higher sulfur, heavier crude oils, which now account for almost all the growth in U.S. crude oil imports. The additional production of heavy crude oils includes increases in bitumen produced syncrudes and bitumen blends.

Major reserves of oil sands are located in Canada, Venezuela, Malagasy, Albania, Trinidad, Russia, Romania and the United States. Venezuela's Orinoco heavy oil belt and Alberta Canada's recoverable bitumen account for 3.6 trillion barrels of heavy oil and bitumen reserves. Canadian oil sands will be a major source of future crude oil supply in North America, projected to increase from 1 million bpd to 3 million bpd by 2015. Heavy crude oils and bitumen contain high amounts of sulfur, nitrogen, carbon residue and metals that concentrate in the heavy gas oil and residue fractions. These contaminants must be removed to meet new heavy fuel oil specifications and to protect down stream refining catalysts. Since the composition of bitumen and bitumen derived crudes and their level of contaminants are fundamentally different than conventional petroleum crude oils, additional refining is required to convert these oils into transportation fuels and fuel oils. Bitumen requires hydrotreating to obtain acceptable FCC yields. Hydrogen content of FCC feedstock is a critical parameter to optimize performance. Hydrocracking can convert the large amount of VGO into distillate fuels [214A015, 214A508, 214A509, 214A565].

Hydrotreating of heavy oil is performed primarily for desulfurization and demetallization of these oils for use as FCC and RFCC feedstocks and, lately, as hydrocracker and coker feedstocks (Figure 4.1). Hydrocracker feed is hydrodesulfurized to protect the metallurgy of the hydrocracker. Coker feed is hydrodemetallized and hydrodesulfurized to meet petroleum coke specifications. In 2007, approximately 46% of FCC feedstock worldwide is resid-based. Hydrotreat FCC feedstock is growing from a base of less than 20% of all FCC feeds. The imposition of new sulfur specifications on residual fuel oils and on marine fuels expected between now and 2015 will require new investment in residue oil hydrotreating (or the rapid development of unproven on-board exhaust gas scrubbing) [214A020, 214A526, 214A527].



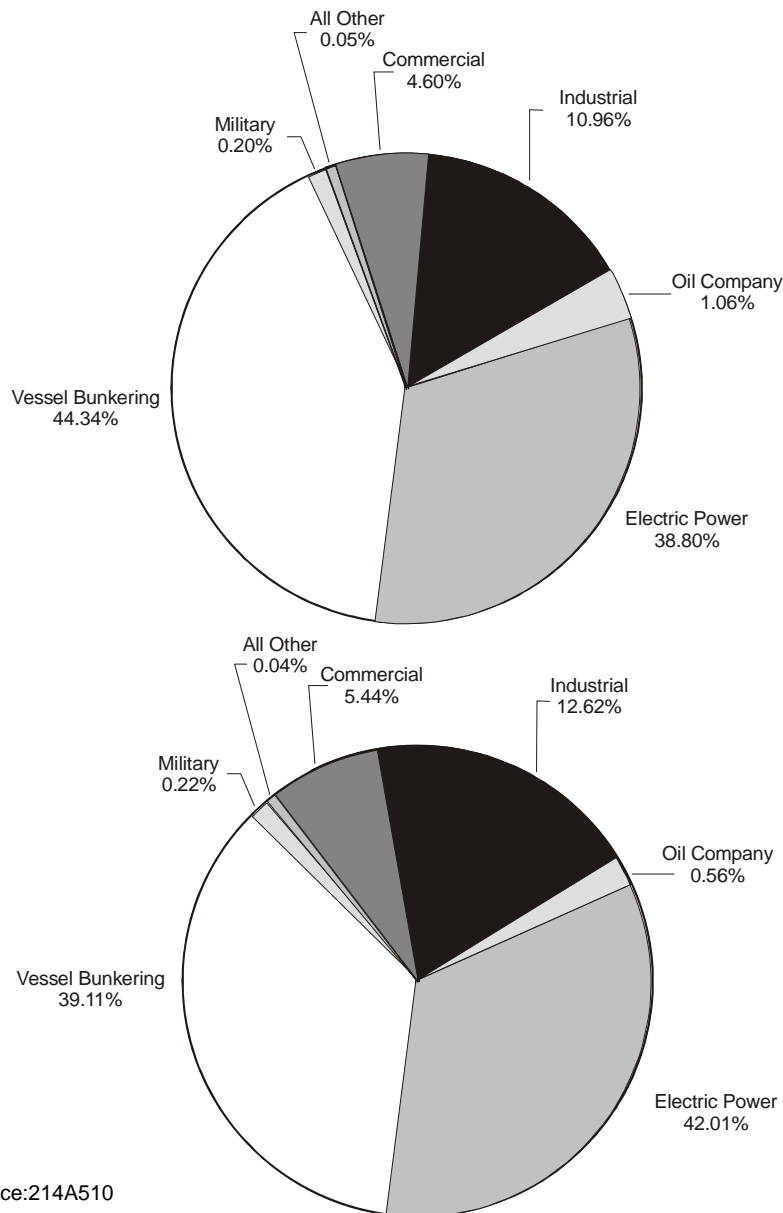
**Figure 4.1**  
**REFINERY HEAVY OIL HYDROTREATING APPLICATIONS**



Residual oil is sold as residual fuel oil or blended with suitable distillate oil to meet fuel oil viscosity specifications for marine vessels, power plants, commercial buildings and industrial furnaces. In the United States, end uses of residual fuel oil have changed little from 2000 to 2005 (Figure 4.2) although total sales (in units of 1,000 B/D) declined and recovered with the economy during this period:

<u>2000</u>	<u>2001</u>	<u>2002</u>	<u>2003</u>	<u>2004</u>	<u>2005</u>
911.0	881.2	699.6	772.1	867.1	920.0

**Figure 4.2**  
**U.S. ADJUSTED SALES OF RESIDUAL FUEL OIL BY END USE**



Residual fuel oil sells for less than the cost of crude oil due to its high sulfur content and the presence of heavy metals. Sulfur in the crude oil is concentrated in the residual oil distillation cut. Residual oil naturally contains 1 to over 6% sulfur. Residual oil may also contain high concentrations of heavy metals, mainly nickel and vanadium, which upon combustion produce ash that can foul burner systems. Hydrotreating residual oil removes sulfur and metals [214A047].

Worldwide overall demand for heavy fuel oil is projected to remain relatively constant. In 2005, about one-third of the 10 million B/D fuel oil market was bunker fuel oil. The inland demand for fuel oil is projected to continue to decline. Due to continued growth in world trade, especially driven by economic growth in China, the demand for bunker fuel could increase by about one-third between 2005 and 2015 [214A418].

## CRUDE OIL SUPPLY

Worldwide crude oil supply will continue well past 2030 to be produced predominantly from conventional oil and gas (as condensate) fields. Unconventional crude oil supplies, defined as any liquid hydrocarbon fuel, including liquids produced from energy crops, natural gas, coal, oil sands, and shale oil, will increase from 3.3 volume % (vol%) in 2005 to 6.9% in 2015 and to 9.3% in 2030. Synthetic crude oil produced from oil sands bitumen will be of increasing supply to U.S. refiners. Supplies of crude oil and synthetic crude oil are briefly discussed next.

### Conventional Crude Oil Supply

Worldwide conventional crude oil supply is projected by the Energy Information Administration to increase from 81.59 million B/D in 2005 to 90.9 million B/D in 2015 and 106.4 million B/D in 2030. This is an annual growth rate of 1.1% from 2005 to 2015 and also 1.1% from 2015 to 2030. Production in North America is forecast to vary about the 2004-2005 average production of 14.2 million B/D as shown in Table 4.1 [214A517].

**Table 4.1**  
**WORLD CRUDE OIL SUPPLY BY REGION**

MILLION B/D

	Actual		Forecast					Annual Growth, %		
	2004	2005	2010	2015	2020	2025	2030	2005-2015	2015-2030	2005-2030
<b>Conventional crude oil<sup>a</sup></b>										
North America	14.43	13.93	14.06	14.47	14.45	14.29	14.26	-0.35	-0.10	0.09
Europe	6.39	5.96	5.73	4.91	4.22	3.64	3.16	-0.69	-2.90	-2.51
Asia-Pacific	8.32	8.14	7.59	7.41	7.60	7.63	7.50	-0.22	0.08	-0.33
South & Central America	6.68	6.78	7.30	7.86	8.16	8.49	9.04	0.15	0.94	1.16
Former Soviet Union	11.48	11.99	13.96	15.21	16.20	17.22	18.10	0.44	1.16	1.66
Middle East	24.28	24.63	24.23	26.23	29.00	32.42	36.10	0.14	2.15	1.54
Africa	9.42	10.15	12.55	14.77	15.72	16.90	18.24	0.75	1.42	2.37
<b>World</b>	81.00	81.59	85.42	90.86	95.35	100.59	106.40	0.07	1.06	1.07
<b>World, Unconventional Production<sup>b</sup></b>	2.44	2.80	5.63	6.78	7.83	9.42	10.93	1.39	3.23	5.60
<b>World, Total</b>	83.45	84.39	91.05	97.64	103.29	110.01	117.33	0.11	1.23	1.33

Source: 214A517

<sup>a</sup> Includes condensates, natural gas liquids, other hydrogen and hydrocarbons for refinery feedstocks, alcohol and other

sources and refinery gains.

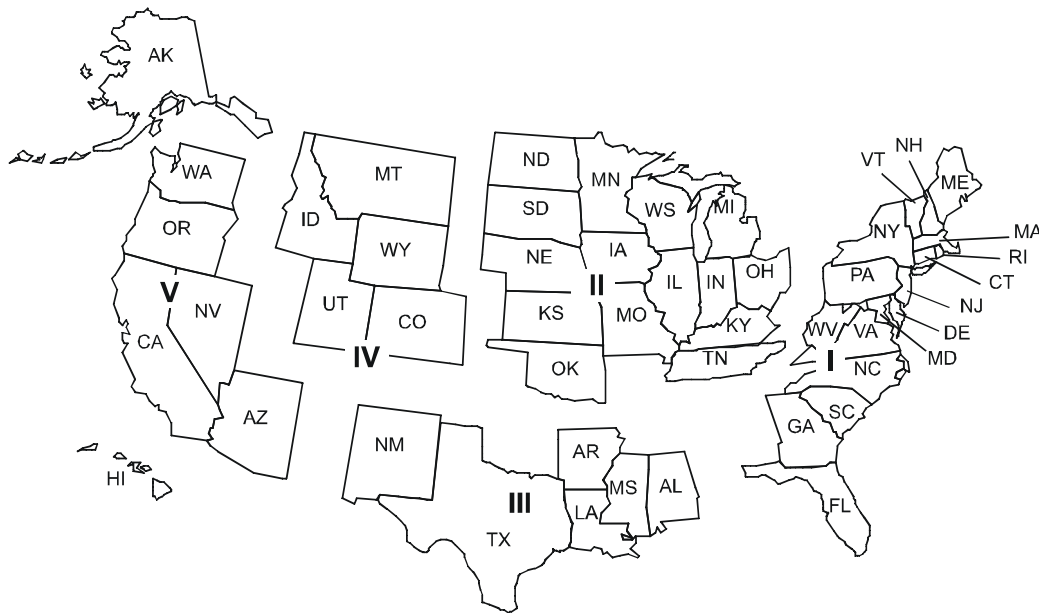
<sup>b</sup> Includes: liquids produced from energy crops, natural gas, coal, oil sands, and shale.

### Synthetic Crude Supply

Canada's recoverable oil sands reserves are estimated to be 175 billion barrels, making Canada's petroleum reserves second largest only to Saudi Arabia's 259 billion barrels. While production from Canada's 4 billion barrels of conventional reserves is projected to remain relatively constant at 2.0 million B/D through 2015, oil sands production is projected to grow very rapidly. Recent annual oil sands production has averaged 150,000 B/D. The U.S. Energy Information Administration forecasts oil sands production to reach 2.3 million B/D in 2015 and 3.7 million B/D in 2030. A second forecast is for world bitumen plus heavy oil production to increase from 1.7 million B/D in 2005 to 6.4 million B/D in 2030. Another forecast is for 23.6 million B/D of world energy demand to be met from unconventional oil or heavy oil by 2025 [214A026, 214A517, 214A565].

Synthetic crude oil is generally understood to be a blend of naphtha, distillate and gasoil range petroleum fractions boiling below the residue fraction (1050°F+, 565°C+). Currently most of the synthetic crude imports to the United States from production in Western Canada is refined in PADDs II and IV (Figure 4.3). Pipeline expansions will increase imports to PADD II and supply PADD V. Expected future pipeline systems will reach Texas (PADD III) and a seaport in British Columbia that could allow shipments to California and the Asia-Pacific region [214A026, 214A509].

**Figure 4.3**  
**U.S. PETROLEUM ADMINISTRATION FOR DEFENSE DISTRICTS**



Each synthetic crude and bitumen blend has a different composition and refining characteristics. Sweet blends comprise the majority of marketed synthetic crudes; the major ones are briefly described:

- Suncor Oil Sands Blend - Light, sweet Syncrude
- Syncrude Sweet Blend - Fully hydrotreated, fluid coker upgraded oil
- Husky Sweet Blend - Sweet, ebullated bed hydroprocessed and delayed coker oils
- Premium Albion Synthetic - Ebullated bed hydroprocessed oils

Suncor makes a range of sour blends customized for specific refinery processing capabilities. For example, their OSE crude is a blend of hydrotreated coker naphtha with non-hydrotreated coker distillate and coker heavy gas oil. OSV crude is a blend of hydrotreated coker naphtha with straight run distillate and straight run vacuum gas oil. Albion Heavy Synthetic is a blend of Premium Albion Synthetic crude with residue containing unconverted oil from the resid hydrocracker.

Greater than 400,000 B/D of bitumen is shipped diluted without upgrading. In addition to the syncrudes, several bitumen blends are marketed. *Dilbits* are blends of 70-75 LV% of bitumen and mostly C<sub>5</sub>-C<sub>12</sub> condensate that are processed in heavy crude refineries. The most common dilbits are Cold Lake Blend, Bow River and various Lloyd blends. *Synbits* are blends of sweet synthetic crudes (typically 50 LV%) and bitumen (50 LV%). They contain significant proportions of distillate range oil and are refined in medium crude refineries. The most common synbits are Christina Lake Blend and MacKay Heavy. *SynDilBits* are blends of condensate, hydrotreated synthetic crude and bitumen (typically about 65 LV%) that are also refined in medium crude refineries. Most common examples are Wabasca Heavy and Western Canadian Select (WCS). WCS may become the new market heavy crude. WCS is a proprietary blend developed by EnCana, Talisman, Canadian Natural Resources Limited and Petro-Canada. Each batch contains condensate, hydrotreated synthetic crude (Suncor Oil Sands Blend), heavy conventional crude, medium conventional crude, Cold Lake bitumen and Athabasca bitumen meeting the following specifications: 19-22 API, 7-9 wt% carbon residue, 2.8-3.2 wt% sulfur and a total acid number of 0.7-1.0 mg KOH/g.

Dilbits and WCS contain about three times the volume of resid than West Texas Intermediate crude oil and about 50% more vacuum gas oil but only half the distillate and naphtha [214A509]. Refinery constraints and modifications required to process Dilbits, Synbits and synthetic crude oil are summarized in Table 4.2. As pipeline system expansions (mentioned above) are built, potentially wide price differentials will provide an incentive for the refineries served to make modifications to process syncrude and bitumen blends [214A026].

**Table 4.2**  
**REFINERY CONSTRAINTS AND MODIFICATIONS FOR OIL SANDS CRUDE PROCESSING**

<u>Oil Sands Product</u>	<u>Constraint<sup>a</sup></u>	<u>Modification</u>
Dilbit	% resid	Larger cokers, ancillaries
	% sulfur	More HDS, recovery <sup>b</sup>
	Total Acid Number <sup>c</sup>	Metallurgy
	Asphalt <sup>d</sup>	Blending
Synbit	% Vacuum Gas Oil	Larger FCC, ancillaries
	% Sulfur	More HDS, recovery <sup>b</sup>
	Total Acid Number <sup>c</sup>	Metallurgy
	Asphalt <sup>d</sup>	Blending
Synthetic Crude Oil	% Vacuum Gas Oil	Hydrocracking
	% Distillate	Hydrocracking
	Diesel aromatics	Aromatics saturation

Source: 214A026

<sup>a</sup> Refinery constraints may also include product blending and environmental emissions.

<sup>b</sup> Refineries must reduce the sulfur content of gasoline and diesel.

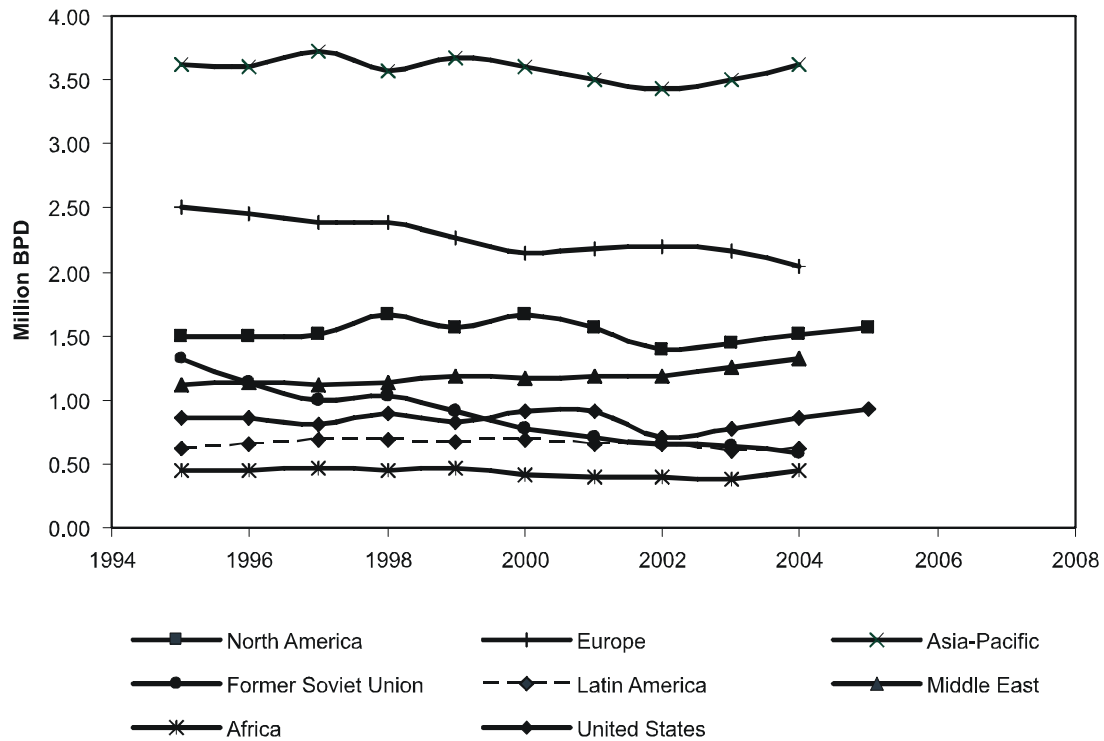
<sup>c</sup> High total acid number (TAN) for Athabasca, not Cold Lake.

<sup>d</sup> Asphalt from mined bitumen may be poor quality. Synbit asphalt quality is uncertain.

## RESIDUAL FUEL OIL MARKET

Worldwide demand for heavy fuel oil is projected to continue to be relatively constant (Figure 4.4). In 2005, about one-third of the 10 million B/D fuel oil market was bunker fuel oil. The inland demand for fuel oil is projected to continue to decline. Due to continued growth in world trade, especially driven by economic growth in China, the demand for bunker fuel could increase by about one-third between 2005 and 2015 [214A418].

**Figure 4.4**  
**WORLD DEMAND FOR RESIDUAL FUEL OIL**



Source: 214A511

The global residual fuel oil market through 2015 is likely to be characterized by

1. Continuing fuel oil contamination problems
2. Declining inland fuel oil demand due to competition from natural gas and further reduction in sulfur specifications
3. Growing international bunker fuel market with a trend towards lower sulfur specifications and
4. Widening price differentials between low and high sulfur fuel oils [241418].

Without new residue desulfurization investments (or development of on-board exhaust gas scrubbing), by 2015 there could be as much as a global 1 million B/D shortage of low sulfur fuel oil concurrent with a surplus of about 2 million B/D of high sulfur fuel oil. The low sulfur fuel oil shortage will be greater in some areas such as the U.S. and parts of Asia and less in other areas such as some regions of Europe. Since this wide an imbalance can not actually persist, equilibrium will be re-established. The key issue for the refining and shipping industries is whether the price spread between low and high sulfur fuel oils will be large enough to support refinery capital investment for hydrotreatment (or the rapid development of on-board exhaust gas scrubbing) [214A418]?

U.S. residual fuel oil consumption is projected by the Energy Information Administration under their most likely crude oil price scenario (reference case) to decrease from 0.92 million B/D in 2005 to 0.82 million B/D in 2020 but increase to 0.83 million B/D in 2030 (Table 4.3). This is an annual growth rate of -1.0%/y from 2005 to 2020, 0.12%/y from 2020 to 2030 and 0.41%/y from 2005 to 2030.

**Table 4.3**  
**FORECAST U.S. RESIDUAL FUEL OIL PRICE AND CONSUMPTION**

	Actual		Forecast					Annual Growth, %		
	<u>2004</u>	<u>2005</u>	<u>2010</u>	<u>2015</u>	<u>2020</u>	<u>2025</u>	<u>2030</u>	<u>2005- 2020</u>	<u>2020- 2030</u>	<u>2005- 2030</u>
<b>Crude Oil Price<sup>a</sup>, \$/B</b>										
High Price Estimate			62.53		82.60		92.93			
Reference Price Estimate	37.09	49.19	51.20	44.61	46.47	49.57	51.63			
Low Price Estimate			44.06		28.91		28.91			
<b>Residual Fuel Oil Price, \$/B</b>										
High Price Estimate			55.99		77.41		86.02			
Reference Price Estimate	32.05	41.41	47.84	41.16	43.97	47.00	48.97			
Low Price Estimate			41.12		26.50		27.64			
<b>Residual Fuel Oil Consumption, million B/D</b>										
Under High Price			0.78		0.73		0.76	-1.09	0.40	-0.76
Under Reference Price		0.92	0.79		0.82		0.83	-1.01	0.12	-0.41
Under Low Price			0.81		1.06		1.16	-0.85	0.91	0.93

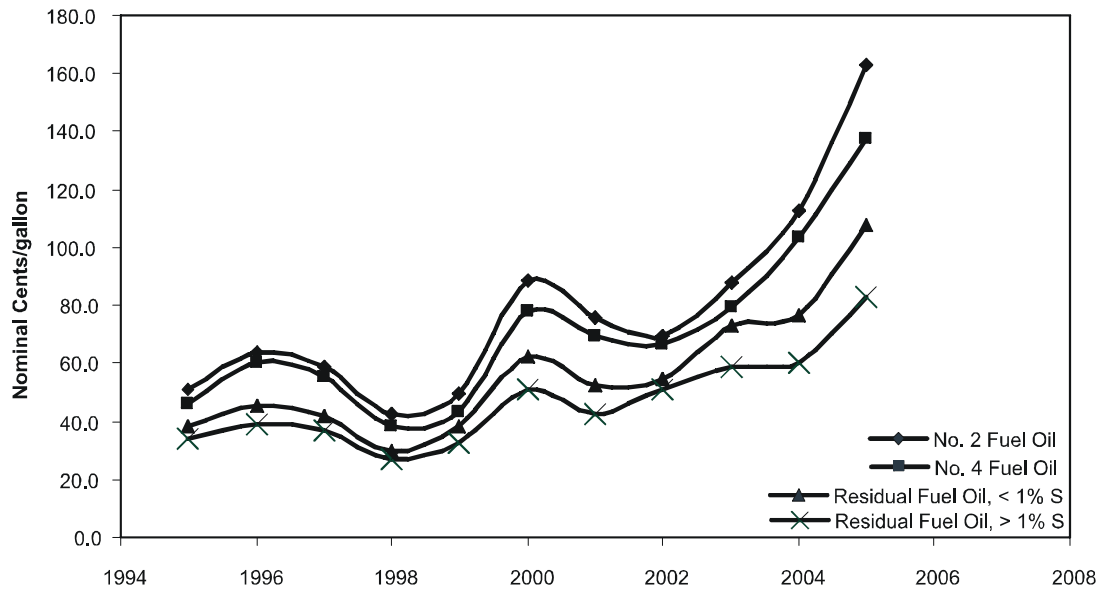
Source: 214A517

<sup>a</sup> Weighted average price delivered to U.S. refineries.

The prices of fuel oils fluctuate in unison (Figure 4.5), the lighter oils increasing faster since 2002 than residual oils. The Energy Information Administration (Table 4.3 above) projects residual fuel oil costs will continue to fluctuate and increase with the price of crude oil. Residual fuel oil sells for less than the cost of crude oil and lighter fuel oil grades due to its high sulfur content and likely higher amount of ash forming heavy metals (see Heavy Fuel Oil Specifications below) that can foul burner systems ([214A047]). Fuel oil prices in Europe, Asia and the United States behaved similarly, plateauing from mid 2005 through mid 2006 before temporarily declining through the end of 2006 (Figure 4.6).

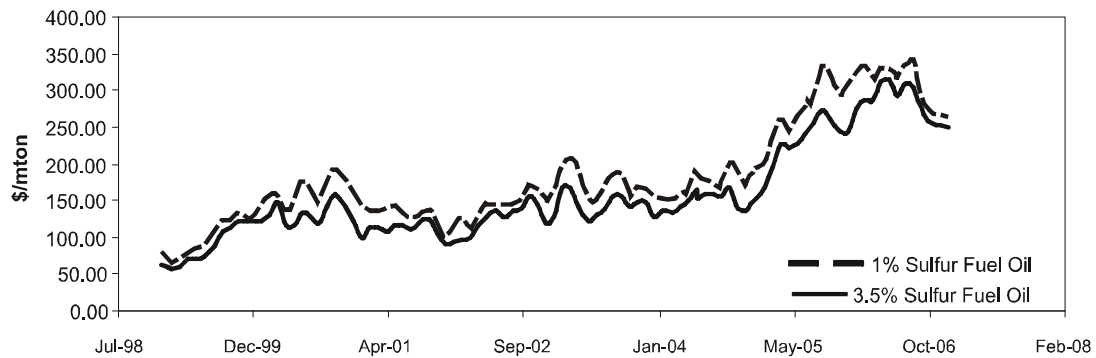


**Figure 4.5**  
**HISTORICAL U.S. FUEL OIL PRICES**



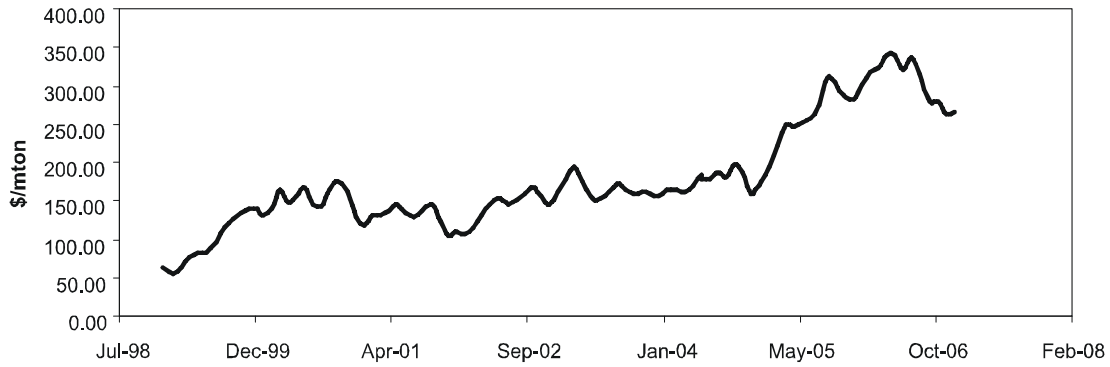
Source:214A512

**Figure 4.6**  
**EUROPEAN, ASIAN AND U.S. FUEL OIL PRICES**  
NORTHWEST EUROPE FUEL OIL PRICES

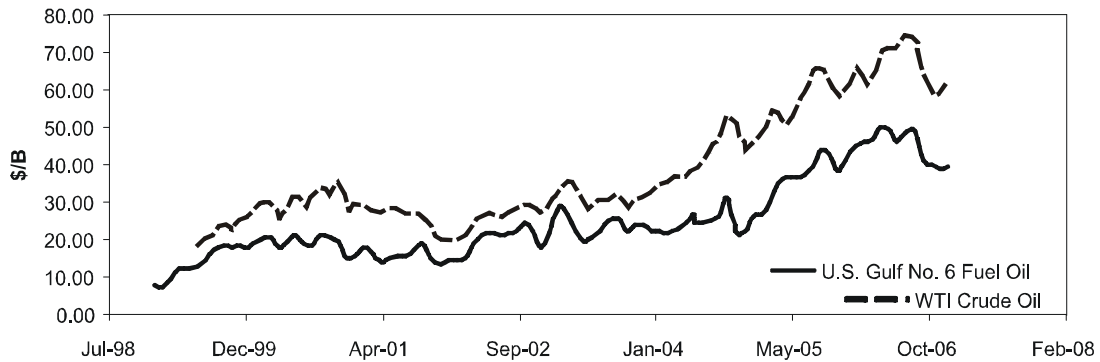


**Figure 4.6 (Continued)**  
**EUROPEAN, ASIAN AND U.S. FUEL OIL PRICES**

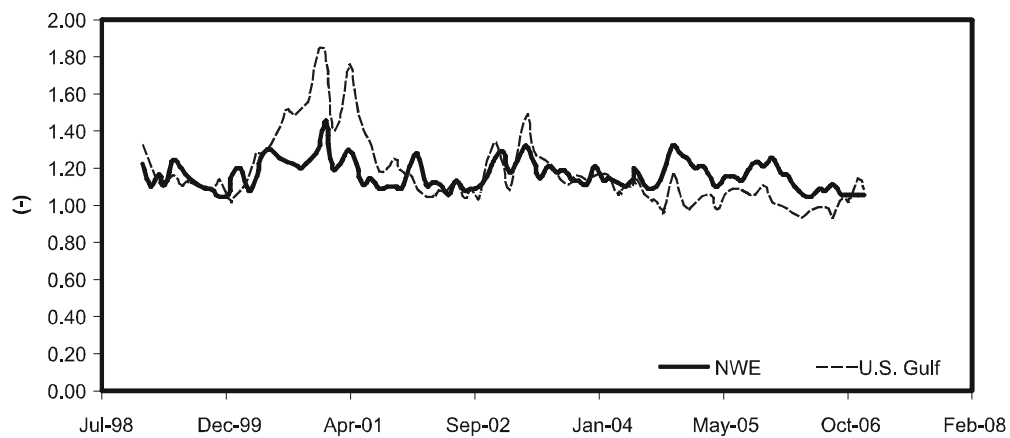
SINGAPORE HIGH SULFUR FUEL OIL PRICE



U.S. GULF COAST NO. 6 (3.5% SULFUR) FUEL OIL

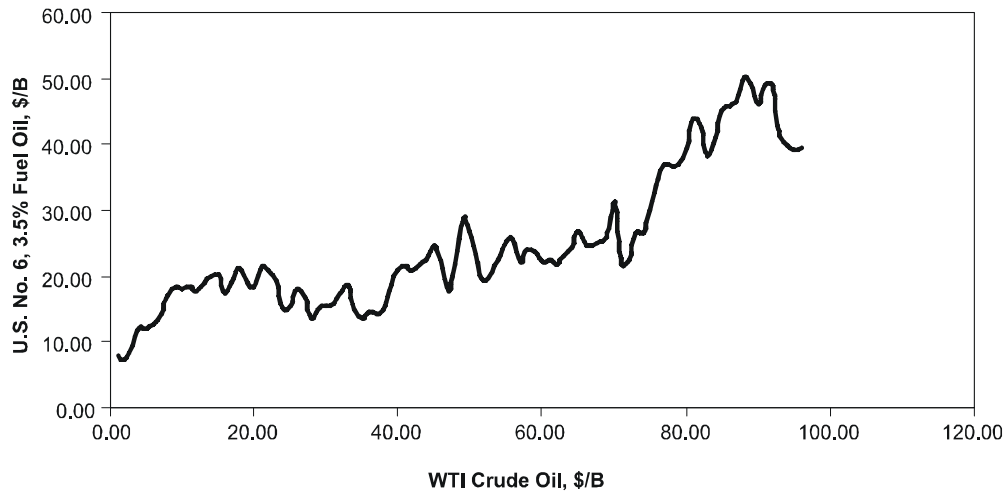


PRICE RATIO 3.5%/1% SULFUR FUEL OILS



**Figure 4.6 (Concluded)**  
**EUROPEAN, ASIAN AND U.S. FUEL OIL PRICES**

U.S. GULF COAST



## REGULATIONS

The global movement to improve air quality through legislating tighter oil product specifications and emission controls is starting to address the residual fuel oil market. Inland residual fuel oil markets can be regulated similar to the gasoline and diesel fuel markets with responsibility and enforcement placed on the refinery and retailer. In 2005, almost half the inland fuel oil market is estimated to be low sulfur fuel oil (1.5 wt% S or less) [214A418]. However, a large portion of the residual oil market is sea-going marine fuel oils, which are much more difficult to regulate due to limited jurisdiction, many selling locations and consumers who usually have several choices in location to purchase. As a result, sulfur in the ocean marine fuel oil market was unregulated. This is starting to change.

On May 19, 2005, the emission regulations protocol adopted by the International Maritime Organization, MARPOL, 73/78 Annex VI, Regulations for the Prevention of Air Pollution from Ships (the International Convention for the Protection of Pollution for Ships) became effective. Thirty amendments to Annex VI that must be adopted by 2008 will result in the shipping industry moving away from high sulfur fuel oil to low sulfur fuel oil. Amendments include lower SO<sub>x</sub> emissions, lowering the sulfur cap in sulfur control areas to 1% or even 0.5%, lower NO<sub>x</sub> emissions limits on existing engines as well as new and establishing NO<sub>x</sub> control areas [214A422, 214A507].

The European Union agreed to legislation to introduce Sulphur Emission Control Areas (SECAs) in the Baltic and North Sea along with legislation covering passenger ferries. This regulation will limit permissible sulfur emissions, resulting in the use of maximum 1.5% sulfur fuel oil or of as yet unproven on-board exhaust gas scrubbers. In 2005, Baltic Sea marine fuel oil sulfur was limited to 4.5 wt% with proposal to reduce the sulfur limit to 0.5% by December 2012. The regulatory history of sulfur limits of other fuels such as middle distillates shows faster political momentum that causes regulations to spread more rapidly than expected throughout the world. By 2010-2015, Canada and the United States are expected to follow with regulations similar to those adopted in parts of Asia. The EU is expected to also extend SECAs. Unlike sulfur

regulation of other fuels, this marine legislation places responsibility on the ship operator since, as mentioned, the bunker fuel market is different than other fuel markets [214A340, 214A418, 214A422].

### Heavy Fuel Oil Specifications

Heavy fuel oils are classified by the American Society for Testing Materials (ASTM) (ASTM standard D 396) into four grades (Table 4.4) and by the International Organization for Standardization (ISO) (ISO 8217) into ten grades of residual fuel oils. ASTM heavy fuel oil grades are designated as No. 4, No. 5 (Light), No. 5 (Heavy) and No. 6. No. 6 fuel oil is the most common and is also called bunker fuel oil or navy special fuel oil. Furnace fuel oil often refers to either No. 5 or No. 6. Marine heavy fuel oils are historically classified on the basis of kinematic viscosity but are now based on the fractions blended as follows:

- Marine Diesel Oil (MDO) – a blend of gasoil (diesel) and heavy fuel oil
- Intermediate Fuel Oil (IFO) – a blend of gasoil and heavy fuel oil containing less gasoil than MDO
- Medium Fuel Oil (MFO) – a blend of gasoil and heavy fuel oil containing less gasoil than IFO
- Heavy Fuel oil (HFO) – pure or nearly pure residual oil, roughly equivalent to No. 6 fuel oil [214A419, 214A422].

**Table 4.4**  
**ASTM FUEL OIL GRADES**

<u>Grade</u>	<u>Type</u>	<u>Heating Value, Btu/gal</u>	<u>Carbon Chain Length</u>
No. 1 Fuel Oil	Distillate	132,900-137,000	9-16
No. 2 Fuel Oil	Distillate	137,000-141,800	10-20
No. 4 Light Fuel Oil	Blend, distillate and residual oils	143,000-148,100	
No. 5 Light Fuel Oil	Residual oil	146,800-150,000	12-70
No. 5 Heavy Fuel Oil	Residual oil	149,400-152,000	12-70
No. 6 Fuel Oil	Residual oil	151,300-155,900	20-70

Source: 214A101; 214A419; 214A421

No. 4 fuel oil is a low viscosity type fuel oil that is customarily made by blending residual oil with distillate oil. The percentage of distillate can range from 50 to 80% depending upon the viscosity of the residual oil. No. 4 fuel oil may also be a catalytically cracked distillate or a blend of cracked and straight run distillate. The API gravity, viscosity and carbon residue can vary widely as illustrated in Table 4.5 for four samples. No. 4 usually does not require preheating for handling or burning. However, the temperature of above ground storage tanks can easily drop lower than the viscosity test temperature resulting in poor atomization unless the oil is preheated. Also, although the pour point may be low, the oil begins to thicken and congeal above its pour point.

**Table 4.5**  
**ANALYSES OF FOUR NO. 4 FUEL OILS**

<u>Sample<sup>a</sup></u>	<u>API Gravity</u>	<u>Viscosity, cSt, 100°F (38°C)</u>	<u>Conradson Carbon</u>	<u>Ramsbottom Carbon</u>
A	18	18	4.50	3.75
B	24	23	6.00	5.00
C	29	3.3	0.010	0.010
D	33	3.6	0.014	0.010

Source: 214A420

<sup>a</sup> A and B are blends of distillate and residue oils. C is a catalytically cracked distillate. D is a blend of cracked and straight run distillates.

No. 5 fuels oils are generally made by blending No. 6 oil (a residual oil) with distillate to meet specifications. Depending upon the residual oil's viscosity, blended distillate may range from 20 to 45%. Preheating may be required for Light No. 5 fuel oil depending upon the climate and burner for the reasons given above for No. 4 oil. Heavy No. 5 may require preheating for burning and, in cold climates, may be required for handling [214A420].

No. 6 fuel oil is totally residual oil. The residue may be straight or further processed. At room temperature, this fuel oil is a thick, gummy semi-fluid black material. No. 6 fuel oil requires preheating for both handling and burning [214A420].

To reduce air pollution, most industrialized countries restrict residual fuel oil sulfur content. Standardized properties of residual fuels typically include [214A047]:

1. Density at 60°F (15°C) ranges from 0.975 to 1.01 g/cm<sup>3</sup>.
2. Kinematic viscosity at 212°F (100°C) ranges from 10 to 55 centistokes (mm<sup>2</sup>/s).
3. Pour point, the lowest temperature at which the oil will continue to flow under prescribed standard conditions, varies from 32 to 113°F (0 to 45°C) depending upon the type of fuel oil. Below the pour point, wax begins to precipitate, which blocks filters and may deposit on heat exchange surfaces. High viscosity fuels should be stored about 18°F (10°C) above the pour point to avoid wax precipitation. Generally, high viscosity oils need to be well above the pour point in order to reduce the viscosity for efficient pumping.
4. Flash point of residual fuels has to be greater than 140°F (60°C).
5. Ash, noncombustible inorganics contained in the crude or contamination during storage or distribution (V, Ni, Na, Ca, Mg, Zn, Pb, Fe), ranges from 0.1 to 0.2%.
6. Carbon residue, a measure of carbonaceous deposits resulting from combustion, ranges from 10 to 22%.
7. Sulfur, which causes corrosive combustion gas below the dew points of sulfurous acid and sulfuric acid, ranges from 3.5 to 5%. These acids cause corrosion between 122-140°F (50-60°C) and 230-302°F (110-150°C) respectively.
8. Vanadium content ranges from 150 to 600 mg/kg.

Specifications of ASTM heavy fuel oil grades (No. 4, No. 5 (Light), No. 5 (Heavy) and No. 6) are summarized in Table 4.6. No sulfur specifications are given since different burners can use fuel oils with varying amounts of sulfur. Where the sulfur level is critical, the buyer will specify the allowable maximum. In the U.S., the EPA regulates the allowable sulfur level, which can vary widely from location to location.

**Table 4.6**  
**ASTM HEAVY FUEL OIL SPECIFICATIONS**

<b>Property</b>	<b>ASTM Test Method</b>	<b>No. 4</b>	<b>No. 5 (Light)</b>	<b>No. 5 (Heavy)</b>	<b>No. 6</b>
Flash Point, °C (°F), min.	D 93	55 (130)	55 (130)	55 (130)	60 (140)
Water and Sediment, vol%, max.	D 95 & D 473 <sup>a</sup>	0.50	1.00	1.00	2.00
Kinematic viscosity, mm <sup>2</sup> /s (cSt) at 100°C (212°F), min./max.	D 445	>5.5/24.0 <sup>b</sup>	5.0/8.9 <sup>c</sup>	9.0/14.9 <sup>c</sup>	15.0/50.0 <sup>c</sup>
Ash, mass%, max.	D 482	0.10	0.15	0.15	---
Pour Point, °C (°F), max.	D 97	-6 (28)	---	---	---

Source: 214A101

<sup>a</sup> The amount of water by distillation Test Method D 95 plus the sediment by extraction by Test Method D 473 shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.50 mass%, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass%.

<sup>b</sup> At 40°C (104°F).

<sup>c</sup> Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower number grade down to and including No. 4 can be supplied by agreement between purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

The ISO physical property specifications for marine residual fuel oils are listed in Table 4.7 and the compositional specifications are listed in Table 4.8.

**Table 4.7**  
**ISO PHYSICAL PROPERTY SPECIFICATIONS FOR MARINE RESIDUAL FUEL OILS**

<u>Fuel Oil</u>	<b>Density at 59°F (15°C), Max., kg/m<sup>3</sup></b>	<b>Viscosity at 122°F (50°C), Max., mm<sup>2</sup>/s or cSt</b>	<b>Flash Point Min., °F (°C)</b>	<b>Pour Point</b>		<b>Total Potential Sediment Max., wt%</b>
				<b>Summer, Max., °F (°C)</b>	<b>Winter, Max., °F (°C)</b>	
RMA 30	960.0	30.0	140 (60)	43 (6)	32 (0)	0.10
RMB 30	975.0	30.0	140 (60)	75 (24)	75 (24)	0.10
RMD 80	980.0	80.0	140 (60)	86 (30)	86 (30)	0.10
RME 180	991.0	180.0	140 (60)	86 (30)	86 (30)	0.10
RMF 180	991.0	180.0	140 (60)	86 (30)	86 (30)	0.10
RMG 380	991.0	380.0	140 (60)	86 (30)	86 (30)	0.10
RMH 380	991.0	380.0	140 (60)	86 (30)	86 (30)	0.10
RMK 380	1010.0	1010.0	140 (60)	86 (30)	86 (30)	0.10
RMH 700	991.0	991.0	140 (60)	86 (30)	86 (30)	0.10
RMK 700	1010.0	1010.0	140 (60)	86 (30)	86 (30)	0.10
Test Reference	ISO 3675 or ISO 12185	ISO 3104	ISO 2719	ISO 3016	ISO 3016	ISO 10307-2

Source: 214A423

**Table 4.8**  
**ISO COMPOSITION SPECIFICATIONS FOR MARINE RESIDUAL FUEL OILS**

<b>Fuel Oil</b>	<b>Water Max., Vol%</b>	<b>Micro Carbon Residue Max., Wt%</b>	<b>Sulfur<sup>a</sup> Max., Wt%</b>	<b>Ash Max., Wt%</b>	<b>Vanadium Max., mg/kg</b>	<b>Aluminum + Silicon Max., mg/kg</b>	<b>Zn<sup>b</sup> Max., mg/kg</b>	<b>P<sup>b</sup> Max., mg/kg</b>	<b>Ca<sup>b</sup> Max., mg/kg</b>
RMA 30	0.5	10	3.5	0.10	150	80	15	15	30
RMB 30	0.5	10	4.00	0.10	150	80	15	15	30
RMD 80	0.5	14	4.50	0.10	350	80	15	15	30
RME 180	0.5	15	4.50	0.10	200	80	15	15	30
RMF 180	0.5	20	4.50	0.15	500	80	15	15	30
RMG 380	0.5	18	4.50	0.15	300	80	15	15	30
RMH 380	0.5	22	4.50	0.15	600	80	15	15	30
RMK 380	0.5	22	4.50	0.15	600	80	15	15	30
RMH 700	0.5	22	4.50	0.15	600	80	15	15	30
RMK 700	0.5	22	4.50	0.15	600	80	15	15	30
Test	ISO	ISO 10370	ISO	ISO	ISO 14597 or	ISO 10478	IP 501/ IP 470	IP 501/ IP 470	IP 501/ IP 470
Reference	3733		14596 or 8754	6245	501				

Source: 214A423

<sup>a</sup> A sulfur limit of 1.5% m/m will apply in SO<sub>x</sub> Emission Control Areas designated by the International Maritime Organization, when its relevant Protocol comes into force. There may be local variations.

<sup>b</sup> The Fuel shall be free of used lubricating oil (ULO). A fuel is considered to be free of ULO if one or more of the elements are below the limits. All three elements shall exceed the limits before deemed to contain ULO.

### Gasoline and Diesel Fuel Specifications

The severity of hydrotreating FCC and RFCC feedstocks is a function of the sulfur specifications for gasoline and diesel fuel. Sulfur content has a high effect on the emission of air toxics and NO<sub>x</sub>. Below we briefly discuss motor fuel regulations. Gasoline regulations and specifications are further discussed in PEP Reports 129B *Advances in Catalytic Reforming* (2006) and 254 *Refinery C<sub>5</sub>s Utilization* (2004). Diesel fuel specifications are discussed in more detail in 195A *Advances in Fluid Catalytic Cracking* (2005).

Specifications for gasoline and diesel fuel are set by each country, or in Europe, the European Commission. Four leading gasoline specifications are summarized in Tables 4.9 and 4.10. The Worldwide Fuel Charter Category 4 is the most stringent category proposed by the automobile and engine manufacturers for future engines. The U.S. Tier 2 and the European Euro 4 specifications come closest to the Worldwide Fuel Charter. Gasoline specifications change according to an implementation schedule and with new information. The trend towards low sulfur gasoline is gaining momentum worldwide.

Future regulations are expected to continue to tighten, especially in urban areas and in developing countries. In parts of California, 15 ppm sulfur is going to be required. U.S. gasoline sulfur limit may be reduced to 10 ppm in the future [214A559]. Sulfur reduction to 10 ppm is being phased into parts of Europe from 2005 to 2009. The expectation is that all of the ECU will have 10 ppm sulfur gasoline by 2009. Sulfur regulations in the advanced Asia-Pacific countries are comparable to Europe's (S. Korea's are stricter) [214A558, 214A560]. Australia is considering 10 ppm sulfur gasoline for 2010. Singapore's long term plan calls for 10 ppm sulfur gasoline. The



Middle East is expected to eventually locally consume 10 ppm sulfur gasoline as well as for export. Brazil recently adopted regulations that will follow the European Union limits, Euro IV in 2009. Ultimately, most gasoline will meet the 10-15 ppm sulfur specification.

**Table 4.9**  
**LEADING 2005-2006 GASOLINE SPECIFICATIONS**

	<b>Reformulated, <u>USA</u></b>	<b>California, <u>USA</u></b>	<b><u>Europe</u></b>	<b>Worldwide Fuel Charter, <u>Category 4</u></b>
Effective	2006	<2004	2005	---
Density, max, lb/ft <sup>3</sup>	48.07	---	48.69	48.07
Kg/m <sup>3</sup>	770	---	780	770
Sulfur, ppmw	30	10	50	5-10
Oxygen, wt%	2 min.	2 min.	---	2.7 max.
Lead, g/l	None	None	None	None
Aromatics, vol%	25	25	35	35
Olefins, vol%	4	6	18	10
T <sub>10</sub> , max., °F (°C)	149-113 (65-45)	---	158-131 (70-55)	149-113 (65-45)
End Point, max., °F (°C)	383 (195)	300 (149)	419 (215)	383 (195)

Sources: 214A561, 214A562

**Table 4.10**  
**SUMMARY OF GASOLINE SULFUR SPECIFICATIONS**

<b><u>Region</u></b>	<b><u>Effective</u></b>	<b><u>Average Sulfur</u></b>	<b><u>Maximum Sulfur</u></b>
U.S. outside California	2005	30 ppmw	80 ppmw
California	2003	15	40
Canada	2005	30	80
European Union	2008/2009		10
Japan	2005	50	
Japan	2008	potentially 10	

Source: 214A563, 214A564

In 2006, the U.S. started changing over to near zero sulfur diesel fuel of less than 15 ppm sulfur. During a transition period from 2006 through 2010, U.S. refiners will be handling two grades of on road diesel. After 2010, only near zero sulfur diesel fuel will be available in the U.S. U.S. and European diesel fuel specifications are summarized in Table 4.11. The U.S. Environmental Protection Agency proposed non-road diesel fuel sulfur be dramatically reduced from 3400 ppm previously to 500 ppm beginning in 2007 and then to 15 ppm in 2010 [214A565, 214A566, 214A567, 214A568, 214A569, 214A570].

**Table 4.11**  
**U.S. AND EUROPEAN DIESEL FUEL SPECIFICATIONS**

	<u>U.S.</u>	<u>Europe</u> <u>1996</u>	<u>2000</u>	<u>Expected 2005</u>
Sulfur, ppm max.		500	350	10-50
Cetane Number, min.		49	51	52-54
Polyaromatics, wt% max.		---	11	1-6
ASTM D-86 T <sub>95</sub> , vol%, °F (°C ) max.	---	---	680 (360)	644-662 (340-350)
T <sub>90</sub> , vol%, °F (°C ) max.	640 (388)	---	---	---

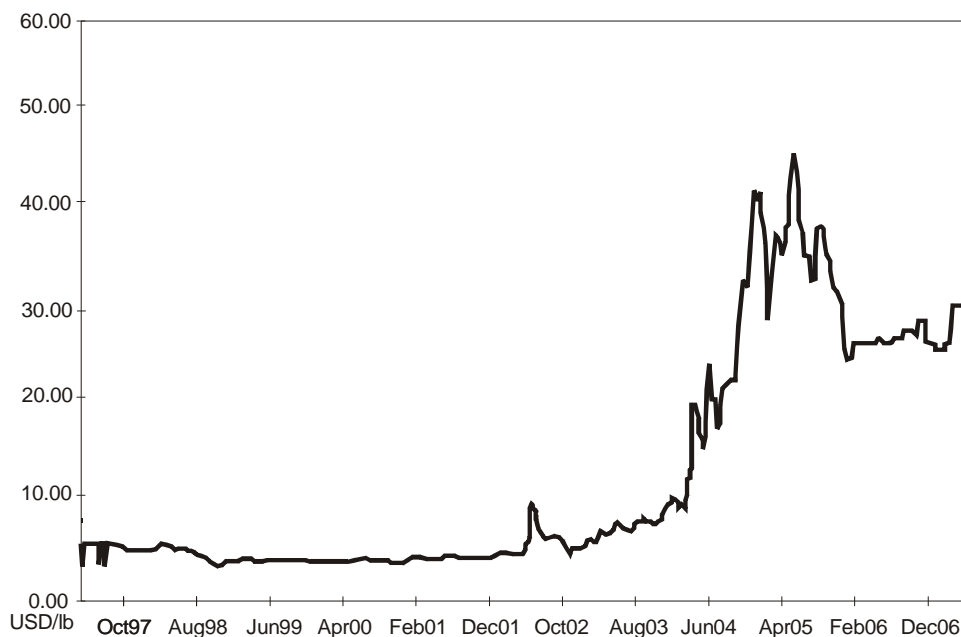
Sources: 214A562, 214A565

### CATALYTIC METAL PRICES

The price history of the hydrotreating catalytic metals (Figures 4.7, 4.8, 4.9 and 4.10) each showed different profiles over the last 10 years. Cobalt and molybdenum are byproducts. In 2005, byproduct molybdenum recovery from copper mining is estimated to account for 63% of worldwide supply. The price of byproduct metals are subject to greater fluctuations as production varies in response to demand for the primary metal. Catalysts account for about 11% of the cobalt market, as carbonate, sulfate, nitrate and acetate salts or metal. Just about 7% of U.S. molybdenum consumption in 2004 and 2005 is estimated to have been used for catalysts [214A519].

**Figure 4.7**  
**PRICE HISTORY OF MOLYBDENUM, 1997-2006**

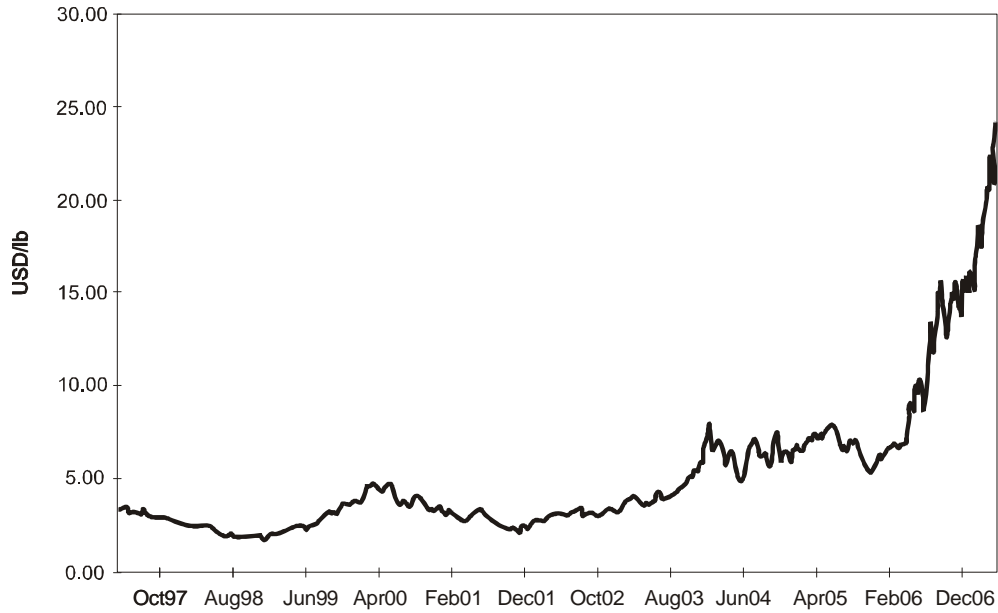
MOLYBDENUM (USD/LB)  
FRIDAY, APRIL 11, 1997 – WEDNESDAY, APRIL 11, 2007



Source:214A515

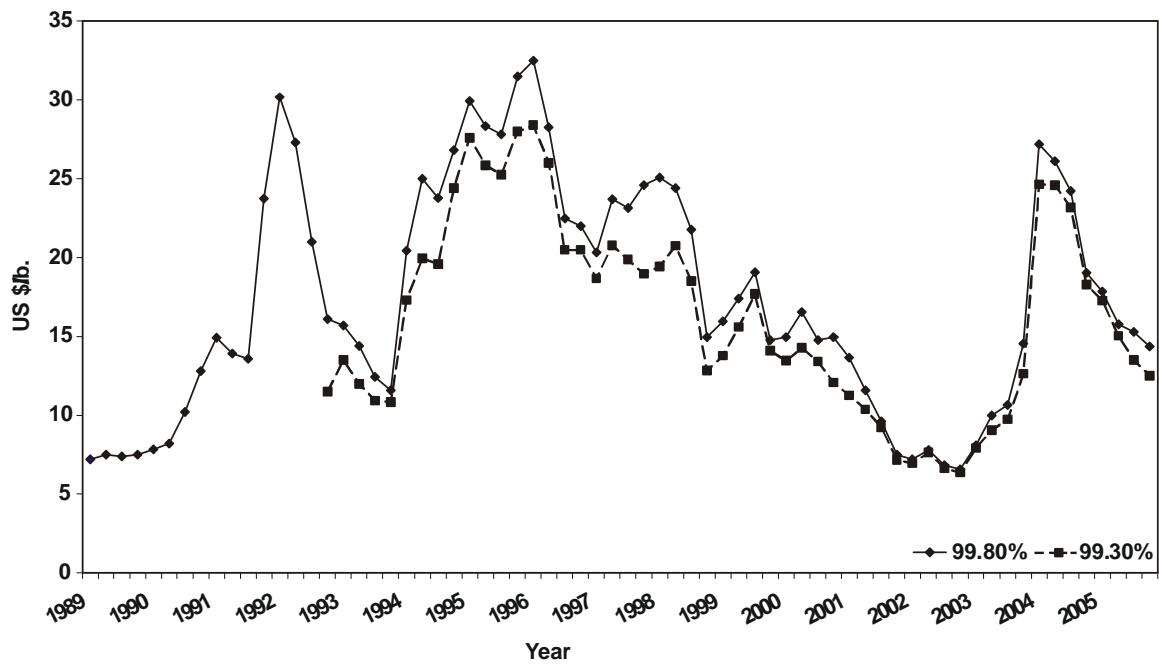
**Figure 4.8**  
**PRICE HISTORY OF NICKEL, 1997-2006**

NICKEL (USD/LB)  
FRIDAY, APRIL 11, 1997 – WEDNESDAY, APRIL 11, 2007



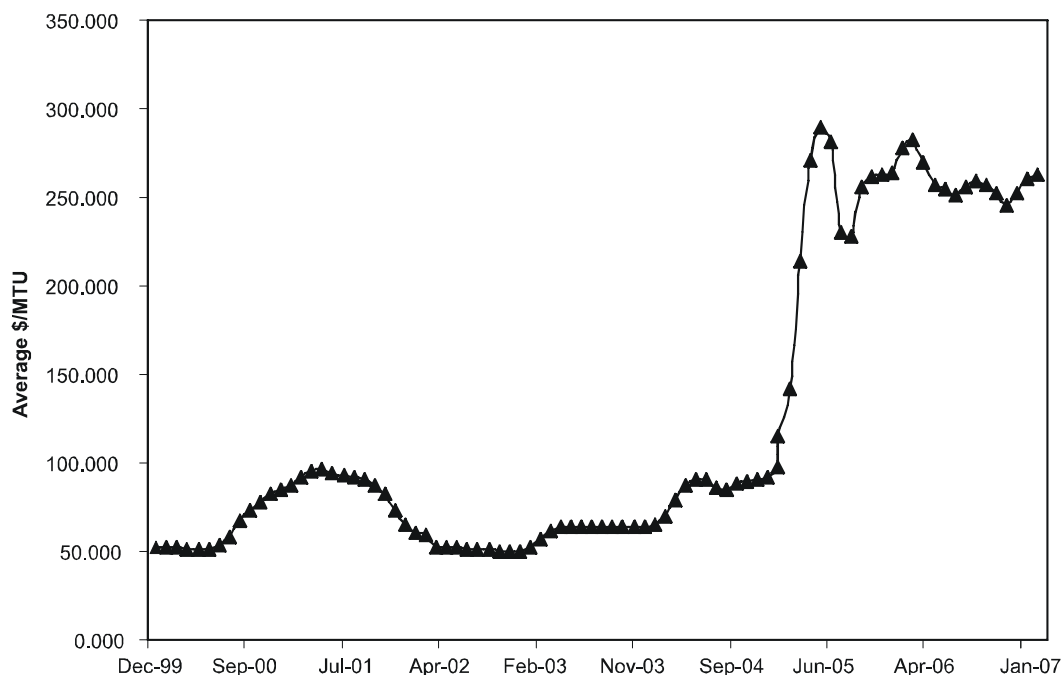
Source: 214A514

**Figure 4.9**  
**PRICE HISTORY OF COBALT, 1997-2006**



Source:214A516

**Figure 4.10**  
**PRICE HISTORY OF TUNGSTEN, 2000-2006**



Source:214A521

Molybdenum was relatively stable, trading below 5 \$/lb through 2002. The price then began an exponential rise in March of 2004 to over 40 \$/lb in 2005 in response to limited world roasting capacity and growing demand. Swing production is from primary molybdenum mines that have a limited capacity to change production rates in response to demand. Production costs from primary mines are 3-4 \$/lb compared to 1-2 \$/lb for copper byproduct costs since the cost of mining the ore is charged to the copper. By early 2006, the price declined to around 25 \$/lb but then increased to 30 \$/lb in early 2007 [214A515, 214A518, 214A520].

Nickel was relatively stable, cycling between 2.50 and 5 \$/lb through September 2003. The price range then rose to 5 to 7.50 \$/lb through March 2006 while molybdenum peaked. The price rose steeply through early 2007 to about 23 \$/lb [214A514].

In contrast, the price trend of cobalt generally declined from over 20 \$/lb in 1997-mid 1998 to below 7.50 \$/lb during 2002 due to the slow down in the world economy. During 2003, the price increased to about 14 \$/lb since very little metal was available at a time of raising demand. Cobalt closed 2003 at over 20 \$/lb. The price jumped to over 25 \$/lb during the first half of 2004 but dropped suddenly to about 18 \$/lb. The price continued to decline through 2005. Cobalt is usually found in combination with nickel or copper and until recently has been produced as a byproduct of copper refining. Cobalt as a byproduct of nickel refining increased significantly. In 2005, nearly 40% of refined cobalt is estimated to be produced as the main product. Since 2002, demand to 2006 in the U.S. and Western Europe remained relatively steady while demand in Asia increased by 80% [214A516].

Tungsten prices are generally quoted in the form of ammonium tungstate in terms of metric ton units (MTU). A MTU is one hundredth of a metric ton (1000 kg) of contained tungsten trioxide

(equivalent to 7.93 kg or 17.478 lb of metal). Tungsten prices ranged from 50 to 100 \$/MTU from January 2000 to 2005 (Figure 4.10). The price increased significantly in 2005 from 65-95 \$/MTU in 2004 to peak at 290 \$/MTU in mid-2005. Since then through early 2007, the price has fluctuated around 250 \$/MTU. China has reduced subsidies for state owned mines and a number have closed. The formerly large Russian stockpile is believed to be close to depletion. Current world demand is believed to be greater than mine output, depleting stockpiles. Demand is growing with the growth of the principal economies causing the price increase [214A521].

## INSTALLED HEAVY OIL HYDROTREATING CAPACITY

In this subsection, we discuss worldwide installed heavy oil hydrotreating capacities as of January 1, 2007, based on information published in the *Oil and Gas Journal*. The reported capacities are on a refinery basis. Since some refineries have multiple units, the total number of units does not necessarily equal the number of refineries reported. Of the world's 656 refineries tabulated by the *Oil & Gas Journal* in their 2006 annual survey [214A551], 145 or 22% were identified as having heavy oil hydrotreating capacity, 24 or 3.7% of which have a residue hydrotreater. Residue hydrotreating is predominately located in the Asia-Pacific region where 20 of the 28 refineries having this unit are located. Worldwide identified heavy oil hydrotreating capacity totals 17,308,000 B/cD or 20.4 vol% of the world's 84,984,000 B/cD crude capacity (Table 4.12). Refineries outside North America have 64% of global heavy oil hydrotreating capacity.

**Table 4.12**  
**HEAVY OIL HYDROTREATING REFINERIES – WORLD SUMMARY**

TOTAL CAPACITIES, 1,000 BPCD

<u>Region</u>	<u>Number of Refineries</u>	<u>Distillation</u>		<u>Total HDT</u>	<u>Residue HDT</u>	<u>FCC Pretreating</u>	<u>Other Heavy Gas Oil</u>
		<u>Crude</u>	<u>Vacuum</u>				
North America	52	8,859.5	4,324.8	8,367.3	182.0	2,079.3	208.4
Western Europe	30	5,175.8	2,020.2	4,144.8	116.3	679.0	257.1
Asia-Pacific	35	7,348.8	2,045.6	5,738.2	909.6	528.1	552.7
Central & Eastern Europe	6	756.2	387.7	567.2	0.0	173.3	0.0
Middle East	6	1,712.9	466.1	954.2	237.4	78.2	73.9
South & Central America	7	2,578.0	1,328.7	1,243.7	0.0	454.0	59.5
Former Soviet Union	7	1,367.8	710.2	792.5	0.0	257.0	0.0
Africa	2	92.6	17.2	40.2	0.0	2.7	10.0
Outside North America	93	19,032	6,975.6	9,506.4	5,400.1	4,376.9	5,061.6
World	145	27,891.5	11,300.4	17,873.7	5,582.1	6,456.2	5,270.0
<b>All Refineries</b>							
United States	131	17,272.6	7,634.9	13,501.0	257.0	2,079.3	175.4
North America	156	20,853.8	9,091.6	15,644.4	182.0	2,079.3	208.4
Outside North America	500	64,130.6	19,082.7	27,601.2	5,400.1	4,376.9	5,061.6
World	656	84,984.4	28,174.3	43,245.6	5,582.1	6,456.2	5,270.0

Hydrotreating of FCC feedstocks worldwide grew 4.0%/year from 2002 to 2007 (Table 4.13). Over the same period growth has been faster outside North America, 4.8%/year compared to 3.2%/year. The growth, although considerable slower than the 1998 to 2002 period, is considerably greater than the growth in crude distillation capacity (0.95%, year worldwide; 0.96%/year outside N. America and 0.90%/year in N. America) or in vacuum distillation capacity (1.12%/year worldwide; 1.34%/year outside N. America and 0.50%/year in N. America).

**Table 4.13**  
**GROWTH IN HYDROTREATING CAPACITY (1998-2007)**

	<b>North America</b>		<b>Outside North America</b>		<b>World</b>	
	<b><u>1,000</u></b>	<b><u>Growth,</u></b>	<b><u>1,000</u></b>	<b><u>Growth,</u></b>	<b><u>1,000</u></b>	<b><u>Growth,</u></b>
	<b><u>BPcD</u></b>	<b><u>%/year</u></b>	<b><u>BPcD</u></b>	<b><u>%/year</u></b>	<b><u>BPcD</u></b>	<b><u>%/year</u></b>
<b>FCC Feedstock</b>						
1998	920.5	---	693.9	---	1,614.3	---
2002	1,770.6	17.8	1,720.8	25.5	3,491.4	21.3
2007	2,079.3	3.2	2,172.3	4.8	4,251.6	4.0
<b>Resid</b>						
1998	---	---	---	---	---	---
2002	283.5	---	1,306.3	---	1,589.8	---
2007	292.0	0.6	1,368.3	0.93	1,660.3	0.87
<b>Total Heavy Oils</b>						
1998	---	---	---	---	---	---
2002	2,224.0	---	4,356.5	---	6,580.4	---
2007	2,579.7	3.0	4,493.9	0.62	7,073.5	1.46
<b>Crude Distillation</b>						
1998	19,806.	---	52,141.	---	71,948.	---
2002	19,939.	0.17	61,132.9	4.0	81,072.	3.0
2007	20,854.	0.90	64,131.	0.96	84,984.	0.95
<b>Vacuum Distillation</b>						
1998	8,382.	---	15,094.	---	23,476.	---
2002	8,866.	1.42	17,855.	4.29	26,721.	3.30
2007	9,092.	0.91	19,083.	1.34	28,362.	1.12

Source: 214A551

In North America in 2007, heavy oil hydrotreating capacity of all types totaled 2.58 million B/cD, equaling 28.3% of crude oil distillation capacity of those refineries. North American refineries having heavy oil hydrotreaters are summarized in Table 4.14 and listed individually in Table 4.15. FCC feed hydrotreaters are in 44 or 28% of North American refineries. In these refineries, FCC feedstock hydrotreating capacity equals 2.08 million B/cD or 31% of their 6.60 million B/cD of FCC capacity.

Outside of North America, 93 refineries have heavy oil hydrotreaters totaling 4.49 million B/cD capacity (summarized in Table 4.14 and listed individually in Table 4.16). FCC feed pretreating totals 2.17 million B/cD, which is 72% of their 3.02 million B/cD FCC capacity.

**Table 4.14**  
**SUMMARY OF HEAVY OIL HYDROTREATING REFINERIES CAPACITIES, JANUARY 1, 2007**  
CAPACITY (1,000 B/CD)

<u>Region</u>	<u>Number of Refineries</u>	<u>Distillation</u>		<u>Catalytic Hydrotreating</u>			
		<u>Crude</u>	<u>Vacuum</u>	<u>Total HDT</u>	<u>Resid_ HDT</u>	<u>FCC Pre-treatment</u>	<u>Other Heavy Oil</u>
United States	52	8,984.5	4,413.8	8,521.3	257.0	2,079.3	175.4
North America	53	9,084.5	4,454.8	8,630.3	292.0	2,079.3	208.4
Western Europe	30	5,175.8	2,020.2	4,144.8	116.3	679.0	257.1
Eastern Europe	6	756.2	387.7	567.2		173.3	
Asia-Pacific	37	7,848.8	2,081.6	5,843.2	1,014.6	528.1	552.7
Central & South America	7	2,578.0	1,328.7	1,243.7		454.0	59.5
Former Soviet Union	7	1,367.8	710.2	792.5		257.0	
Middle East	6	1,712.9	466.1	954.2	237.4	78.2	73.9
Africa	<u>2</u>	<u>92.6</u>	<u>17.2</u>	<u>40.2</u>		<u>2.7</u>	<u>10.0</u>
Outside North America	95	19,532.1	7,021.7	13,585.8	1,368.3	2,172.3	953.2
World	148	28,616.5	11,466.4	22,216.2	1,660.3	4,251.6	1,161.6
<b>All Refineries</b>							
United States	131	17,272.6	7,634.9	13,501.0	257.0	2,079.3	175.4
North America	156	20,853.8	9,091.6	15,644.4	292.0	2,079.3	208.4
Western Europe	96	14,175.5	5,714.0	9,586.4	116.3	679.0	257.1
Eastern Europe	30	2,347.2	997.2	1,179.3		173.3	
Asia-Pacific	156	22,115.4	4,075.7	8,641.2	1,014.6	528.1	552.7
Central & South America	66	6,602.7	2,845.8	1,899.5		454.0	59.5
Former Soviet Union	59	7,925.4	2,762.3	3,087.8		257.0	
Middle East	48	7,752.4	2,177.5	2,320.4	237.4	78.2	73.9
Africa	45	3,212.1	510.1	886.6		2.7	10.0
Outside North America	500	64,130.6	19,082.7	27,601.2	1,368.3	2,172.3	953.2
World	656	84,984.4	28,174.3	43,245.6	1,660.3	4,251.6	1,161.6

**Table 4.15**  
**NORTH AMERICAN HEAVY OIL HYDROTREATING REFINERIES CAPACITIES**

CAPACITY (1,000 B/CD)

<u>State/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Catalytic Hydrotreating (HDT)</u>			
		<u>Crude</u>	<u>Vacuum</u>	<u>Total HDT</u>	<u>Resid HDT</u>	<u>FCC Pre-treatment</u>	<u>Other Heavy Oil</u>
UNITED STATES							
Pennsylvania ConocoPhillips	Trainer	185.0	75.4	130.2		38.3	
West Virginia Ergon-West Virginia Inc.	Newell	19.4	8.4	10.6			6.0
<b>Total PADD 1</b>		<b>204.4</b>	<b>83.8</b>	<b>140.8</b>		<b>38.3</b>	<b>6.0</b>
Kansas Frontier Oil Corp.	El Dorado	110.0	41.0	136.0		45.0	
Kentucky Marathon Petroleum Co.	Catlettsburg	222.0	114.5	251.3		96.9	
Michigan Marathon Petroleum Co.	Detroit	100.0	48.5	92.3		31.4	
Minnesota Flint Hills Resources	Rosemount	279.3	185.3	285.8		91.4	
Marathon Petroleum Co.	St. Paul Park	70.0	30.4	73.7		25.7	
		<b>349.3</b>	<b>215.7</b>	<b>359.5</b>		<b>117.1</b>	
Ohio BP PLC	Toledo	147.3	65.6	123.5		38.0	
Marathon Petroleum Co.	Canton	73.0	28.5	59.0		25.7	
		<b>220.3</b>	<b>94.1</b>	<b>182.5</b>		<b>63.7</b>	
Oklahoma ConocoPhillips	Ponca City	187.0	80.0	193.0		21.0	
Valero Energy Corp.	Ardmore	91.5	32.0	86.5		32.0	
		<b>278.5</b>	<b>112.0</b>	<b>279.5</b>		<b>53.0</b>	
<b>Total PADD 2</b>		<b>1,280.1</b>	<b>625.7</b>	<b>1,301.1</b>		<b>407.1</b>	
Alabama Hunt Refining Co.	Tuscaloosa	35.0	15.0	42.0		10.0	
Shell Chemical Co.	Saraland	85.0	28.0	43.0			18.0
		<b>120.0</b>	<b>43.0</b>	<b>85.0</b>		<b>10.0</b>	<b>18.0</b>



**Table 4.15 (Continued)**  
**NORTH AMERICAN HEAVY OIL HYDROTREATING REFINERIES CAPACITIES**

CAPACITY (1,000 B/CD)

State/Company	Location	Distillation		Catalytic Hydrotreating (HDT)			Other Heavy Oil
		Crude	Vacuum	Total HDT	Resid HDT	FCC Pre-treatment	
UNITED STATES (Continued)							
Arkansas							
Lion Oil Co.	El Dorado	70.0	27.1	74.1		18.9	
Louisiana							
Chalmette Refining LLC	Chalmette	192.5	112.0	172.5		62.0	
Citgo Petroleum Corp.	Lake Charles	440.0	79.8	233.1		64.8	
Marathon Petroleum Co.	Garyville	245.0	127.3	331.6		100.7	
Motiva Enterprises LLC	Convent	235.0	100.0	218.0		38.0	
Murphy Oil USA Inc.	Meraux	125.0	50.0	123.8			12.0
Valero Energy Corp.	Norco	186.0	200.0	131.1		35.1	
		1,423.5	669.1	1,210.1		300.6	12.0
Mississippi							
Chevron Corp.	Pascagoula	330.0	240.0	238.5			87.5
Ergon Refining Inc.	Vicksburg	23.0	10.2	12.0			12.0
		353.0	250.2	250.5			99.5
Texas							
Alon USA	Big Spring	70.0	24.0	68.0		6.5	
Citgo Petroleum Corp.	Corpus Christi	156.8	73.6	148.2		56.9	
ConocoPhillips	Borger	146.0		166.0	73.0		
ConocoPhillips	Sweeny	247.0	125.5	268.3		99.2	
ExxonMobil Refining & Supply Co.	Baytown	563.0	270.0	725.5		105.5	
ExxonMobil Refining & Supply Co.	Beaumont	348.5	143.0	294.5			
Flint Hills Resources	Corpus Christi	279.3	83.1	225.1		47.7	
Lyondell-Citgo Refining LP	Houston	282.6	191.1	307.9		98.0	
Motiva Enterprises LLC	Port Arthur	290.0	138.0	220.4		23.0	
Shell Deer Park Refining Co.	Deer Park	331.7	170.6	279.2		46.6	39.9
Total SA	Port Arthur	231.5	51.8	154.5		50.4	
Valero Energy Corp.	Corpus Christi	205.0	95.0	254.7	74.0	28.0	
Valero Energy Corp.	Port Arthur	250.0	145.0	282.0		65.0	
Valero Energy Corp.	Texas City	225.0	130.0	263.0	110.0		
Valero Energy Corp.	Three Rivers	96.0	35.0	100.8		20.0	
		3,722.3	1,675.7	3,758.1	257.0	646.8	39.9

**Table 4.15 (Continued)**  
**NORTH AMERICAN HEAVY OIL HYDROTREATING REFINERIES CAPACITIES**

CAPACITY (1,000 B/CD)

State/Company	Location	Distillation		Catalytic Hydrotreating (HDT)			
		Crude	Vacuum	Total HDT	Resid HDT	FCC Pre-treatment	Other Heavy Oil
UNITED STATES (Concluded)							
Total PADD 3		5,688.8	2,665.1	5,377.7	257.0	976.3	169.4
Colorado							
Suncor Energy Products	Commerce City	92.0	34.5	43.1		12.0	
Montana							
CHS Inc.	Laurel	59.6	31.3	51.6		15.7	
ConocoPhillips	Billings	58.0	34.0	72.0		23.0	
Montana Refining Co.	Great Falls	10.0	5.0	7.1		3.0	
		127.6	70.3	130.7		41.7	
Utah							
Chevron Corp.	Salt Lake City	45.0	25.6	39.0		15.0	
Total PADD 4		264.6	130.4	212.8		68.7	
California							
BP PLC	Carson	247.0	123.5	171.0		90.0	
Chevron Corp.	El Segundo	260.0	136.0	228.0		65.0	
ConocoPhillips	Los Angeles	138.7	78.0	135.9		50.0	
ExxonMobil Refining Supply Co.	Torrance	149.5	98.5	143.5		102.0	
Shell Oil Products US	Martinez	157.6	95.1	189.6		75.3	
Shell Oil Products US	Wilmington	100.0	62.0	101.3		38.0	
Tesoro Petroleum	Golden						
	Eagle	161.0	144.0	172.5		62.0	
Valero Energy Corp.	Benicia	139.5	78.5	146.0		37.0	
Valero Energy Corp.	Wilmington	80.0	46.0	139.5		62.5	
		1,433.3	861.6	1,427.2		581.8	
Washington							
Tesoro West Coast Co	Anacortes	113.3	47.2	61.6		7.1	
Total PADD 5		1,546.6	908.8	1,488.8		588.9	
Total United States		8,984.5	4,413.8	8,521.3	257.0	2,079.3	175.4

**Table 4.15 (Concluded)**  
**NORTH AMERICAN HEAVY OIL HYDROTREATING REFINERIES CAPACITIES**

CAPACITY (1,000 B/CD)

<u>State/Company</u>	<u>Location</u>	Distillation		Catalytic Hydrotreating (HDT)			
		<u>Crude</u>	<u>Vacuum</u>	<u>Total HDT</u>	<u>Resid HDT</u>	<u>FCC Pre-treatment</u>	<u>Other Heavy Oil</u>
CANADA							
Consumers' Cooperative Refineries Ltd.	Regina, Saskatchewan	100.0	41.0	109.0	35.0		33.0
Total North America		9,084.5	4,454.8	8,630.3	292.0	2,079.3	208.4

**Table 4.16**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Total HDT</u>	<u>Catalytic Hydrotreating</u>		<u>Other Heavy Oil</u>
		<u>Crude</u>	<u>Vacuum</u>		<u>Resid HDT</u>	<u>FCC Pre- treatment</u>	
Austria							
OMV AG	Schwechat	208.6	65.0	139.4		38.3	12.6
Belgium							
ExxonMobil Refining & Supply Co.	Antwerp	298.0	128.0	272.0		93.0	
Fina Raffinderij Antwerpen	Antwerp	356.6	92.6	333.1	83.3		
		654.6	220.6	605.1	83.3	93.0	
Finland							
Neste Oil	Naantali	51.8	28.1	39.2		6.0	
Neste Oil	Porvoo	200.0	70.1	163.8		40.5	
		251.8	98.2	203.0		46.5	
France							
Cie. Rhenane de Raffinage	Reichstett-Vendenheim	79.8	30.6	37.8			18.9
ExxonMobil Refining & Supply Co.	Port Jerome/NDG	233.0	103.0	212.5		52.0	
Total SA	Feyzin	115.6	50.9	58.7		45.7	
Total SA	Grandpuits	98.9	47.8	67.4		37.4	
		527.3	232.3	376.5		135.1	18.9
Germany							
BP PLC	Gelsenkirchen	267.5	163.1	182.6			36.0
ConocoPhillips	Wilhelmshaven	260.0	103.0	207.0			16.0
Mineraloelraaffinerie Oberrhein GmbH	Karlsruhe	302.0	130.0	351.0		74.0	
OMV AG	Burghausen	72.0		65.0		65.0	
PCK Raffinerie GmbH	Schwedt	220.0	140.0	210.0		60.0	
		1,121.5	536.1	1,015.6		199.0	52.0
Greece							
Hellenic Petroleum SA	Aspropyrgos	146.5	68.0	181.5		43.8	

**Table 4.16 (Continued)**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Total HDT</u>	<u>Catalytic Hydrotreating</u>		
		<u>Crude</u>	<u>Vacuum</u>		<u>Resid HDT</u>	<u>FCC Pre- treatment</u>	<u>Other Heavy Oil</u>
Italy							
AgipPetroli SpA	Gela, Ragusa	105.0	52.5	94.0			35.0
ExxonMobil Refining Supply Co.	Augusta, Siracusa	198.0	93.0	112.0		21.0	
Iplom SpA	Busalla	39.5	19.5	20.5			9.5
		<b>342.5</b>	<b>165.0</b>	<b>226.5</b>		<b>21.0</b>	<b>44.5</b>
Netherlands							
ExxonMobil Refining Supply Co.	Rotterdam	188.0	80.0	141.0			21.0
Norway							
Statoil Mongstad	Mongstad	200.0		70.0		16.9	17.1
Portugal							
Galp Energia	Sines	212.9	71.4	124.7		13.5	
Spain							
Cia. Espanola de Petroles SA	Cadiz	240.0	40.0	119.0		30.0	
Cia. Espanola de Petroles SA	Huelva	100.0	38.0	45.0		15.0	
Repsol YPF SA	La Coruna	120.0	52.0	89.9		26.8	
		<b>460.0</b>	<b>130.0</b>	<b>253.9</b>		<b>71.8</b>	
Sweden							
Preem Raffinaderi AB	Gothenburg	106.0		103.5			6.5
Shell Raffinaderi AB	Gothenburg	77.0	30.0	61.0			28.0
		<b>183.0</b>	<b>30.0</b>	<b>164.5</b>			<b>34.5</b>
Switzerland							
Petroplus	Cressier	60.0	24.0	62.0			27.0
Tamoil SA	Collombey	72.0		33.2			7.6
		<b>132.0</b>	<b>24.0</b>	<b>95.2</b>			<b>34.6</b>

**Table 4.16 (Continued)**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Catalytic Hydrotreating</u>			<u>Other Heavy Oil</u>
		<u>Crude</u>	<u>Vacuum</u>	<u>Total HDT</u>	<u>Resid HDT</u>	<u>FCC Pre-treatment</u>	
United Kingdom, Eng.							
ConocoPhillips	South Killingholme, England	221.0	157.0	251.5			21.9
ExxonMobil Refining Supply Co.	Fawley, England	326.0	142.5	296.5	33.0		
		<b>547.0</b>	<b>299.5</b>	<b>548.0</b>	<b>33.0</b>		<b>21.9</b>
<b>Total Western Europe</b>		<b>5,175.8</b>	<b>2,020.2</b>	<b>4,144.8</b>	<b>116.3</b>	<b>679.0</b>	<b>257.1</b>
Bulgaria							
Neftochim	Bourgas	115.2	49.9	64.2		23.3	
Hungary							
MOL Hungarian Oil & Gas Co.	Szazhalombatta	161.0	77.5	120.7		35.0	
Lithuania							
JSC Mazeikiu Nafta	Mazeikiai	190.0	89.3	153.9		54.0	
Romania							
Petromidia SA	Midia	105.0	46.0	73.0		15.0	
Rafo SA	Onesti, Bacau	70.0	70.0	67.6		24.0	
		<b>175.0</b>	<b>116.0</b>	<b>140.6</b>		<b>39.0</b>	
Slovakia							
Slovnaft, Joint Stock Co.	Bratislava	115.0	55.0	87.8		22.0	
<b>Total Eastern Europe</b>		<b>756.2</b>	<b>387.7</b>	<b>567.2</b>		<b>173.3</b>	
Australia							
Shell Refining (Australia) Pty. Ltd.	Geelong	110.0	10.0	75.0		3.0	
China							
West Pacific Petrochemical Corp.	Dalian	160.0	40.0	85.0	35.0		19.0

**Table 4.16 (Continued)**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Total HDT</u>	<u>Catalytic Hydrotreating</u>			<u>Other Heavy Oil</u>
		<u>Crude</u>	<u>Vacuum</u>		<u>Resid HDT</u>	<u>FCC Pre- treatment</u>		
China, Taiwan								
Chinese Petroleum Corp.	Kaohsiung	270.0	75.5	75.0	30.0	25.0		
Chinese Petroleum Corp.	Ta-Lin	300.0		60.0	60.0			
Chinese Petroleum Corp.	Tao-Yuan	200.0	36.0	45.0	45.0			
Formosa Petrochemical Co.	Mailiao	520.0	80.0	339.0	161.0	52.0		
		790.0	155.5	414.0	191.0	77.0		
Japan								
Cosmo Oil Co. Ltd.	Chiba	228.0	57.0	251.1	64.8			31.5
Cosmo Oil Co. Ltd.	Sakai	76.0	36.1	76.5				18.0
Cosmo Oil Co. Ltd.	Sakaide	114.0	39.4	112.7	27.0			15.5
Cosmo Oil Co. Ltd.	Yokkaichi	147.3	70.3	113.4				37.4
Fuji Oil Co. Ltd.	Sodegaura	192.0	55.0	168.5				47.0
Idemitsu Kosan Co. Ltd.	Chita, Aichi	152.0	15.2	152.1	54.0			
Idemitsu Kosan Co. Ltd.	Ichihara, Chiba	209.0	62.7	187.2	36.0	35.1		
Idemitsu Kosan Co. Ltd.	Shunan, Yamaguchi	114.0	52.3	108.0		40.5		
Idemitsu Kosan Co. Ltd.	Tomakomai, Hokkaido	133.0	22.8	111.0	34.2			
Japan Energy Co.	Mizushima, Okayama			241.1		63.0		
Kashima Oil Col Ltd.	Kashima, Ibaragi	180.5	39.9	174.6	27.0	22.5		
Kyushi Oil Co. Ltd.	Oita	130.0	66.0	69.0				33.0
Nippon Oil Co. Ltd.	Marifu, Yamaguchi	127.0	64.0	65.0				22.0
Nippon Oil Co. Ltd.	Mizushima	250.0	77.0	256.3	37.0			40.0
Nippon Oil Co. Ltd.	Muroran	180.0	65.0	170.1	45.0			22.0
Nippon Oil Co. Ltd.	Negishi	340.0	130.0	339.0	81.0			62.5
Nippon Oil Co. Ltd.	Sendai	145.0	60.0	100.0	35.0			29.0
Nippon Oil Co. Ltd.	Takaishi, Osaka	115.0	60.0	120.0				21.0
Okinawa Sekiyu Seisei	Yonashiro, Okinawa	100.0		129.0	38.0			20.0
Seibu Oil Co. Ltd.	Yamaguchi	110.0	40.0	142.0	50.0			
Showa Yokkaichi Sekiyu Co. Ltd.	Yokkaichi	222.0	96.3	173.2				36.9
Toa Oil Co. Ltd.	Mizue Factory, Kawasaki	65.0	57.0	117.0		46.0		

**Table 4.16 (Continued)**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Total HDT</u>	<u>Catalytic Hydrotreating</u>		
		<u>Crude</u>	<u>Vacuum</u>		<u>Resid HDT</u>	<u>FCC Pre- treatment</u>	<u>Other Heavy Oil</u>
Japan (Concluded)							
Toa Oil Co. Ltd.	Ohgimachi Factory, Kawasaki	120.0	30.0	92.0			16.0
Tonen/General Sekiyu Seisei KK	Kawasaki	296.0	94.5	299.0		79.0	
Tonen/General Sekiyu Seisei KK	Sakai	139.5	53.0	160.5		39.0	
Tonen/General Sekiyu Seisei KK	Wakayama	154.5	54.5	145.5		29.0	
		<b>4,039.8</b>	<b>1,398.0</b>	<b>4,073.7</b>	<b>529.0</b>	<b>354.1</b>	<b>451.7</b>
Philippines							
Pilipinas Shell Petroleum Corp.	Tabangao	153.0		78.4			47.3
Singapore							
Shell Eastern Petroleum (Pte.) Ltd.	Pulau Bukom	458.0	74.8	196.9	77.6		
South Korea							
SK Corp.	Ulsan	817.0	78.9	316.1	27.0	54.0	
S-Oil Co. Ltd.	Onsan	520.0	160.0	258.0	50.0	40.0	
		<b>1,337.0</b>	<b>238.9</b>	<b>574.1</b>	<b>77.0</b>	<b>94.0</b>	
Thailand							
Alliance Refining Co. Ltd.	Map Ta Phut, Rayong	301.0	128.4	241.1			34.7
		<b>7,848.8</b>	<b>2,081.6</b>	<b>5,843.2</b>	<b>1,014.6</b>	<b>528.1</b>	<b>552.7</b>
Aruba							
Valero Aruba Refining Co. NV	San Nicolas	270.8	166.3	214.2		117.0	
Brazil							
Petroleo Brasileiro SA	Duque de Caxis,Rio de Janeiro	232.2	112.2	45.0		11.7	



**Table 4.16 (Continued)**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Total HDT</u>	<u>Catalytic Hydrotreating</u>		<u>Other Heavy Oil</u>
		<u>Crude</u>	<u>Vacuum</u>		<u>Resid HDT</u>	<u>FCC Pre- treatment</u>	
Colombia							
Empresa Colombiana de Petroleos	Barrancaberme ja-Santander	205.0	101.0	19.8		19.8	
Ecuador							
Petroecuador	Esmeraldas	110.0	45.3	24.5			24.5
Netherlands Antilles							
Refineria Isla Curazao SA	Emmastad	320.0	195.0	119.5		26.0	
Venezuela							
Paraguana Refining Center	Cardon Falcon/Judiban a Falcon	940.0	504.0	380.7		184.5	
Virgin Islands							
Hovensa LLC	St. Croix	500.0	205.0	440.0		95.0	35.0
<b>Total Central &amp; South America</b>		<b>2,578.0</b>	<b>1,328.7</b>	<b>1,243.7</b>		<b>454.0</b>	<b>59.5</b>
Azerbaijan							
SOCAR	New Baku	160.0	71.0	67.5		42.2	
Kazakhstan							
Kazakoil	Pavlodar	162.7	94.0	123.1		46.0	
Russia							
Bashneftekhim-zavody	Ufa	235.0	98.7	90.5		42.2	
Central Fuel Co.	Moscow	243.0	90.2	142.7		42.2	
Sibneft	Omsk	286.2	195.0	159.2		42.2	
		<b>764.1</b>	<b>383.9</b>	<b>392.4</b>		<b>126.6</b>	
Ukraine							
TNK-Ukraina	Lisichansk	175.0	115.6	178.7		42.2	

**Table 4.16 (Continued)**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Total HDT</u>	<u>Catalytic Hydrotreating</u>		
		<u>Crude</u>	<u>Vacuum</u>		<u>Resid HDT</u>	<u>FCC Pre- treatment</u>	<u>Other Heavy Oil</u>
Uzbekistan							
Uzbekneftegaz	Fergana	106.0	45.7	30.8			
<b>7 Total Former Soviet Union</b>		<b>1,367.8</b>	<b>710.2</b>	<b>792.5</b>		<b>257.0</b>	
<hr/>							
Kuwait							
Kuwait National Petroleum Co.	Mina Abdulla	256.5	142.5	188.1	107.1		
Kuwait National Petroleum Co.	Mina Al-Ahmadi	442.7	80.8	318.8	130.3		
		<b>699.2</b>	<b>223.3</b>	<b>506.9</b>	<b>237.4</b>		
<hr/>							
Saudi Arabia							
Petromin-Shell	Al-Jubail	305.0	84.0	182.0			49.0
<hr/>							
Syria							
Homs Refinery Co.	Homs	107.1	12.2	43.3			3.1
<hr/>							
Turkey							
Turkish Petroleum Refineries Corp.	Izmit	251.6	89.9	139.0		39.0	
<hr/>							
United Arab Emirates							
Abu Dhabi National Oil Co.	Ruwais, Abu Dhabi	350.0	56.7	83.0		39.2	21.9
<b>Total Middle East</b>		<b>1,712.9</b>	<b>466.1</b>	<b>954.2</b>	<b>237.4</b>	<b>78.2</b>	<b>73.9</b>
<hr/>							
Egypt							
Ameriya Petroleum Refining Co.	Alexandria	78.0	15.0	37.5			10.0
<hr/>							
Eritrea							
Pertroleum Corp. of Eritrea	Assab	14.6	2.2	2.7		2.7	
<hr/>							

**Table 4.16 (Concluded)**  
**CAPACITIES OF WORLD HEAVY OIL HYDROTREATING REFINERIES OUTSIDE OF NORTH AMERICA**

CAPACITY (1,000 B/CD)

<u>Country/Company</u>	<u>Location</u>	<u>Distillation</u>		<u>Catalytic Hydrotreating</u>			
		<u>Crude</u>	<u>Vacuum</u>	<u>Total HDT</u>	<u>Resid HDT</u>	<u>FCC Pre-treatment</u>	<u>Other Heavy Oil</u>
<b>Total Africa</b>		<b>92.6</b>	<b>17.2</b>	<b>40.2</b>		<b>2.7</b>	<b>10.0</b>
<b>Total North America</b>		<b>9,084.5</b>	<b>4,454.8</b>	<b>8,630.3</b>	<b>292.0</b>	<b>2,079.3</b>	<b>208.4</b>
<b>Total World</b>		<b>28,616.5</b>	<b>11,466.4</b>	<b>22,216.2</b>	<b>1,660.3</b>	<b>4,251.6</b>	<b>1,161.6</b>

Worldwide, the average hydrotreating refinery's combined resid, FCC feed and other heavy oil hydrotreating capacity is 48,000 B/cD. The average capacity is about the same in or outside North America (48,500 B/cD versus 47,700 B/cD outside). Of the world's heavy oil hydrotreating refineries, 66% have FCC feed pretreaters while 85% of the North American refineries do. FCC feed hydrotreating capacity ranges from 3,000 to 105,500 B/cD in North America and 2,742 to 184,500 B/cD outside North America. Resid hydrotreating capacities range from 27,000 to 161,000 B/cD. The distribution of total heavy oil hydrotreating capacity in the refineries is summarized in Table 4.17. Refineries with 80,000 B/cD or larger total heavy oil hydrotreating capacity comprise 17% worldwide of these hydrotreating refineries and 23% in North America. These large capacity refineries account for 37% of worldwide and 45% of North American heavy oil hydrotreating capacity. In North America, 50% of the refineries have less than 40,000 B/cD of heavy oil hydrotreating. The 50% of North American refineries with at least 40,000 B/cD capacity produce about 77.5 vol% of the products. Outside of North America, capacity shows a similar distribution as North America: 51.5% of the 40,000 B/cD or greater capacity hydrotreating refineries have 77.2% of the total heavy oil hydrotreating capacity.

**Table 4.17**  
**HEAVY OIL<sup>a</sup> HYDROTREATERS – DISTRIBUTION OF CAPACITIES**

<b>Capacity Range, 1,000 BPcD</b>	<b>% by Number</b>			<b>% by Volume</b>		
	<b>North America</b>	<b>World Excl. N.A.</b>	<b>World</b>	<b>North America</b>	<b>World Excl. N.A.</b>	<b>World</b>
Below 10	7.7	7.5	7.6	0.9	0.9	0.9
10-20	15.4	10.8	12.4	4.4	3.4	3.8
20-30	11.5	15.1	13.8	5.4	7.5	6.7
30-40	15.4	15.1	15.2	11.2	11.0	11.1
40-50	3.8	18.3	13.1	3.6	16.8	12.0
50-60	5.8	8.6	7.6	6.1	9.5	8.3
60-70	13.5	6.5	9.0	17.4	9.8	12.6
70-80	3.8	5.4	4.8	5.7	8.4	7.5
80-110	23.1	12.9	16.6	45.3	32.7	37.3
Total	100.0	100.0	100.0	100.0	100.0	100.0

<sup>a</sup> FCC feed pretreatment plus resid hydrotreating and other heavy gas oil hydrotreating

### **New Construction**

Announced new or planned construction (revamps and expansions are excluded) of hydrotreaters for all types of feedstocks is listed in Table 4.18 by location. Of the 49 projects, announced new world capacity for 43 units totals 1.38 million B/D. The country with the most new units announced is Brazil with 14 units totaling 309,700 B/D followed by the U.S. with 12 units totaling 376,500. The Middle East region has 8 projects totaling 300,000 B/D.

**Table 4.18**  
**ANNOUNCED NEW HYDROTREATING CONSTRUCTION PROJECTS**

<b><u>Company</u></b>	<b><u>Location</u></b>	<b><u>Capacity, B/D</u></b>	<b><u>Status</u></b>	<b><u>Contractor/Licenser</u></b>
Eastern Refinery Ltd.	Chittagong, Bangladesh	20,000	Planning, 2009	---
		250,000	Planning, 2009	---
JSC Mozyr	Mozyr, Belarus	5,840	Engineering, 2008	Fluor/Albemarle
Alberto Pasqualini Refinery	Canoas, RGS, Brazil	---	Construction, 2006	---
		30,157	Planning, 2009	---
Duque de Caxias Refinery	Rio de Janeiro, Brazil	12,063	Construction, 2006	---
		30,157	Planning, 2009	---
Gabriel Passos Refinery	Betim, MG, Brazil	19,084	Planning, 2009	---
		24,126	Planning, 2009	---

**Table 4.18 (Continued)**  
**ANNOUNCED NEW HYDROTREATING CONSTRUCTION PROJECTS**

<b>Company</b>	<b>Location</b>	<b>Capacity, B/D</b>	<b>Status</b>	<b>Contractor/Licenser</b>
Ladulpho Alves Refinery	San Francisco do Conde, BA, Brazil	18,094	Planning, 2009	---
Paulina Refinery	Paulinia, SP, Brazil	24,126	Planning, 2009	---
		24,126	Planning, 2009	---
		36,189	Planning, 2009	---
Presidente Bernardes Refinery	Cubatao, SP, Brazil	13,206	Under Construction, 2009	---
		30,157	Planning, 2009	---
Presidente Getulio Vargas Refinery	Araucaria, Parana, Brazil	18,094	Planning, 2009	---
		30,157	Planning, 2009	---
Imperial Oil	Edmonton, Alberta, Canada	---	Construction, 2006	Fluor
Empresa Colombiana de Petroleos	Barrancabermeja, Santander, Colombia	19,000	Engineering, 2007	Axens
Ceska Rafinerska AS	Kralupy, Czech Republic	7,750	Engineering, Nov. 2007	ABB Lummus
Saras SPA	Sarroch, Italy		Engineering, 2008	Foster Wheeler, Axens
Kyokuto Petroleum Industries Ltd.	Ichihara, Chiba, Japan	14,000	Planning, 2007	ExxonMobil Corp.
Amakpe International Refineries Ltd.	Eket, Akwa Ibom, Nigeria	4,000	Planning, Dec. 2007	---
PKN Orlen SA	Plock, Poland	---	Engineering, June 2009	Technip
Oman Refining Co.	Sohar, Oman	---	Construction, 2006	JGC/Chiyoda
		1,309	Construction, 2006	UOP LLC, JGC/Chiyoda
		26,858	Construction, 2006	UOP LLC, JGC/Chiyoda
		40,540	Construction, 2006	UOP LLC, JGC/Chiyoda
Alliance Oil Co.	Khabarovsk, Russia	---	Engineering, 2006	Shell Global Solutions
Saudi Aramco	Riyadh, Saudi Arabia	45,000	Engineering, 2006	Foster Wheeler Ltd., Technip, Axens
	Yanbu, Saudi Arabia	95,000	Engineering, 2006	Foster Wheeler Ltd., Axens

**Table 4.18 (Concluded)**  
**ANNOUNCED NEW HYDROTREATING CONSTRUCTION PROJECTS**

<b>Company</b>	<b>Location</b>	<b>Capacity, B/D</b>	<b>Status</b>	<b>Contractor/Licenser</b>
BP PLC	Castellon de la Plana, Spain	6,000	Engineering, 2007	Intecsa-Uhde; ExxonMobil
Chinese Petroleum Corp.	Ta-Lin, Taiwan	20,000	Planning, 2008	---
	Tao-Yuan, Taiwan	30,000	Planning, 2008	---
Turkish Petroleum Refineries Corp.	Izmit, Turkey	10,100	Engineering, 2006	Axens
		53,500	Construction, 2006	UOP
	Kirikale, Turkey	28,000	Construction, 2007	ABB Lummus Global
BP PLC	Whiting, IN USA	105,000	Engineering, 2011	Fluor
Frontier Oil Corp.	Cheyenne, WY USA	18,500	Engineering, 2006	Haldor Topsoe
Lyondell-Citgo LP	Houston, TX USA	70,000	Construction, 2006	Fluor; S&B Constructors
Tesoro Corp.	Anacortes, WA USA	10,000	Planning, 2007	---
	Kenai, AK USA	10,000	Planning, 2007	---
	Mandan, ND USA	14,000	Engineering, 2006	Haldor Topsoe
United Refining	Warren, PA USA	26,000	Engineering, 2007	Foster Wheeler
Valero Energy Corp.	Lima OH USA	25,000	Engineering, 2006	Jacobs
	Memphis, TN USA	33,000	Engineering, 2006	Jacobs
	Port Author, TX USA	45,000	Engineering, 2006	Jacobs
Western Refining	El Paso, TX USA	---	Engineering, 2006	Haldor Topsoe
Wynnewood Refining Co.	Wynnewood, OK USA	20,000	Construction, 2007	Koch Partners LP
Dzung Quat Refinery	Quang Ngai, Vietnam	29,000	Engineering, 2009	Axens

Source: 214A549, 214A550

## 5 GENERAL PROCESS REVIEW

Worldwide, the importance of hydrotreating heavy oils for FCC feedstocks and fuel oil is increasing as discussed in Section 4 due to worldwide crude oil supply and environmental factors:

- More heavy crude oils and oil sands bitumen is being refined
- Demand for near zero sulfur vehicle fuels is increasing
- Growing regulatory requirements specify that marine and stationary boiler fuels be low sulfur
- Benefits of removing catalyst poisons of further downstream processes are increasingly recognized and required for optimum performance

Hydrotreating is a preferred process for removing the high levels of sulfur, nitrogen and oxygen found in heavy crude oils, which concentrate in the heavier distillation fractions [214A292]. The lowest sulfur heavy fuel oil commercially produced by hydrotreating sour crude (about 3 wt% sulfur in the atmospheric residue) is about 0.1 wt% sulfur. Properties of that premium fuel oil produced by the Chevron Lummus Global Residuum Desulfurization (RDS) process (described in Section 6) are summarized in Table 5.1.

**Table 5.1**  
**PREMIUM LOW SULFUR FUEL OIL AND FEEDSTOCK PROPERTIES<sup>a</sup>**

	<u>RDS Feed</u>	<u>RDS 650°F+ (343°C+) Product</u>
Gravity, API	16.0	23.9
Specific gravity, 59°F/39°F (15°C/4°C)	0.9590	0.9105
Sulfur, wt%	3.75	0.09
Nitrogen, ppm	2060	644
Ni, ppm	13	<1
V, ppm	40	<1
Carbon residue, %	7.95	2.28
Viscosity, cSt at 122°F (50°C)	248	84

**Table 5.1 (Concluded)**  
**PREMIUM LOW SULFUR FUEL OIL AND FEEDSTOCK PROPERTIES<sup>a</sup>**

	<u>RDS Feed</u>	<u>RDS 650°F+ (343°C+) Product</u>
Distillation, °F (°C)		
IBP	495 (257)	522 (272)
5%	617 (325)	626 (330)
10	667 (353)	676 (358)
20	756 (402)	739 (393)
30	815 (435)	797 (425)
40	873 (467)	842 (450)
50	936 (502)	896 (480)
60	999 (537)	959 (515)
70	---	1031 (555)

Source: 214A530

<sup>a</sup> Commercial data from Idemitsu Kosan's Aichi, Japan unit.

Benefits of hydrotreating FCC feed include lower sulfur of the full boiling range of FCC products, possible avoidance or simplification of post FCC desulfurization and much less H<sub>2</sub> is consumed than in conventional post FCC hydrotreatment [214A455].

Since the heavy oils contain high percentages of asphaltenes and metal compounds not found in the lighter distillates, hydrotreating heavy oils is more complex a process than hydrotreating middle distillates for diesel fuel (discussed in PEP Report 246, *Near Zero Sulfur Diesel Fuel* (2002)). Asphaltenes and metals can deactivate hydrotreating catalysts very fast through the formation of coke and through plugging of the catalyst's pores by metal deposits. Metals that must be removed from feedstocks in order to ensure further safe and effective catalytic processing are summarized in Table 5.2.

**Table 5.2**  
**NEGATIVE EFFECTS OF METALLIC COMPOUNDS IN CRUDE OIL**

<u>Metal</u>	<u>Negative Effects</u>
Ni	Deposits on catalytic cracking catalyst, causing excess coke and gas formation and causes adverse product selectivity.
V	Same as Ni. Also V is a heavy metal that is thought to cause lung disease. It also causes deterioration of fire brick and corrosion of boiler tubes and turbine blades.
Na	Sodium buildup can reduce catalytic activity. Sodium in fuels is an ash-forming constituent and corrosive.
Cu	Destabilizes various petroleum products by accelerating gum and sediment formation. Also Cu is a catalyst poison for catalytic cracking but less so than Ni or V.
Fe	An ash former and also acts as a catalyst poison-like Ni and V but to a lesser degree.
As	Permanent poison for catalytic reforming catalysts.

Source: 214A525



Hydrotreating catalysts are made in various average pore sizes, in several pellet shapes and with active metal combinations of primary, secondary and even tertiary elements. Pore diameter is an important property for residue hydrotreating due to the large asphaltene molecules and associated metals deposition and diffusion considerations. Large pore demetallization catalyst is used in the first bed while smaller pore, more active HDS/HDN catalyst is used in the final bed. Trilobe and pentalobe extrudate geometries reduce pressure drop and provide higher surface area compared to cylinders. The active metals are usually molybdenum or tungsten promoted by nickel or cobalt and enhanced by phosphorus. There is an optimum balance of catalyst pore size and surface area that balances the diffusion, dispersion of active metals and deactivation rate.

The performance of a hydrotreating process depends upon the nature and concentration of the heteroatoms (sulfur, nitrogen, oxygen and metals) present in the feedstock, the product specifications, the catalyst properties (activity, selectivity and rate of deactivation), reactor design and operating conditions.

Selected patents and patent applications since 1994 of general interest for heavy oil hydrotreating are summarized in Appendix A. Table A.1 (in Appendix A) contains summaries of catalysis patents and applications. Table A.2 similarly contains process related patents and applications.

In this section, we review the properties of the major heavy oil feedstocks and products, the chemistry of the process and its catalysts with emphasis on research reported since PEP Report 214 *Hydrotreating* (1996). Developments in the hydrotreating process and reactors for heavy oils are reviewed in Section 6.

## **HYDROTREATER FEEDSTOCK PROPERTIES**

Heavy oils can be envisioned as composed of three major components: oil, resins and asphaltenes, which also contain heteroatoms (sulfur, nitrogen, oxygen and metals).

Most of the nitrogen present in heavy crude oils resides in heterocyclic organonitrogen compounds of either basic or nonbasic ring structures. The nonbasic nitrogen compounds are more difficult to remove with conventional sulfided NiMo catalysts than the basic compounds since the nonbasic compounds adsorb weaker on the catalyst. In HDN of mixtures of basic and nonbasic nitrogen compounds, reactivity of the basic compounds is always greater than their nonbasic analogs. This can be explained by the higher adsorption energy of all basic nitrogen compounds than non-basic compounds [214A218].

We review the properties of two major heavy oil feeds for hydrotreaters, FCC gas oil feedstock and oil sands bitumen with emphasis on bitumen derived gas oils. Properties of residual oils and their catalytic cracking are reviewed in PEP Report 228, *Refinery Residue Upgrading*, (2000). FCC feedstocks and the FCC process with emphasis on gas oil cracking are reviewed in PEP Report 195A, *Advances in fluid catalytic cracking*, (2005).

### **FCC Feedstock Properties**

A typical FCC feedstock and hence FCC pretreater feed is a blend of about 38 vol% heavy atmospheric gas oil, 18% light vacuum gas oil and 44% heavy vacuum gas oil. Properties of light and heavy gas oils from four crude oils summarized in Table 5.3 show wide variation with crude source. Atmospheric and vacuum residues or their blends, which may include vacuum gas oil, are feeds for residue FCC (RFCC) units. Coker gas oil and deasphalted oil may also be blended into the RFCC feed. The range of typical RFCC feedstock properties are summarized in Table 5.4. Residue feedstocks are more difficult to hydrotreat than gas oils due to higher concentrations

of contaminants, especially sulfur, nitrogen, metals, asphaltenes, sediment and carbon residue [214A011, 214A175].

**Table 5.3**  
**SELECTED PROPERTIES OF LIGHT AND HEAVY VACUUM GAS OILS**

<u>Crude Source</u>	<u>Oil Cut</u>	<u>Sulfur, wt%</u>	<u>Nitrogen, ppm</u>	<u>Saturates, wt%</u>	<u>Aromatics, wt%</u>	<u>Polars, wt%</u>
South China Sea	LVGO	0.06	147	7.7	11.6	0.7
	HVGO	0.09	798	73.5	23.7	2.8
Mexico	LVGO	3.17	1524	42.5	35.0	22.5
	HVGO	3.68	2362	28.3	46.4	25.3
Central America	LVGO	4.81	809	30.1	66.3	3.6
	HVGO	5.49	1211	18.9	75.5	5.6
West Coast	LVGO	4.22	3107	39.6	54.3	6.1
	HVGO	4.94	3904	26.6	63.2	10.2

Source: 214A147

LVGO = light vacuum gas oil; HVGO = heavy vacuum gas oil

**Table 5.4**  
**TYPICAL RFCC FEEDSTOCK PROPERTIES**

	<u>Coker Gas Oil &amp; DAO Mixtures</u>	<u>Mid East Mixture Atm. Residue</u>	<u>Mid East Mixture Vacuum Residue</u>
Specific Gravity	0.95-1.00	0.955-0.985	1.010-1.040
Viscosity at 212°F (100°C), cSt	5-250	25-70	800-2,000
Sulfur, wt%	2.0-4.5	3.4-4.3	4.2-5.0
Nitrogen, ppmw	2,500-3,400	1,800-2,300	3,100-3,700
Conradson Carbon Residue, wt%	1-10	9-14	18-22
Asphaltenes, wt%	<<1	2-5	6-9
Metals (Ni+V), ppmw	5-50	50-110	110-200

Source: 214A011

Physical properties alone do not adequately characterize FCC feedstocks sufficiently to enable the satisfactory prediction of FCC yields (Table 5.5). Mass spectra analysis shows significant compositional differences between commercial samples. The 5% more di+ aromatics in Sample A than sample B can significantly increase the cycle oil yield and reduce conversion. Samples B and C have almost identical physical properties, but differ in aromatics and saturates.

**Table 5.5**  
**PROPERTIES OF THREE COMMERCIAL FCC FEEDSTOCKS**

	<u>Feed A</u>	<u>Feed B</u>	<u>Feed C</u>
<b>Physical Properties</b>			
Gravity, API	24.6	24.5	24.6
Sulfur, wt%	1.01	0.28	0.25
Hydrogen, wt%	12.48	12.54	12.60
Conradson Carbon Residue, wt%		0.19	0.21
Nickel, ppmw		<0.5	0.23
Vanadium, ppmw		<0.2	<0.5
<b>Molecular type by mass-spec analysis</b>			
Saturates, wt%	59.6	60.8	72.9
Monoaromatics, wt%	14.6	18.4	13.1
Di+ Aromatics, wt%	25.8	20.8	14.0
Total, wt%	100.0	100.0	100.0

Source: 214A179

Significantly improved predictions of FCC yields compared to conventional methods are obtained by characterizing the feedstock using a combination of conventional physical properties coupled with detailed high-resolution electron-impact mass spectrometry (Hreims) and a nuclear magnetic resonance (NMR) based magnetic imaging of FCC feedstock (MIFF) system (Table 5.6) [214A179].

**Table 5.6**  
**FCC YIELD ESTIMATE COMPARISON**

<u>Products</u>	<u>Mass Spec, wt%</u>	<u>Mass Spec. &amp; NMR, wt%</u>	<u>Plant Data, wt%</u>
H <sub>2</sub> S	0.49	0.49	0.36
H <sub>2</sub> -C <sub>2</sub>	4.75	3.50	3.51
LPG	14.86	17.03	16.53
Gasoline	37.53	43.81	43.70
Light Cycle Oil	20.37	17.44	19.22
Decant Oil	16.79	12.56	11.58
Coke	5.21	5.17	5.10
Total	100.00	100.00	100.00
Conversion, %	62.84	70.0	69.3

Source: 214A179

Mercaptans crack mainly to H<sub>2</sub>S. Alkylthiophenes in the FCC feed contribute significantly to gasoline sulfur. The alkyl chains are cracked from the thiophene species and isomerize into a range of alkylated thiophene species. Alkyl groups can also cyclize and dehydrogenate to benzothiophenes [214A552].

## Oil Sand Bitumen Properties

Bitumen is a very viscous, heavy crude oil that will not flow unless diluted with lighter oil or heated. Bitumen comprises 10-12% of oil sands; sand and clay account for 80-85% and water for 4-6%. The API gravity of bitumens ranges from 7 to 14 while the sulfur content ranges from 4% to 5%. Analysis of one bitumen (Table 5.7) shows residue is 50-55 LV% of the oil. One bitumen is composed of 83.2% carbon, 10.4% hydrogen, 0.94% oxygen, 0.36% nitrogen and 4.8% sulfur. Bitumen is upgraded through four main processes into synthetic crude oil: (1) coking to reduce carbon and to crack large molecules into smaller ones, (2) distillation, (3) catalytic conversion and (4) hydrotreating to reduce sulfur and nitrogen while adding hydrogen [214A508].

**Table 5.7**  
**ANALYSIS OF TYPICAL BITUMEN**

API gravity	7-8
Sulfur, wt%	4-5
Boiling Fractions, LV%	
Naphtha, C <sub>5</sub> -350°F (C <sub>5</sub> -177°C)	<1
Distillate, 350-649°F (177-343°C)	15-20
Gasoil, 650-975°F (343-524°C)	20-30
Residue, 975°F+ (524°C+)	50-55

Source: 214A508

Oil sand bitumen and its gas oil contain high levels of nitrogen (~4000 ppm) and sulfur (~4 wt%) compared to conventional crude oils and gas oils. The high nitrogen level adversely affects these oils during storage and deactivates refining catalysts at a higher rate than conventional oils [214A318]. The properties of bitumen derived gas oils are unique; the oils are difficult to hydrotreat [214A313].

The properties of a virgin gas oil derived from Canadian oil-sands bitumen are listed in Table 5.8 and compared with a hydrotreated coker gas oil and a hydrotreated deasphalted oil, both also made from Canadian oil-sands bitumen.

**Table 5.8**  
**SELECTED PROPERTIES OF CANADIAN OIL-SANDS BITUMEN OILS**

	<u>Virgin Gas Oil</u>	<u>Hydrotreated Coker Gas oil</u>	<u>Hydrotreated Deasphalted Oil</u>
Density at 60°F (15.6°C), g/ml	0.9712	0.9511	0.9430
API gravity	14.2	17.3	18.55
Sulfur, wt%	3.25	0.43	0.70
Total nitrogen, wppm	1930	2150	2450
Basic nitrogen, wppm	610	439	613
Conradson carbon residue, wt%	0.33	0.50	2.00
Aromatic carbon, %	25.4	24.7	20.9
975°F (524°C) + by simulated distillation, wt%	2.0	8.3	36.9

**Table 5.8 (Concluded)**  
**SELECTED PROPERTIES OF CANADIAN OIL-SANDS BITUMEN OILS**

	<u>Virgin Gas Oil</u>	<u>Hydrotreated Coker Gas oil</u>	<u>Hydrotreated Deasphalted Oil</u>
Hydrocarbon Type Analysis, wt%			
Saturates	28.7	34.4	35.4
Paraffins	1.8	4.7	5.0
Cycloparaffins	26.9	29.7	30.4
Aromatics	65.6	61.8	57.5
Mono-	22.5	29.5	29.5
Di-	14.4	13.6	12.7
Tri-	7.2	6.3	5.4
Tetra- and up	10.8	8.2	6.5
Aromatic sulfur			
Benzothiophenes	5.0	0.7	1.2
Dibenzothiophenes	4.6	3.0	2.0
Benzonaphthophenes	1.1	0.5	0.2
Polar Compounds	5.7	3.8	7.1

Source: 214A162

### Bitumen Gas Oil

Properties of a narrow cut, mid-boiling gas oil (811-901°F, 433-483°C) derived from Athabasca oil sands bitumen are shown in Table 5.9. Also presented are properties of its products after hydrotreating at three temperatures: 707°F (375°C), 725°F (385°C) and 752°F (400°C). The H/C ratios and <sup>13</sup>CNMR aromaticity (f<sub>a</sub>) for three products are similar, but show significant hydrotreating when compared to the feed. Hydrotreating reduced the concentrations of the heteroatoms, especially sulfur. Hydrotreating did not significantly change the molecular weight.

**Table 5.9**  
**CHARACTERIZATION OF ATHABASCA BITUMEN DERIVED GAS OIL AND**  
**HYDROTREATED PRODUCTS**

<u>Property</u>	<u>Feed</u>	<u>Product, hydrotreated at</u>		
		<u>707°F (375°C)</u>	<u>725°F (385°C)</u>	<u>752°F (400°C)</u>
C	84.6	87.33	87.19	87.55
H	10.43	11.74	11.92	11.82
N	0.43	0.30	0.20	0.17
S	4.03	0.30	0.39	0.09
O	0.54	0.34	0.31	0.37
H/C	1.48	1.61	1.64	1.62
f <sub>a</sub>	35.0	25.1	26.0	25.8

**Table 5.9 (Concluded)**  
**CHARACTERIZATION OF ATHABASCA BITUMEN DERIVED GAS OIL AND**  
**HYDROTREATED PRODUCTS**

<b>Property</b>	<b>Feed</b>	<b>Product, hydrotreated at</b>		
		<b><u>707°F (375°C)</u></b>	<b><u>725°F (385°C)</u></b>	<b><u>752°F (400°C)</u></b>
Molecular Weight				
GPC M <sub>number ave.</sub>	278	281	287	284
GPC M <sub>weight ave.</sub>	294	333	338	337
GC-MS	340	---	332	---

Source: 214A052

GPC = gel permeation chromatography; GC-MS = gas chromatography-mass spectroscopy

The effects of hydrotreating are shown by fractionating the feed and products by preparative high performance liquid chromatography into four fractions characterized as saturate, mono-, di- and poly-aromatics (3-5 rings). The poly-aromatic fraction is further separated into three subfractions corresponding to elution times for three, four and five ring model compounds. The yields and H/C ratio of the fractions and subfractions are summarized in Table 5.10. The yields of saturates and mono-aromatics of the products increase due to saturation and cracking of the polyaromatics. The mono-aromatics are essentially independent of reaction temperature. Di- and poly-aromatics yields both decrease as hydrotreating temperature increases. The atomic H/C ratio generally decreases from the saturated to the poly-aromatic fraction. The aromaticity and molecular formulas of the fractions and subfractions for the feed and the 725°F (385°C) product shown in Table 5.11. The product fractions are more aromatic than the feed. The relative changes in the heteroatom content of the fractions of product and feed show only minor differences in nitrogen among the saturated, mono- and di-aromatics. Hydrotreating reduces the overall amount of heteroatoms; the remaining heteroatoms in the product are concentrated in the polyaromatic fraction, which accounts for more than 90 wt% of the total nitrogen, 30 wt% of total oxygen and 60 wt% of total sulfur [214A052].

**Table 5.10**  
**YIELDS AND H/C RATIOS OF ATHABASCA BITUMEN DERIVED 811-901°F (433-483°C)**  
**GAS OIL AND HYDROTREATED PRODUCT**

		Product hydrotreated at		
HPLC Fraction	Feed	707°F (375°C)	725°F (385°C)	752°F (400°C)
Yield, wt% of parent sample				
Saturated	26.6	41.8	43.0	46.3
Mono-aromatic	19.7	30.9	30.6	30.8
Di-aromatic	20.1	18.1	17.0	16.2
Poly-aromatic	33.6	9.2	9.5	6.8
Three ring	23.3	6.3	6.8	5.1
Four ring	8.5	2.4	2.1	1.4
Five ring	1.8	0.5	0.6	0.3

**Table 5.10 (Concluded)**  
**YIELDS AND H/C RATIOS OF ATHABASCA BITUMEN DERIVED 811-901°F (433-483°C)**  
**GAS OIL AND HYDROTREATED PRODUCT**

<b>HPLC Fraction</b>	<b>Feed</b>	<b>Product hydrotreated at</b>		
		<b>707°F (375°C)</b>	<b>725°F (385°C)</b>	<b>752°F (400°C)</b>
			H/C ratio	
Saturated	1.78	1.84	1.89	1.88
Mono-aromatic	1.55	1.55	1.54	1.53
Di-aromatic	1.31	1.22	1.25	1.23
Poly-aromatic				
Three ring	1.08	1.08	1.08	1.04
Four ring	1.18	1.21	1.21	1.23
Five ring	1.17	1.18	1.27	1.24

Source: 214A052

**Table 5.11**  
**AROMATICITY AND MOLECULAR FORMULAS OF ATHABASCA BITUMEN DERIVED 811-901°F (433-483°C) GAS OIL AND 725°F (385°C) HDT PRODUCT**

<b>HPLC Fraction</b>	<b>Feed</b>	<b>Product</b>
	$f_a (^{13}\text{CNMR})$	
Saturated	0	0
Mono-aromatic	17.7	28.8
Di-aromatic	48.4	51.2
Poly-aromatic		
Three ring	68.0	70.0
Four ring	65.3	69.0
Five ring	---	---
	<b>Molecular Formula</b>	
Saturated	$\text{C}_{32.4}\text{H}_{57.8}\text{N}_{0.03}\text{S}_{0.02}\text{O}_{0.12}$	$\text{C}_{33.4}\text{H}_{62.8}\text{N}_{0.03}\text{S}_{0.00}\text{O}_{0.08}$
Mono-aromatic	$\text{C}_{23.8}\text{H}_{37.0}\text{N}_{0.02}\text{S}_{0.23}\text{O}_{0.1}$	$\text{C}_{26.0}\text{H}_{40.1}\text{N}_{0.02}\text{S}_{0.01}\text{O}_{0.10}$
Di-aromatic	$\text{C}_{19.9}\text{H}_{26.2}\text{N}_{0.02}\text{S}_{0.54}\text{O}_{0.14}$	$\text{C}_{21.0}\text{H}_{26.4}\text{N}_{0.02}\text{S}_{0.06}\text{O}_{0.07}$
Poly-aromatic		
Three ring	$\text{C}_{16.9}\text{H}_{18.2}\text{N}_{0.11}\text{S}_{0.58}\text{O}_{0.15}$	$\text{C}_{17.9}\text{H}_{19.4}\text{N}_{0.11}\text{S}_{0.03}\text{O}_{0.11}$
Four ring	$\text{C}_{17.9}\text{H}_{21.1}\text{N}_{0.41}\text{S}_{0.41}\text{O}_{0.41}$	$\text{C}_{18.2}\text{H}_{22.1}\text{N}_{0.66}\text{S}_{0.09}\text{O}_{0.27}$
Five ring	$\text{C}_{18.8}\text{H}_{22.0}\text{N}_{0.67}\text{S}_{0.33}\text{O}_{0.49}$	$\text{C}_{19.0}\text{H}_{24.3}\text{N}_{0.82}\text{S}_{0.1}\text{O}_{0.38}$

Source: 214A052

Due to the large polyaromatics content, gas oils derived from bitumen are poor FCC feedstocks without hydrotreating or hydrocracking. The most difficult to treat feeds gain the most advantage by hydrotreating. During catalytic cracking, alkyl side chains with a carbon number of three or greater cleave off polyaromatics molecules close to the aromatic ring as olefins and, if long enough, may crack again. FCC will not open aromatic ring structures. If a three ring aromatic molecule is hydrotreated to partially saturate two of the rings, consuming four molecules of H<sub>2</sub> before FCC, the two saturated rings would open during FCC far more easily than the corresponding aromatic ring. The majority of partially saturated ring structures will crack to a monoaromatic product cleaved of large side chains, usually high octane number toluene or xylene but seldom benzene, while a smaller amount will crack to diaromatics also free of long side chains. If the three ring compound is fully saturated in a hydrotreater prior to FCC, seven molecules of H<sub>2</sub> are consumed in saturating the rings. During FCC, all three rings mostly crack open to form various normal paraffins, isoparaffins and olefins. The normal and isoparaffins are much lower octane number compounds than aromatic compounds of the same carbon number. Some of the saturated three compounds will partially dehydrogenate back to form monoaromatics plus several paraffins. Fully saturating the aromatic rings reduces gasoline yield and octane number and slightly increases LPG and dry gas yields compared to the partial saturation case. The cracking of saturate and aromatic ring structures is summarized in Table 5.12.

**Table 5.12**  
**CRACKING OF AROMATIC RINGS**

Multi-ring aromatics	<ul style="list-style-type: none"> <li>• High cycle oil yield</li> <li>• Low gasoline yield</li> <li>• Gasoline, mostly paraffins and olefins</li> <li>• Low gas yield</li> </ul>
Mono-ring aromatics	<ul style="list-style-type: none"> <li>• High gasoline yield</li> <li>• Gasoline mostly aromatics (high octane)</li> <li>• Low gas yield</li> </ul>
Naphthenes	<ul style="list-style-type: none"> <li>• Reasonably high gasoline yield</li> <li>• Gasoline mostly paraffins and olefins (lower octane)</li> <li>• Higher gas yield</li> </ul>

---

Sources: 214A028, 214A509

To maximize FCC gasoline production, the feed hydrotreating conditions should be set to saturate all multi-ring aromatics to monoaromatics. A hydrotreater product hydrogen content of 12-12.5 wt% is suggested as optimal for bitumen derived heavy gas oils. Further H<sub>2</sub> consumption would lower the gasoline yield and octane number. To maximize light olefin production for alkylation feed or chemicals, conditions resulting in higher H<sub>2</sub> consumption are optimal [214A028, 214A509].

Hydrotreating of bituminous feedstocks prior to FCC also reduces the volume of the feed if the distillate and lighter hydrotreating products are fractionated from the FCC feedstock. Severe hydrotreating of a VGO feed converts about 10-15 LV% of the feed to distillate and lighter products due to removal of sulfur and nitrogen and to some hydrocracking. The FCC unit is debottlenecked or additional feed can be cracked, improving the economics [214A028, 214A509].



## Bitumen Coker Gas Oil

Properties of a coker gas oil derived from Athabasca oil sands bitumen are shown in Table 5.13 for the whole and narrow boiling fractions. The 811-901°F (433-483°C) cut was further fractionated by preparative high pressure liquid chromatography into four fractions characterized as saturate, mono-, di- and poly-aromatics (3-5 rings). The poly-aromatic fraction was then separated into three subfractions corresponding to elution times for three, four and five ring model compounds. The properties of the fractions and subfractions are summarized in Tables 5.14 and 5.15. The atomic H/C ratio generally decreases from the saturated to the poly-aromatic fraction. The concentrations of the heteroatoms are highest in the poly-aromatic fraction (90 wt% of total nitrogen and 60 wt% of the total oxygen) and generally low in the saturates. This combined with the low molecular weight indicates that the fraction is extremely polar. The poly-aromatic subfractions show only minor differences in molecular weights and average structural parameters, each subfraction comprises an average of two aromatic rings with virtually the same H/C ratios and aromaticities. The concentration of nitrogen in the subfractions (a) and (b) may allow its selective removal in only a small fraction (<10%) of the coker gas oil [214A313].

**Table 5.13**  
**CHARACTERIZATION OF ATHABASCA BITUMEN DERIVED COKER GAS OIL AND ITS**  
**NARROW BOILING FRACTIONS**

Fraction		Yield, wt%	Molecular Weight		Sulfur, wt%	Nitrogen, wt%	H/C	f <sub>a</sub>
°F	°C		VPO	GPC Mn				
Bulk oil		100.0	na	210	4.07	0.40	1.51	34.5
IBP-650	IBP-343	19.2	na	158	3.82	0.17	1.55	34.5
650-739	343-393	19.1	266	176	3.86	0.24	1.52	34.3
739-811	393-433	18.0	318	196	3.93	0.32	1.47	34.5
811-901	433-483	21.2	362	221	3.90	0.42	1.49	35.0
901-939	483-504	5.6	404	239	4.38	0.52	1.41	37.4
939-975	504-524	7.8	470	340	4.49	0.57	1.45	39.4
>975	>524	9.1	590	450	4.61	0.68	1.30	42.7

Source: 214A313

f<sub>a</sub> = aromaticity

**Table 5.14**  
**CHARACTERIZATION OF ATHABASCA BITUMEN DERIVED 811-901°F (433-483°C) COKER**  
**GAS OIL CUT HPLC CLASS FRACTIONS**

<b>HPLC Fraction</b>	<b>Yield, wt%</b>	<b>Molecular Weight</b>		<b>Heteroatoms, wt%</b>			<b>Atomic H/C</b>
		<b>VPO</b>	<b>GPC Mn</b>	<b>N</b>	<b>S</b>	<b>O</b>	
Saturated	26.6	412	329	0.09	0.16	0.42	1.78
Mono-aromatic	19.7	385	245	0.07	2.14	0.46	1.55
Di-aromatic	20.1	324	224	0.12	5.99	0.75	1.31
Poly-aromatic	33.6	---	190	1.10	6.33	1.51	1.12
Poly-aromatic (a)	23.3	347	176	0.59	7.47	0.97	1.08
Poly-aromatic (b)	8.5	406	179	2.10	4.6	2.42	1.18
Poly-aromatic (c)	1.8	---	201	3.32	3.69	2.78	1.17

Source: 214A313

**Table 5.15**  
**HETEROATOM DISTRIBUTION AND MOLECULAR FORMULAS OF ATHABASCA BITUMEN**  
**DERIVED 811-901°F (433-483°C) COKER GAS OIL CUT HPLC CLASS FRACTIONS**

<b>HPLC Fraction</b>	<b>Heteroatom Distribution, % bulk</b>			<b>Molecular Formula</b>
	<b>N</b>	<b>S</b>	<b>O</b>	
Saturated	5.5	1.1	13.4	C <sub>32.4</sub> H <sub>57.8</sub> N <sub>0.03</sub> S <sub>0.02</sub> O <sub>0.12</sub>
Mono-aromatic	3.1	10.8	10.8	C <sub>23.8</sub> H <sub>37.0</sub> N <sub>0.02</sub> S <sub>0.23</sub> O <sub>0.1</sub>
Di-aromatic	5.5	30.9	18.0	C <sub>19.9</sub> H <sub>26.2</sub> N <sub>0.02</sub> S <sub>0.54</sub> O <sub>0.14</sub>
Poly-aromatic	85.9	56.9	57.9	C <sub>18.0</sub> H <sub>19.7</sub> N <sub>0.21</sub> S <sub>0.53</sub> O <sub>0.25</sub>
Poly-aromatic (a)	31.4	44.6	27.0	C <sub>16.9</sub> H <sub>18.2</sub> N <sub>0.11</sub> S <sub>0.58</sub> O <sub>0.15</sub>
Poly-aromatic (b)	40.8	10.0	24.6	C <sub>17.9</sub> H <sub>21.1</sub> N <sub>0.41</sub> S <sub>0.41</sub> O <sub>0.41</sub>
Poly-aromatic (c)	13.6	1.7	6.0	C <sub>18.8</sub> H <sub>22.0</sub> N <sub>0.67</sub> S <sub>0.33</sub> O <sub>0.49</sub>

Source: 214A313

### Bitumen Vacuum Residue

Vacuum residue (>975°F, >524°C) from Athabasca bitumen (Table 5.16) was fractionated by supercritical fluid extraction into ten fractions that were characterized. The end cut comprising 18 wt% of the bitumen contained 30% of the total sulfur, 44% of the total nitrogen, 62% of the total microcarbon residue (MCR) and 80% of the total nickel or vanadium. The carbon and hydrogen were evenly distributed through the 82 wt% point, suggesting that molecules in most of the bitumen fractions, except the end cut, may have had a similar structure (i.e. big molecules composed of several smaller molecules found in the lighter fractions). The SARA (saturates, aromatics, resins and asphaltenes) components were unevenly distributed. Saturates decreased with boiling point and are found only in the lighter 50% of the oil. Aromatics were essentially constant up to the end cut, which contained a much lower concentration. The resins increased in concentration as the fractions got heavier. The end cut contained all the asphaltenes and ash with a small amount (about 8%) of resins and aromatics (about 2%) [214A449].

**Table 5.16**  
**CHARACTERIZATION OF ATHABASCA BITUMEN**

Gravity, API	7.8	MCR, wt%	14
Carbon, wt%	85.48	Nickel, ppm	80
Hydrogen, wt%	11.02	Vanadium, ppm	220
Sulfur, wt%	4.65	Ash, wt%	0.75
Nitrogen, wt%	0.43		

Source: 214A449

## HEAVY FUEL OIL PROPERTIES

Properties of the heavy fuel oils of a given grade vary depending upon the crude oil origin, processing and blending. The properties presented below are therefore representative and not absolute values of each shipment. Specifications for heavy fuel oils are presented in Section 4.

### Composition and Physical Properties

The composition of several No. 6 fuel oils (Bunker C oils) show large variation in asphaltene contents as illustrated in Table 5.17. The detailed analysis of a No. 6 fuel oil is compared to a No. 2 fuel oil, a distillate fuel oil, in Table 5.18. Table 5.19 shows the metal content of one No. 6 fuel oil. Physical properties of a couple No. 6 fuel oils are shown in Table 5.20.

**Table 5.17**  
**SARA ANALYSIS OF SELECTED NO. 6 FUEL OILS**

	<u>Composite</u>	<u>Shell, 1999</u>	<u>Alaskan Sample</u>	<u>Canadian, 1970</u>
Gravity, API	---	14.1 wt%	11.4wt%	11.6wt%
Saturates	24.4 wt%	24	25	32
Aromatics	54.6	55	47	32
Resins (Polars)	14.9	15	17	17
Asphaltenes	6.2	6	11	19
Sulfur	2.0	2.4	0.53	1.93

Source: 214A424, 214A425

**Table 5.18**  
**COMPOSITIONS OF A NO. 2 AND A NO. 6 FUEL OIL**

	<u>No. 2 Fuel Oil</u>	<u>No. 6 Fuel Oil</u>	<u>No. 2 Fuel Oil</u>	<u>No. 6 Fuel Oil</u>
Gravity, API	31.6	7.3		
Sulfur, wt%	0.32	1.46		
Nitrogen, wt%	0.024	0.94		
Nickel, ppm	0.5	89		
Vanadium, ppm	1.5	73		

**Table 5.18 (Concluded)**  
**COMPOSITIONS OF A NO. 2 AND A NO. 6 FUEL OIL**

	<u>No. 2 Fuel Oil</u>	<u>No. 6 Fuel Oil</u>		<u>No. 2 Fuel Oil</u>	<u>No. 6 Fuel Oil</u>
<b>COMPOSITION</b>					
<b>Saturates, wt%</b>	61.8	21.1	<b>Isoparaffins, wt%</b>	22.3	5.0
n-Paraffins	8.07	1.73	1-ring cycloparaffins	17.5	3.9
C <sub>10</sub> + C <sub>11</sub>	1.26	0	2-ring cycloparaffins	9.4	3.4
C <sub>12</sub>	0.84	0	3-ring cycloparaffins	4.5	2.9
C <sub>13</sub>	0.96	0.07	4-ring cycloparaffins	0	2.7
C <sub>14</sub>	1.03	0.11	5-ring cycloparaffins	0	1.9
C <sub>15</sub>	1.13	0.12	6-ring cycloparaffins	0	0.4
C <sub>16</sub>	1.05	0.14	<b>Aromatics, wt%</b>	38.2	34.2
C <sub>17</sub>	0.65	0.15	Benzenes	10.3	1.9
C <sub>18</sub>	0.55	0.12	Indans and tetralins	7.3	2.1
C <sub>19</sub>	0.33	0.14	Dinaphthenobenzenes	4.6	2.0
C <sub>20</sub>	0.18	0.12	Naphthalenes	0.2	
C <sub>21</sub>	0.09	0.11	Methylnaphthalenes	2.1	2.6
C <sub>22</sub>	0	0.10	Dimethylnaphthalenes	3.2	
C <sub>23</sub>	0	0.09	Other naphthalenes	0.4	
C <sub>24</sub>	0	0.08	Acenaphthenes	3.8	3.1
C <sub>25</sub>	0	0.07	Acenaphthalenes	5.4	7.0
C <sub>26</sub>	0	0.05	Phenanthrenes	0	11.6
C <sub>27</sub>	0	0.04	Pyrenes	0	1.7
C <sub>28</sub>	0	0.05	Chrysenes	0	0
C <sub>29</sub>	0	0.04	Benzothiophenes	0.9	1.5
C <sub>30</sub>	0	0.04	Dibenzothiophenes	0	0.7
C <sub>31</sub>	0	0.04	<b>Resins (Polars)</b>	0	30.3
C <sub>32</sub> Plus	0	0.05	<b>Asphaltenes</b>	0	14.4

Source: 214A424

**Table 5.19**  
**METALS CONTENT OF ONE NO. 6 FUEL OIL<sup>a</sup>**

Barium, ppm	<0.3	Molybdenum	<0.6
Chromium	<1.5	Nickel	8.6
Copper	1.2	Titanium	<0.6
Iron	35	Vanadium	42
Lead	<3	Zinc	1.6
Magnesium	23.9		

Source: 214A425

<sup>a</sup> Shell, 1999

**Table 5.20**  
**PHYSICAL PROPERTIES OF SELECTED NO. 6 FUEL OILS**

	<u>Shell, 1999</u>	<u>Alaskan Sample</u>	<u>Canadian, 1970</u>
Gravity, API	14.1	11.4	11.6
Sulfur, wt%	2.4	0.53	1.93
Nitrogen, wt%	0.34	---	---
Pour Point, °F (°C)	43 (6)	28 (-2)	43 (6)
Flash Point, °F (°C)	208 (9)	181 (83)	239 (115)
Viscosity at 59°F (15°C), cP	45,030	8,706	40,340
Kinematic Viscosity at 122°F (50°C), cSt	211 to 640		---
Surface Tension at 59°F (15°C), dynes/cm	---	32.5	---
at Room Temperature, dynes/cm	27	---	---
Distillation, °F (°C)			
IBP, wt%	---	---	228 (109)
5	477 (247)	410 (210)	288 (142)
10	615 (324)	457 (236)	421 (216)
15	696 (369)	522 (272)	450 (232)
20	752 (400)	622 (328)	491 (255)
25	804 (429)	685 (363)	469 (243)
30	874 (468)	729 (387)	487 (253)
35	982 (528)	765 (407)	500 (260)
40	1045 (563)	799 (426)	507 (264)
45	1081 (583)	835 (446)	---
50	1107 (597)	874 (468)	---
55	1134 (612)	918 (492)	---
60	1159 (626)	966 (519)	538 (281)
65	1184 (640)	1018 (548)	---
70	1213 (656)	1074 (579)	---
75	1247 (675)	1132 (611)	---
80	1287 (697)	1193 (645)	---
85	1333 (723)	1263 (684)	---
90	---	1326 (719)	---

Source: 214A425

### Heating Value

Fuel oil is purchased for its (lower) heating value per gallon. Heavy fuel oils have higher volumetric heating values than lighter fuel oils as illustrated in Table 5.21. This table also shows cracked fuel oils have a higher volumetric heating value than straight run oils. Also, as the API gravity of fuel oil increases, the volumetric heating value decreases but the mass heating value increases since the percentage of hydrogen increases (Table 5.22). The density decreases with increasing API gravity at a faster rate than the increase the mass heating value.

**Table 5.21**  
**COMPARISON OF HEATING VALUES OF HEAVY AND LIGHT FUEL OILS**

	Gravity	High Heating Value	
	<u>API</u>	<u>Btu/gal</u>	<u>kJ/liter</u>
No. 2 Straight-run	38	134,960	37,789
No. 2 Cracked	30	139,660	39,105
No. 5 Straight-run	22	144,600	40,488
No. 5 Cracked	13	150,310	42,087

Source: 214A420

**Table 5.22**  
**RELATIONSHIP OF GRAVITY, HYDROGEN CONTENT AND HEATING VALUE OF FUEL OIL**

<u>Gravity, API</u>	<u>Hydrogen Content, %</u>	<u>Density, lb/gal</u>	Heating Value	
			<u>Btu/lb</u>	<u>Btu/gal</u>
10.0	10.00	8.328	18,260	152,280
14.0	10.41	8.099	18,450	149,720
18.0	10.80	7.882	18,650	147,160
22.0	11.37	7.676	18,820	144,600
26.0	11.72	7.481	18,980	142,140
30.0	12.06	7.296	19,130	139,660
34.0	12.62	7.119	19,270	137,310
38.0	12.93	6.951	19,390	134,960

Source: 214A420

### Stability of Fuel Oils

Stability of fuel oil is the resistance to breakdown. Heavy fuel oils may breakdown due to heating-cooling cycles, contact with air and water during shipment and storage as well as improper handling or the customer adding improper additives. Unless the instability is very great, a fuel oil can be unstable and instability not be noticed since a long storage time is usually needed for an unusual amount of sludge to accumulate. Under normal, constant operation, sediment found in all residual oils that would eventually settle to the bottom of the tank would not have sufficient time to accumulate but would be burned without difficulty. Stability is especially important for stand-by fuel oil (No. 5 and No. 6 fuel oils are the most susceptible to storage problems and should be stored in tanks having steam coils). Although blended oils tend to be more unstable than unblended oils, many blended fuel oils are stable.

Sludge generally includes:

- Emulsions of heavy fuel oil and water found on tank bottoms
- Settled heavy hydrocarbons plus some coke and free carbon
- Insoluble oxidation products
- Precipitated polymers
- Dirt and rust scale

For unblended oils, resistance to oxidation by oxygen from air or water and reactions under hot temperatures are important. Oxidation can form insoluble products that float around a storage tank until eventually settling out as sludge. Sludge can also form by polymerization of olefins upon heating. Asphaltenes can be precipitated from oil by adding saturates (non-solvent), removing small ring aromatics (solvent), removing resins (dispersant) or cracking pendant groups from asphaltene molecules. Insoluble asphaltenes exist in some unblended oils, called “self-incompatible” oils. Insoluble asphaltene sediments arise from the crude, from thermal conversion such as visbreaking or from catalytic hydroconversion such as hydrotreating.

Self-incompatibility of a hydrotreated atmospheric residuum FCC feedstock was accidentally discovered when the liquid product cooling exchanger consistently fouled near the end of three consecutive one year runs. Examination of the product revealed insoluble asphaltenes except one sample made at low reactor temperature and high space velocity. The asphaltenes were soluble in the product made with fresh hydrotreater catalyst and the feed itself. The atomic hydrogen-to-carbon ratio of the asphaltenes in the self-incompatible oil was lower (1.18) than the feed (1.23) while the ratio was higher (1.36) than the feed (1.25) at the start of run when the product asphaltenes were soluble. The mechanism producing the self-incompatibility and fouling is the accumulation of metals (mainly nickel and vanadium) in the pores so late in the run asphaltene molecules are prevented from entering the pores and becoming hydrotreated as at the start-of-run. Near the end-of-run, the asphaltenes are not hydrotreated but slightly thermally cracked, reducing the sulfur, yield and asphaltene hydrogen-to-carbon ratio. The smaller resins (polar aromatics) could still enter the catalyst pores and be converted more than the asphaltenes. Near the end-of-run, the ratio of resins to asphaltenes greatly decreases to about 1.3, decreasing the asphaltene solubility and causing precipitation on cooling [214A059].

Blending of residual oil with distillates or even other residual oil can greatly decrease the stability and increase the probability of sludge formation. When blended with large amounts of distillate oil, insoluble materials stably suspended in residual oils have a tendency to settle during storage due to the lower viscosity of the blend. Also, incomplete blending does not permit the light and heavy oils to reach stable equilibrium, producing stratification in the storage tank so the burner receives different viscosity oils, heavy from the bottom, blended, and light from the top, causing combustion trouble and inefficiency.

Adding distillate also often precipitates asphaltenes in the residual oil. The amount of sludge produced is a function of the composition of both the residual oil and the distillate oil. The amount of sludge produced depends upon the amount and type of distillate, its composition and the asphaltene content of the residual oil. Asphaltenes are maintained in equilibrium by resins and aromatic compounds surrounding the asphaltenes. Blending distillates dilutes the resins. Equilibrium may be maintained when small amounts of distillate are added in which case large amounts of asphaltenes are not precipitated. As the amount of distillate increases, the equilibrium balance can not be maintained, producing more sludge as the amount of distillate increases until all asphaltenes are precipitated. Thermally cracked distillates blend better than catalytically cracked or straight run distillates since they contain a higher concentration of aromatics that help maintain the equilibrium and are better solvents for heavy compounds. For example, blending 30% to 90% of a catalytically cracked distillate with a cracked residual oil resulted in 6.0% to 30% of precipitate while the same percentage of a thermally cracked distillate precipitated only 0.4% for each blend [214A420].

The flocculation onset titration method is commonly used as an indicator of the stability of the oil related to asphaltene precipitation. A solution of crude or heavy oil is titrated with the asphaltene precipitant. Onset is defined as the minimum amount of added precipitant necessary to induce precipitation of asphaltenes. This amount is an indicator of the stability of the oil. The onset point is related both to properties of the oil and the solute, the asphaltenes. Single point

titration, although often reported in the literature, may give poor results due to the oil, solvent and solute. Instead, titration of several (four) different concentrations is recommended. Besides the usual qualitative and empirical evaluation, the method may be extended to determine the critical solubility parameter of the solvent mixture in which the asphaltene will begin to precipitate can be evaluated [214A439, 214A440, 214A443, 214A444].

Wiehe developed an oil compatibility model and tests that predict the proportions and order of blending that will cause asphaltenes to precipitate. When asphaltenes will adsorb onto process surfaces from compatible, but nearly incompatible oils can also be predicted. Two dimensionless solubility parameters of the model, the insolubility number and the solubility blending number, are measured by mixing the individual oils with a nonpolar solvent, such as toluene, and with a nonpolar nonsolvent, such as n-heptane, to determine the points of incipient asphaltene precipitation. When the volumetric average solubility blending number is greater than the insolubility number of any oil in the mixture, the compatibility of the mixture is predicted. A "region of near incompatibility exists when the mixture is predicted to be compatible but the volumetric average solubility blending number is less than 1.4, especially less than 1.3, times the maximum insolubility number of the oils in the mixture" [214A059, 214A433, 214A434, #2114435, US 5871634, US 5997723]. Solubility parameters and heavy oil interactions are briefly reviewed in PEP Report 228, *Refinery Residue Upgrading*, (2000).

## HYDROTREATING CHEMISTRY

In this subsection, hydrotreating chemistry relating to heavy oil hydrotreating is reviewed. Reaction pathways and mechanisms, asphaltene structural changes and kinetics are covered before reviewing catalysis.

Model compound studies are performed to study the fundamental aspects of hydrotreating catalysis, but can not reliably predict results for heavy oil feedstocks. Studies using actual heavy oils feedstocks are required to confirm predictions derived from model studies [214A292].

The complexity of single compound hydrotreating is increased greatly by competitive or interactive effects that exist, especially in the hydrotreating of heavy oils, when a mixture of compound types containing multiple heteroatoms is processed. Table 5.23 summarizes the general effects of some interactions [214A525].



**Table 5.23**  
**INTERACTIVE AND COMPETITIVE EFFECTS IN COMMERCIAL HYDROTREATING**

<b>Reaction Type</b>	<b>Product or Reactant Type</b>			
	<b>H<sub>2</sub>S</b>	<b>NH<sub>3</sub> and/or organo N<sup>(a)</sup></b>	<b>H<sub>2</sub>O</b>	<b>P<sub>H</sub><sup>(b)</sup></b>
Hydrodesulfurization	inhibits <sup>c</sup>	inhibits		benefits
Hydrodenitrogenation	benefits <sup>d</sup>	inhibits	benefits	benefits greatly
Hydrodeoxygenation	benefits <sup>e</sup>	Inhibits		benefits greatly
Hydrodeasphalting		Inhibits		benefits complex aromatics greatly

Source: 214A525

<sup>a</sup> Strong adsorption of N compounds inhibits most of the reactions.

<sup>b</sup> Because HDN, HDO and HAD are rate limited by hydrogenation, these reactions are most favorably affected by higher hydrogen partial pressure (P<sub>H</sub>). Above a certain pressure typical of each feed type, other rate controlling steps take charge and further increase in P<sub>H</sub> show no advantages. The typical hierarchy of rates at high P<sub>H</sub> is HDS > HDN > HDO.

<sup>c</sup> Inhibiting effect reduced by increase in temperature in two-phase systems because H<sub>2</sub>S concentration in liquid then declines.

<sup>d</sup> H<sub>2</sub>S increases the rate of C-N bond cleavage possibly due to increased surface acidity.

<sup>e</sup> Keeps catalyst in sulfided form and prevents over reduction of the surface an essential for HDO.

### Reaction Pathways (Mechanisms)

The reaction mechanisms of HDS and HDN are complex and derived largely from model compound studies. The HDS mechanism of thiophenic compounds can follow two routes; the dominant one depends upon the catalyst and operating conditions. The generally accepted pathway for HDS of 4,6 dimethyldibenzothiophene follows the same mechanism over three types of catalysts: Mo, CoMo and NiMo; H<sub>2</sub>S inhibits HDS with each type of catalyst. The HDS of real feedstocks is also inhibited by nitrogen compounds in the oils. Organonitrogen compounds also suppress the HDN rates of other compounds. We briefly review the mechanisms of HDS and HDN [214A038].

### Hydrodesulfurization

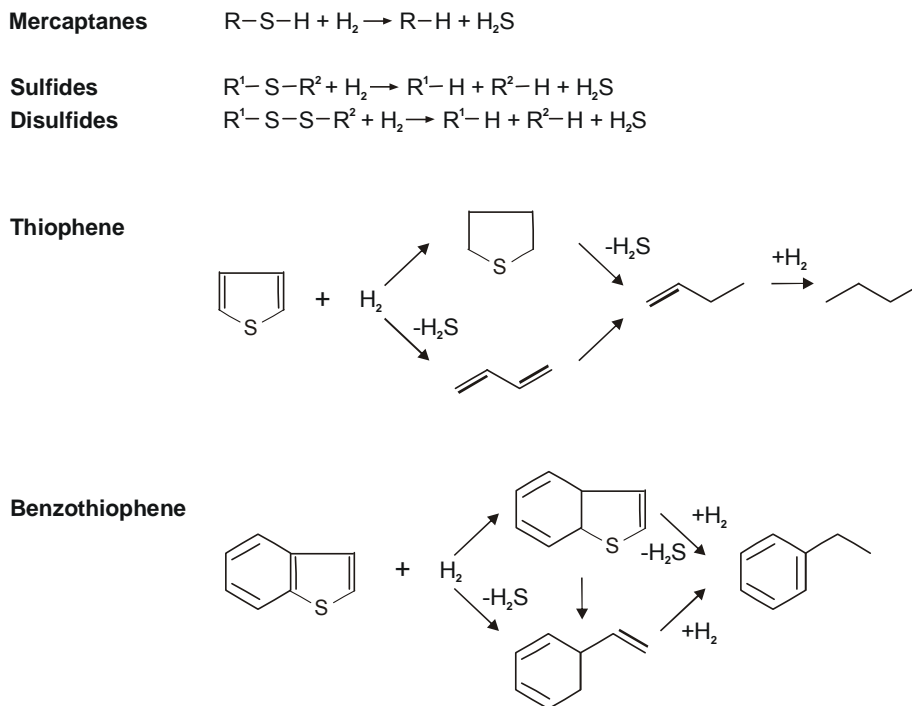
The surface of HDS catalysts are generally believed to contain two types of adsorption sites: one site competitively adsorbs the sulfur molecule such as dibenzothiophene and its products; he other site adsorbs H<sub>2</sub> [214A042]. Adsorbed hydrogen is dissociated into hydrogen atoms. The hydrogen atoms migrate (spillover) to the adsorbed sulfur molecule (the catalyst's MoS<sub>2</sub> phase) where hydrogenation occurs on weakly reduced sites or hydrogenolysis occurs on strongly reduced sites [214A039].

Organosulfur compounds are usually present in all distillation fractions of crude oil, the concentration usually increasing with boiling point. The low boiling fraction contains mainly mercaptans, sulfides and disulfides, which are very reactive in hydrotreating and are easily completely removed. For medium distillates (such as straight run and light naphthas, diesel or kerosene), thiophenes, benzothiophenes and their alkylated derivatives predominate. These are more difficult to desulfurize than the mercaptans and sulfides, but not as difficult as sulfur compounds found in the heavier distillate fractions (heavy FCC naphtha, coker naphtha, FCC light cycle oil and coker light cycle oil) or in the residue oil fractions. The heavy distillates contain

mainly alkylated benzothiophenes, dibenzothiophenes and alkylated dibenzothiophenes plus some polynuclear aromatic sulfur compounds.

Hydrotreating pathways for the lighter sulfur compounds are shown in Figure 5.1 [214A455]. Thiophenic compounds hydrotreat via two parallel pathways, the direct or hydrogenolysis pathway (upper route in the figure) or the two step hydrogenation pathway. Which route predominates depends upon the compound, conditions and catalyst. The direct pathway predominates for dibenzothiophene, but at the same conditions both routes are significant for 4,6-dibenzothiophene. The HDS reactivity follows the order from most to least reactive: thiophene > alkylated thiophene > benzothiophenes > alkylated benzothiophenes > dibenzothiophene > alkylated dibenzothiophenes excluding 4,6- > alkylated dibenzothiophene with a 4- or 6-substituent > 4,6-dibenzothiophenes [, 214A455].

**Figure 5.1**  
**TYPICAL HYDRODESULFURIZATION PATHWAYS OF LIGHTER ORGANOSULFUR**  
**COMPOUNDS [214A455]**



Source:214A455

Full geometry optimization and vibrational analysis shows thiophene is adsorbed on the coordinately unsaturated edge Mo atom of the (303'0) plane. The most stable configuration is a bridged and rotated parallel geometry, which comes closest and almost parallel to the (303'0) plane. Activation of the C-S bond is indicated by the longer bond distances for all configurations [214A486].

Experiments using radioisotopes  $^{35}\text{S}$  and  $^3\text{H}$  in the HDS of thiophene over sulfided CoMo or NiMo on alumina or activated carbon catalysts showed the catalyst sulfur participates in  $\text{H}_2\text{S}$  formation. During the reaction, some catalyst sulfur (called mobile sulfur) reacts with  $\text{H}_2$  to form the  $\text{H}_2\text{S}$  and is replaced by sulfur from the thiophene. The amount of mobile sulfur depends upon

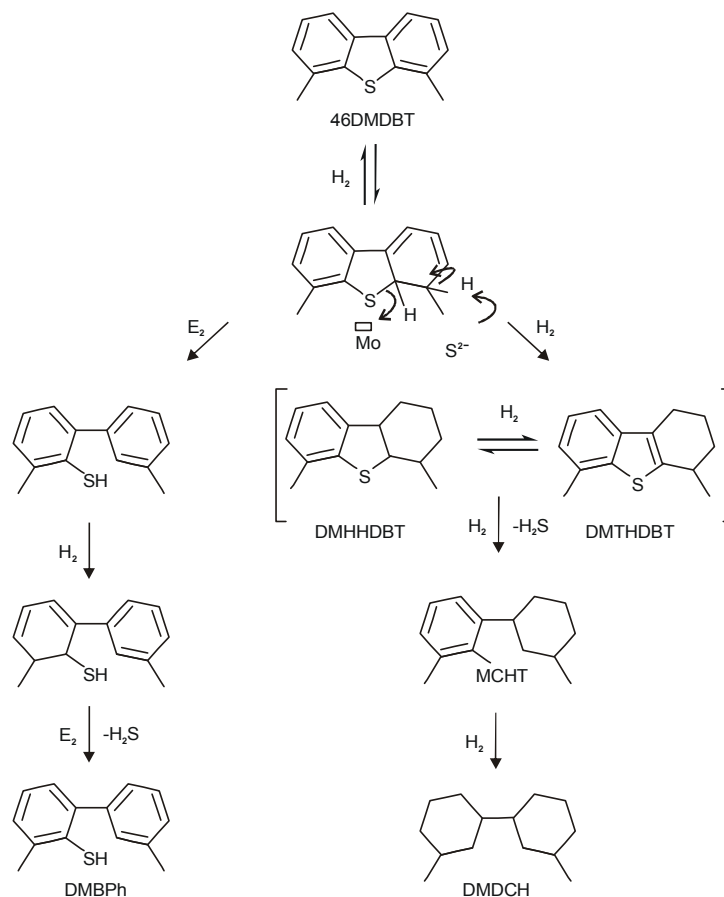
the catalyst composition and sulfidizing method. In other experiments, the degree (wt% desulfurized) of West Siberian residual oil desulfurization correlated linearly with the amount of mobile sulfur on the catalyst. Sulfur from the thiophene does not react directly to form H<sub>2</sub>S but is deposited on the catalyst. SH groups of Ni-sulfide demonstrate greater reactivity to H<sub>2</sub>S formation during thiophene HDS than SH groups of a similar Co catalyst [214A069].

A radioisotope <sup>35</sup>S investigation of CoMo/MCM-41 and NiMo/MCM-41 also showed that sulfur atoms extracted from dibenzothiophene molecules were not released directly to H<sub>2</sub>S but resided on the catalyst surface. The surface sulfur was not released by H<sub>2</sub> even after a couple hours of purging. Sulfur atoms were released by introducing new DBT molecules, indicating sulfur atoms exchange between DBT molecules and the surface must be involved during HDS of DBT. The surface sulfur atoms may serve as active sites. Other work showed introducing other heteroatoms with lone pairs such as nitrogen or oxygen also released sulfur atoms on the active sites of Mo/γ-alumina catalysts. Since CoMo and NiMo nitrides were active HDS catalysts and CoMo and NiMo sulfides were good HDN catalysts, Wang et al. suggested that both sulfur and nitrogen atoms on the active sites were exchangeable, which should be an important step in closing the catalytic cycle. Introducing oxygen containing molecules may substantially increase the period of the cycle because oxygen atoms have stronger affinity for these transition metal cations. Evidence for this was the long time (several hours) to completely replace oxygen with sulfur atoms when presulfiding CoMo or NiMo catalysts. Furthermore, experiments by others indicated alternating HDS and hydrodeoxygenation (HDO) feeds to a commercial presulfided CoMo/γ-alumina catalyst showed HDS conversion decreased following a HDO period. The HDS activity slowly restored with time on sulfur feedstock [214A042].

In the hydrodesulfurization of lighter distillate oils such as diesel fuel, polycyclic aromatic sulfur heterocycles are the most resistant to desulfurization. Some sulfur remains in deeply desulfurized oils, mainly dibenzothiophenes alkylated adjacent the sulfur atom. The alkyl groups sterically hinder the approach to the catalyst's active sites. Hydrodesulfurization of heavy oils is less efficient than the lighter oils. Most of the heavy oil molecules resistant to hydrodesulfurization are in the aromatic fractions. The characterization of high molecular weight sulfur containing aromatics in vacuum residues using Fourier transform ion cyclotron resonance mass spectrometry is discussed by Muller and Anderson. In the aromatic fraction of a vacuum residue, compounds with one or two sulfur atoms dominated. Compounds with three sulfur atoms were negligible. Partial HDS removed primarily compounds with one sulfur atom; those with two sulfur atoms were largely unaffected [214A340].

The generally accepted reaction pathway for the hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT) is shown in Figure 5.2. Hydrogen first adds to the 4,6-DMDBT with the aid of both the molybdenum atom and a S atom of the active site to form an intermediate. The reaction then continues via two separate pathways from the common intermediate: direct desulfurization (DDS) and "hydrogenation" (HYD). DDS involves the direct cleavage of the S-C bonds to eventually produce dimethylbiphenyl (DMBPh). In the HYD route, hydrogen of one of the benzene rings occurs to form 4,6-dimethyltetrahydrodibenzothiophene (4,6-DMTHDBT). The final product of the HYD route is methylcyclohexyltoluene (MCHT) [214A056]. A similar scheme is proposed for dibenzothiophene (DBT) [214A417]. DDS is the main reaction pathway. Whether DDS or HYD routes predominate is determined by adsorption confirmation of the reactant molecule on the catalyst surface. DDS occurs via σ electron adsorption; HYD requires π electron adsorption. 4,6-DMTHDBT is sterically hindered [214A057].

**Figure 5.2**  
**REACTION PATHWAY FOR HYDRODESULFURIZATION OF 4,6**  
**DIMETHYLDIBENZOTHIOPHENE**



Source: 214A056

The same reaction network applies to HDS over three types of catalysts: Mo, CoMo and NiMo. Cobalt and nickel promoters noticeably improve the DDS activity of Mo catalyst for DBT and to a lesser extent 4,6-DMDBT. Over all three catalysts,  $H_2S$  suppresses catalytic activity; NiMo is most affected, Mo the least. The DDS path is inhibited more strongly by  $H_2S$  than the HYD path for all three catalysts. The final sulfur atom removal step in the HYD path is affected to the same extent as the DDS path (constant  $k_{DDS}/k_{HYD}$  desulfurization ratio at all  $H_2S$  partial pressures over all three catalysts). This suggests the same mechanism is active in DDS and the final HYD step [214A057].

The results of a study of a commercial Mo/alumina catalyst and a commercial NiMo/alumina catalyst reveal the quality of liquid products formed from Kuwait export crude atmospheric residue depends strongly on the operating severity and catalyst type. With increasing temperature, the residue becomes more purified (Table 5.24). Hydrogenation activity plays a predominant role in determining the nature of the asphaltenes in the product oil. The asphaltenes and resins are converted to resins and saturates. Polynuclear aromatic rings in the asphaltene

remain in the product oil but become more condensed and less alkyl substituted with increasing temperature for either catalyst. The aromaticity and degree of condensation in the product asphaltenes are higher with the low hydrogenation activity Mo catalyst than with the high activity NiMo catalyst [214A189].

**Table 5.24**  
**REACTION TEMPERATURE EFFECT ON THE LIQUID PRODUCT QUALITY IN HDS AND**  
**HDM OF KUWAIT ATMOSPHERIC RESIDUE**

	Temperature			
	680°F <u>360°C</u>	716°F <u>380°C</u>	752°F <u>400°C</u>	788°F <u>420°C</u>
	HDM Catalyst (Mo/alumina)			
Sulfur, wt%	3.23	2.79	2.62	1.55
Nitrogen, ppmw	2600	2570	2486	2255
Conradson carbon residue, wt%	10.50	9.52	8.54	6.83
Asphaltenes, wt%	2.22	1.68	1.21	---
Vanadium, ppmw	35	23	11	6
Nickel, ppmw	12	10	8	4
Density @ 59°F (15°C)	0.9837	0.9655	0.9609	0.9225
	HDS Catalyst (NiMo/alumina)			
Sulfur, wt%	1.38	1.08	0.56	0.22
Nitrogen, ppmw	2510	2430	1960	1780
Conradson carbon residue, wt%	7.56	6.95	4.76	3.66
Asphaltenes, wt%	2.93	2.40	1.75	1.32
Vanadium, ppmw	26	22	12	5
Nickel, ppmw	10	8	6	4
Density @ 59°F (15°C)	0.9737	0.9510	0.9444	0.9100

Source: 214A189

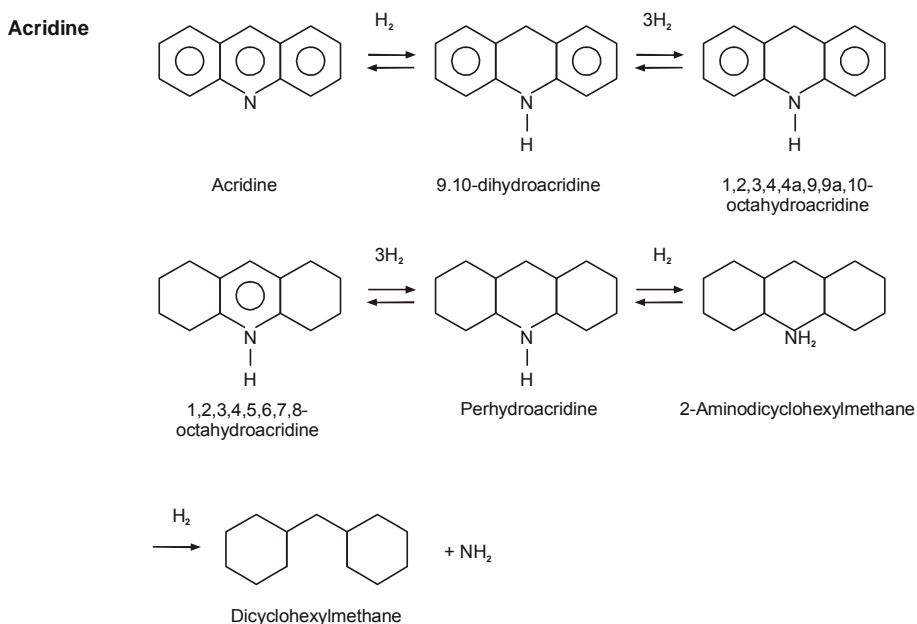
In the competitive hydrodesulfurization of 4,6-DMDBT and the HDN of 2-methylpyridine and 2-methylpiperidine over sulfided NiMo/γ-alumina catalyst, both nitrogen containing molecules strongly inhibited the HDS. 2-methylpiperidine was slightly stronger an inhibitor than 2-methylpyridine for both the DDS and HYD pathways. The nitrogen containing molecules made the desulfurization of the 4,6-dimethyltetrahydrodibenzothiophene intermediate of the HYD path extremely difficult. Meanwhile, 4,6-DMDBT and DBT suppressed the hydrogenation of 2-methylpyridine but the 2-methylpiperidine C-N bond cleavage was not affected. Adsorption of 2-methylpiperidine on both DDS and HYD sites is thus assumed to be much stronger than that of 4,6-DMDBT or DBT. Toluene solvent had no effect on the HDS rates or product distributions. Therefore, toluene molecules did not compete with the reactant for active sites. Naphthalene inhibited the DDS and HYD pathways during HDS of 4,6-DMDBT and DBT to the same extent. The hydrogenation of naphthalene thus occurs at both the DDS and HYD sites. The hydrogenation of naphthalene was inhibited to the same extent by 4,6-DMDBT and DBT to the same extent. The adsorption of naphthalene is expected to be much weaker than that of sulfur containing molecules [214A058].

## Hydrodenitrogenation

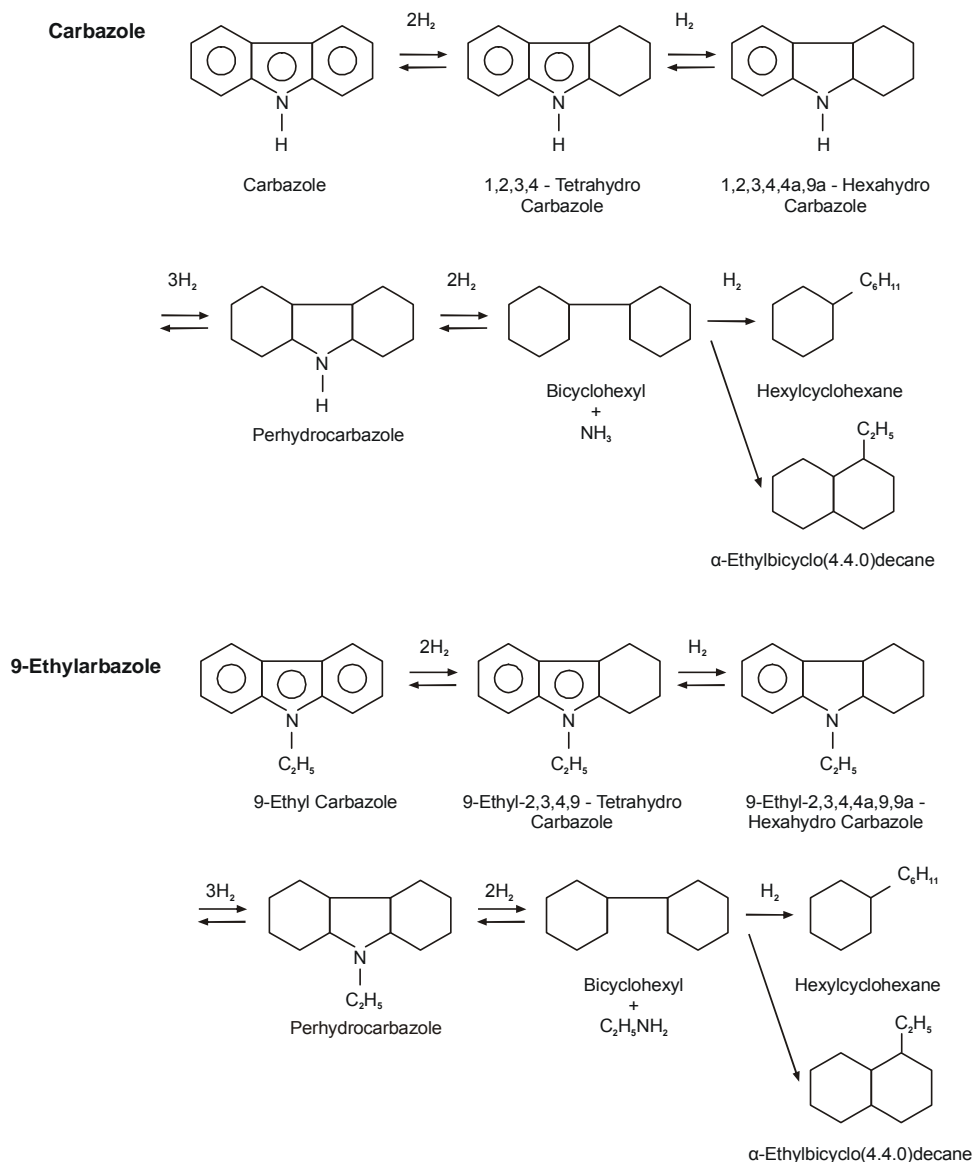
Hydrodenitrogenation (HDN) of petroleum chemistry is reviewed by Furimsky and Massoth with emphasis on model compound reaction networks and reactivities, kinetics, mechanisms, catalysis and simultaneous HDN, HDS, HYD and hydrodeoxygenation (HDO) reactions [214A036].

Besides reducing environmental emission of  $\text{NO}_x$ , it is desirable to remove nitrogen containing compounds because they cause coke formation that deactivates hydrotreating catalyst. Hydrodenitrogenation (HDN) reactions are more complex and difficult to catalyze than HDS. HDN of a Syncrude oil shows the carbon rings are hydrotreated before nitrogen rings, which are resistant to the reaction. HDN reactions usually involve many intermediate aromatic ring hydrogenation and C-N bond cleavage steps, which requires a balanced dual function catalyst. The catalytic mechanism for HDN of model compounds have been studied but the mechanism for heavy oils is unknown. Model compound studies of carbazole and acridine indicate scission of the N-containing aromatic ring occurs only after saturation of the heterocyclic ring. Possible reaction pathways for HDN of acridine, carbazole and 9-ethylcarbazole are shown in Figure 5.3. Experimentally with a commercial NiMo/alumina catalyst, acridine yields only different alkane products at 100% conversion. Aromatics are detected from carbazole (at ~94% conversion), however, 9-ethylcarbazole does not produce aromatics, only alkanes indicating complete hydrogenation (at ~97% conversion).

**Figure 5.3**  
**POSSIBLE REACTION PATHWAYS FOR HDN OF ACRIDINE, CARBAZOLE AND 9-ETHYLCARBAZOLE [214A318]**



**Figure 5.3 (Concluded)**  
**POSSIBLE REACTION PATHWAYS FOR HDN OF ACRIDINE, CARBAZOLE AND 9-CARBAZOLE [214A318]**



Source:214A318

Sulfur compounds depress hydrogenolysis of the C-N bond of polynuclear aromatic compounds regardless of the compound type. Studies of quinoline show that nitrogen compounds, sulfur compounds and aromatics compete for the same catalytic site, but quinoline is preferentially adsorbed. The presence of  $H_2S$  significantly increases the reaction rate of quinoline. During HDN of pyridine, sulfur compounds increased the rate of HDN but only at temperatures above 617°F (325°C). Below 617°F (325°C), the overall reaction rate decreased.

This effect is possibly due to competition between H<sub>2</sub>S and nitrogen-containing compounds for the same catalyst site [214A268].

Analysis of petroleum and Syncrude oils identified two main types of aromatic nitrogen compounds: nonbasic pyrrole benzologues (with a five-membered heterocyclic ring) and basic pyridine benzologues (with a six membered heterocyclic ring) [214A268].

Analysis of a nitrogen-concentrated narrow fraction (901-939°F, 483-504°C), both untreated and hydrotreated, from Syncrude coker gas oil shows compounds containing two or more heteroatoms (N, S, O), except oxygen-sulfur compounds, are more susceptible to hydrotreating than compounds containing only one heteroatom. A possible reason is steric hindrance of access of the single heteromolecules to the catalyst's active sites. Hydrotreatment reduces the relative abundances of the multiple heteroatomic compound classes N<sub>2</sub>, S<sub>3</sub>, NS<sub>2</sub>, NOS, O<sub>3</sub>, OS<sub>2</sub>, and O<sub>x</sub>S<sub>y</sub> to below detectability. N-, S-, O-, O<sub>2</sub>-, OS- and NO-containing compounds survive hydrotreatment and require a higher hydrogen partial pressure for full hydrogenation than the multiple heteroatomic compounds. Nitrogen compounds that resist hydrogenation are typically compounds containing a single nitrogen atom, both pyridinic benzalogs and pyrrolic benzalogs. [214A268, 214A292].

Adsorption of organonitrogen from heavy oil onto sulfided NiMo catalysts occurs prior to reaction so the adsorption energy of the nitrogen compound affects its reactivity. In nickel promoted molybdenum sulfide catalysts, nickel atoms are incorporated preferentially into the MoS<sub>2</sub> structure by substitution of Mo atoms at the (10 $\bar{1}$ 0) Mo-edge to form what is called a "Ni-edge surface". Basic compounds pyridine, quinoline and acridine adsorb essentially perpendicular to the catalyst surface via a strong "end-on bond" between the lone pair electrons of the nitrogen and a nickel atom, which makes the nitrogen ring more likely to be hydrogenated. Acridine contains an additional phenyl ring that decreases the adsorption energy compared to quinoline. End-on adsorption through N-Ni bonding is not possible for non-basic molecules due to the electronic structure of the pyrrolic ring. The calculated most stable configuration for adsorbed nonbasic pyrrole is with the molecular plane flat on the Ni edge plane with bonding through an  $\alpha$  carbon to a nickel site. Nonbasic indole is preferentially adsorbed on the Ni-edge surface through a "side-on bond" between the  $\beta$ -carbon atom in the ring through the  $\pi$  bonds and a nickel atom in the edge. Hydrogenation of the nitrogen ring is the first step in HDN of indole. Nonbasic carbazole has an additional phenyl ring compared to indole and bonds parallel to the catalyst surface through the phenyl ring. Hydrogenation of the phenyl ring is the first step in carbazole HDN. Tetrahydrocarbazole likely adsorbs through the phenyl ring with energy similar to carbazole. Generally the basic nitrogen compounds have larger adsorption energy ( $-\Delta E_a = 16-26$  kcal/mole) than the nonbasic compounds ( $-\Delta E_a =$  about 12-19 kcal/mole), which results in their higher HDN reactivities and stronger inhibition of hydrotreating catalysts. The energetically preferred adsorption geometry is always hydrogenated preferably in the HDN reaction [214A218, 214A491].

The reaction network for HDN of indole is complex. It consists of multiple hydrogenation, hydrogenolysis,  $\beta$ -elimination, Hofmann degradation and dehydrogenation steps [214A402].

### Asphaltene Structural Changes

Asphaltenes are defined as components that are soluble in toluene but precipitate by the addition of an excess of liquid hydrocarbon, most often n-heptane (or n-pentane or n-hexane). Asphaltenes are extremely large, high molecular weight compounds, which generally boil above 1000°F (538°C). Maltenes are components that dissolve in n-hexane. Maltenes are generally smaller molecules than asphaltenes [214A320, 214A495].



A 20 year debate on the molecular weight order of magnitude now appears to be resolved by new analytical techniques and studies. The molecular weight range of 1000 to about 20,000 (by gel permeation chromatography and vapor pressure osmometry) is now believed to be high due to agglomeration during preparation or measurement. Bimodal molecular weight distributions from size exclusion chromatography are mainly due to association-dissociation rather than co-existence of two distinct molecular size groups. Traces of water in toluene solutions are found to promote aggregation of asphaltene sheets or particles. This observation implies polar forces are also important in the intermolecular binding of asphaltenes. Fluorescence depolarization (FD) and field ion mass spectroscopy both give a typical mean value of about 750 amu with a mass distribution width of roughly a factor of two. FD measures asphaltenes in very dilute solutions so aggregation is not a problem nor is fragmentation. Laser desorption mass spectroscopy, atmospheric pressure chemical ionization mass spectroscopy and electrospray ionization mass spectroscopy are in rough agreement. Size exclusion chromatography, although highly dependent on operating conditions, can be used for routinely providing only relative molecular weight distributions but suffers from association, adsorption on the column material and lack of appropriate standards. Concentration, temperature and solvent are important conditions to control along with the column material [214A327, 214A363].

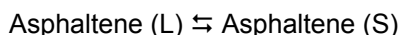
Molecular weight of the asphaltenes is the main parameter in thermodynamic models for asphaltene solubility and precipitation. Uncertain molecular weight and molecular weight distribution data is one factor hampering the development of a sufficiently accurate model to predict precipitation and solubility. Better understanding of the mechanism of flocculation of the asphaltenes and better understanding of asphaltene chemistry are also needed [214A431].

### Unit Structure

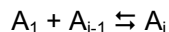
The asphaltene unit structure traditionally is viewed as parallel sheets of fused aromatic rings linked by aliphatic chains. The sheets contain heterocyclic sulfur, nitrogen and oxygen compounds. The sheets are surrounded by polar resin molecules associated with alkyl side chains on the edges of aromatic compounds and form a particle of diameter of about 20Å. The particles link with organometallic porphyrin compounds to form micelles of molecular weight up to ten thousands. This asphaltene “self-assembly” in solution through  $\pi$  and hydrogen bonds results in micellar and colloidal behavior [214A327, 214A363, 214A495].

Asphaltene solubility consists of a number of different equilibria that can be generalized into three types [214A431]:

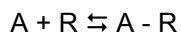
1. Solubility or distribution between liquid (L) and solid (S) phases:



2. Aggregation or association of asphaltene molecules (A):



3. Interaction or solubilization by resins (R):



Asphaltene fractions separated by solubility increase a small amount (1.9Å) in size (by FD) with decreasing solubility. The results of the study indicate the solubility fractions all contain the same molecular species but the fractions vary in the ratio at which each species is present. Thus it appears the solubility of a fraction from a given source affects the population distribution but not the molecular structure. Asphaltenes from similar source material have similar molecular dimensions; asphaltenes from very different source materials such as coal have different molecular sizes too. Recent FD results further showed most asphaltene molecules or micelles in

petroleum have one fused aromatic ring system per molecule with peripheral alkane chain substituents. The asphaltene molecule is surrounded by resins. One study of Middle Eastern vacuum residue indicates the lightest fraction of asphaltenes also function as resins. Carbon Raman x-ray spectroscopy indicates the fused ring systems have a circular arrangement (pericondensed) [214A327, 214A363, 214A437, 214A448, 214A495].

### Characteristics

Characteristics of selected asphaltenes obtained from 968°F+ (520°C+) vacuum residue from five crude oils originating from different types of organic matter are shown in Table 5.25. The Duri asphaltenes have a high H/C ratio indicating long alkyl chains; the Arjuna asphaltenes have a low H/C ratio and essentially no long paraffinic chains. The molecular weight is measured by size exclusion chromatography and should be regarded as relative values. The main differences between the asphaltenes are due to their origin, maturity and biodegradation state as well as their tendency to associate or dissociate under the analytical conditions [214A327].

**Table 5.25**  
**CHARACTERIZATION OF ASPHALTENES FROM VACUUM RESIDUE FROM SELECTED**  
**CRUDE OILS**

Asphaltenes in 968°F+						
<u>Crude (Source)</u>	<u>Origin</u> <u>Type</u>	<u>(520°C)</u> <u>cut, wt%</u>	<u>Asphaltene</u> <u>H/C</u>	<u>M<sub>w</sub>,</u> <u>g/mol</u>	<u>M<sub>z+1</sub>,</u> <u>g/mol</u>	
Duri (Indonesia)	lacustrine	5.7	1.10	7,430	24,200	
Safanyia (Arabian Heavy)	marine	17.1	1.07	6,330	19,700	
Arjuna (Indonesia)	terrestrial	3.5	1.04	5,200	18,300	
Ural (Russia)	marine	5.6	1.04	5,170	15,000	
Aramco (Arabian Light)	marine	7.1	0.98	5,180	14,400	

Source: 214A327

Weighted average molecular weights:  $M_w = \sum N_i M_i^2 / \sum N_i M_i$ ;  $M_{z+1} = \sum N_i M_i^4 / \sum N_i M_i^3$  where  $N_i$  is the number of molecules of molecular weight  $M_i$

FD studies show asphaltenes lacking long alkane side chains are relatively small molecules with small fused ring systems whereas molecules with alkane side chains are larger molecules. Asphaltene solubility is determined by two competing effects: steric hindrance from long alkane chains and intermolecular binding by van der Waals interactions between the ring stacks. The balance between these effects determines the solubility. If the ring systems are large with little alkane substitution, then the molecules can stack efficiently and will not dissolve in toluene (and therefore are not considered to be asphaltenes). This concept is supported by high resolution transmission electron microscopy on asphaltenes and model compounds and by melting point data of alkyl aromatics. These conclusions all depend upon the accuracy of the FD molecular weight results. Two FD studies of solubility fractions of asphaltenes obtained from varying the ratios of toluene and n-heptane concluded the different subfractions appear to consist of the same molecules but in different distributions. A smooth variation of molecular properties of the subfractions could be interpreted by changes in solvating power of the different solutions. However, in another study this time using toluene and acetone, a polar, strongly hydrogen bonding solvent, showed non-monotonically changing asphaltene molecular properties of the subfractions as the solvent ratios changed, indicating a more complex intermolecular interaction than simply the dominant van der Waals forces. This complex behavior is probably related to

dipolar interactions between asphaltenes and the solvent. Whether the effects of polarity are observed or not appears to depend upon the particular solvent system [214A363].

Heavy feedstocks containing high asphaltene contents are difficult to hydrotreat, especially those with a high degree of condensation. When the ratio of internal aromatic carbon atoms to peripheral aromatic carbons is high (over 3), the asphaltene is difficult to process. A ratio of 1.5 to 2.0 indicates more reactive asphaltenes. Asphaltenes both hydrogenate and crack, which changes their structure. Feedstocks with higher ratios of polar to non-polar asphaltenes exhibit a lower reactivity to hydrocracking. Because of the diversity of asphaltene structures, an overall picture of the changes caused by hydrotreating is not possible. Observations with different feeds or at different reaction conditions often appear to be contradictory. The main reported features of asphaltenes that may influence their reactivity include:

1. The components comprising asphaltenes easily are condensed, sulfonated and oxidized.
2. Asphaltenes are highly active in cross-linking reactions.
3. Paramagnetism, low ionization potential and high electron affinity exhibited by asphaltenes affect their reactivity and their propensity to associate.
4. Asphaltenes tend to easily adsorb on the catalyst surface.
5. The shape of the aromatic fragments from asphaltene molecules allows the segregation of aromatic and paraffinic-naphthenic fragments during thermal treatment [214A289].

Changes in asphaltene structure during thermal processing are discussed by Simanzhenkov and Idem. Based on thermodynamics, they also evaluate the possibility of various asphaltene reactions. The possibility of deep cracking of bitumen or vacuum residues at low temperature is also discussed [214A041].

### **Effects of Hydrotreating**

Hydrotreating of atmospheric residue from Safanyia crude oil shows the effects of increased reaction temperature at constant pressure. The oil designated as AR(T<sub>1</sub>) in Table 5.26 is the hydrotreater reactor effluent obtained at a relatively low reactor temperature to minimize thermal cracking. Oil AR(T<sub>2</sub>) is effluent hydrotreated at a higher temperature to induce more thermal cracking of the asphaltenes. Molecular weights are relative values obtained by size exclusion chromatography. As HDT severity increases, the high asphaltene molecular weight compounds decrease while the lower molecular weight asphaltenes increase significantly due to hydrocracking. Table 5.26 also shows changes in asphaltenes from an Arab medium atmospheric residue feed after hydrodemetallization (stage 1) and after subsequent hydrodesulfurization (stage 2). HDM did not significantly affect the asphaltene average molecular weight. HDS significantly decreases the low molecular weight compounds as the smaller asphaltene molecules are converted into smaller resin and aromatic molecules, which increases the average molecular weight of the remaining asphaltenes [214A327].

**Table 5.26**  
**EFFECT OF HYDROTREATING TEMPERATURE AND HDM AND HDS ON ASPHALTENES IN**  
**ATMOSPHERIC RESIDUES**

	Asphaltenes, <u>wt%</u>	Asphaltene <u>Conversion,</u> <u>%</u>	Asphaltene <u>H/C</u>	<u>M<sub>w</sub>,</u> <u>g/mol</u>	<u>M<sub>z+1</sub>,</u> <u>g/mol</u>
Safanyia AR, feed	14.6	---	1.09	6,770	23,000
Effluents					
AR(T1)	7.2	50	1.05	5,670	19,700
AR(T2)	4	72	0.96	3,060	11,300
Arab Medium AR, feed	12.4	---	1.06	5,730	15,600
Effluents					
After HDM	7.1	42	1.03	5,260	15,300
After HDS	4.4	65	1.02	6,490	15,400

Source: 214A327

Weighted average molecular weights:  $M_w = \sum N_i M_i^2 / \sum N_i M_i$ ;  $M_{z+1} = \sum N_i M_i^4 / \sum N_i M_i^3$  where  $N_i$  is the number of molecules of molecular weight  $M_i$

Hydrogenation of aromatic rings produces a trend towards decreasing aromatic content with increasing hydrotreating. Cleavage of side chains produces an opposite trend: increasing aromatic content with increasing hydrotreatment. Molecules without side chains may have better access to the active sites on the catalyst, so these opposite trends may be coupled. As a result, no real trend is observed in  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra between feedstock asphaltene spectra and increasingly hydrotreated samples. Nor is there a trend in the H:C ratio (Tables 5.27 and 5.28). At low temperature, the main reaction is hydrogenation, which leads to stable products. At high temperature, cracking reactions dominate, producing smaller molecules with a lower solubility in the oil. The transition temperature (in the range of 700-735°F (370-390°C)) between the two dominate reactions depends upon the feedstock and other process conditions. The destruction of asphaltene micelles is pronounced in asphaltenes with high vanadium content. Depolymerization dominates when vanadium content is low. The solvent oil properties also change, weakening the solvent power. The oil solvent power decreases as the solubility parameter required to keep the asphaltenes in solution increases. As the temperature increases, asphaltene content decreases and instability and the tendency to form sludge increases. Asphaltenes form sediments that are the main limitation to conversion. During hydrotreating, asphaltenes are coke precursors that precipitate on the catalyst surfaces deactivating the catalyst [214A289, 214A327, 214A363, 214A445, 214A543].

**Table 5.27**  
**SELECTED PROPERTIES OF ASPHALTENES FROM ARABIAN HEAVY ATMOSPHERIC RESIDUE**

<b>Hydrotreating Temperature, °F (°C)</b>	<b>H/C</b>	<b>Asphaltenes, wt%</b>	<b>NSO<sup>a</sup>, wt% asphaltenes</b>
Feed	1.10	5.91	10.4
680 (360)	1.14	2.87	10.1
698 (370)	1.11	1.77	9.9
716 (380)	1.10	2.04	9.0
734 (390)	0.98	1.35	8.4
761 (405)	0.93	0.86	6.3

Source: 214A445

<sup>a</sup> wt% nitrogen, sulfur plus oxygen

**Table 5.28**  
**SELECTED PROPERTIES OF ASPHALTENES AND OIL PRODUCT FROM KUWAIT ATMOSPHERIC RESIDUE**

<b>Temperature °F (°C)</b>	<b>Asphaltenes, WT%</b>	<b>H/C Mol/Mol</b>		<b>Sulfur WT%</b>		<b>Ni + V ppm</b>
	<b>Oil</b>	<b>Asphaltene</b>	<b>Oil</b>	<b>asphaltene</b>	<b>Oil</b>	<b>Oil</b>
Feed	4.07	1.05	1.58	8.26	4.40	86
680 (360)	1.18	1.07	1.80	6.81	0.34	17
698 (370)	1.47	1.08	1.75	7.52	0.33	14
716 (380)	1.01	1.03	1.81	5.93	0.22	10
734 (390)	0.72	1.12	1.83	6.78	0.12	5

Source: 214A445

Analysis of two asphaltenes obtained from a residual oil before and after hydrotreating showed as the asphaltene fractions obtained by preparative gel-permeation chromatography increased in molecular weight, the more aromatic and condensed is their structure. Fractions with the highest molecular weight of both residues show very similar structures. This suggests during hydrotreating the low molecular weight asphaltenes are converted to distillates. The higher molecular weight, refractory fractions remain unaltered during hydrotreating and can cause severe coking in downstream processing. The higher weight asphaltenes of both residues consist of clusters of 4-5 aromatic rings that are interlinked by aliphatic chains of 9-11 carbon atoms [214A427].

N-heptane precipitated asphaltenes from Maya crude oil are changed in composition and structure depending upon the hydrotreating reaction severity. Asphaltene aromaticity increases during hydrotreating as temperature and pressure increase and space velocity decreases. Heteroatoms located in the aromatic ring structure remain unchanged while the average number of carbons per alkyl side chain decreases [214A049].

During hydrotreating of asphaltene containing oils, the asphaltenic sulfur is more resistant than the sulfur in the oil portion. Asphaltenic sulfur may be less than 20% of the total feed oil sulfur but in the hydrotreated product, greater than 60% of the sulfur may be asphaltenic. Generally for less than 50% sulfur removal, very little asphaltenic sulfur is removed. The asphaltene structure is not appreciably decreased in the range of 50-80% desulfurization. Destruction of the asphaltene structure occurs when total sulfur removal exceeds 80%. A major part of the asphaltene sulfur is located in the rings. Hydrogen facilitates the removal of this difficult to remove heterocyclic sulfur. Sulfur-carbon bonds are easier to break than carbon-carbon bonds. As reactor temperature is increased, the asphaltene sulfur did not change significantly until 743°F (394.8°C) or above where sulfur decreased with increasing temperature. When the hydrotreating transition temperature is reached, cracking dominates over hydrogenation and the product sulfur (and total elemental sulfur, nitrogen and oxygen content of the asphaltenes) is reduced with the remaining sulfur in the asphaltenes. Although the sulfur content of asphaltenes decreases with increasing temperature, the change in sulfur content is not proportional to the change in temperature. Sulfur in the side chains is easier to remove than nitrogen and metals, which remain in the unaffected asphaltene aromatic structure [214A048, 214A289, 214A363, 214A444, 214A445, 214A447, 214A495].

Almost all nitrogen in asphaltenes resides in the aromatic rings inside the asphaltene molecule. Hydrogenation of these compounds is thermodynamically unfavorable. As a result, the nitrogen content of asphaltenes does not change under hydrotreating conditions [214A289]. In the hydrotreating of Maya crude oil, nitrogen concentration of the asphaltenes increases as reaction temperature increases; however, the nitrogen compounds are almost unchanged after hydrotreating and are concentrated while other asphaltene molecules react. The H:C ratio also decreases as the temperature increases [214A048, 214A447].

The metals in Maya crude oil asphaltenes also increased with increasing hydrotreating temperature. Like the effect on nitrogen, this is attributed to concentration due to the location of the metals within the asphaltene molecules. Nickel plus vanadium content follows linearly the asphaltene conversion. Asphaltene removal from Maya asphaltenes parallels metal removal, which suggests that metal porphyrin complexes tend to concentrate and precipitate as part of the asphaltenes [214A048].

### **Product Stability**

The stability of the hydrotreated product may change significantly from that of the feed and lead to solids precipitation and increased downstream coking. During hydrotreating both the oil and the asphaltenes undergo reactions that may produce unstable products. New findings suggest the main source of hydrotreated product instability is decreased solubility resulting from changes in molecular structure caused by removal of peripheral chains and not, as previously believed, condensation of molecules into large fused ring systems. The structural changes favor self-aggregation, believed to be the first step in the formation of particles that precipitate from oil. Cracking off of peripheral alkyl substituents (at about 716°F, 380°C) decreases the solubility of the fused ring system resulting from increased ring stacking due to decreased steric hindrance. The stabilized solid decreases solubility. Thermodynamically, the heat of fusion increases. As cracking proceeds, the asphaltenes become smaller molecules containing smaller fused ring systems. Hydrotreating also causes the asphaltene content to decrease significantly. This finding suggests cleavage of alkyl side chains occurs to a larger extent than the formation of asphaltenes by cleavage of alkyl side chains from smaller aromatics. A large portion of the feed asphaltenes is converted into resin type compounds soluble in heptane, assumed caused by hydrogenation of structures enhancing the solubility in alkane solvents [214A363, 214A433, 214A442, 214A443, 214A447].

Asphaltene properties influence the stability of hydroprocessed oils. Asphaltenes with low hydrogen content and high aromaticity start to aggregate at lower concentrations than those with high hydrogen content and low aromaticity. Asphaltenes from stable crude oils are lower in density and lower in aromaticity than asphaltenes from unstable crude oils. Asphaltene fractions differ in solubility. The insoluble fractions have an increased tendency to aggregate. Asphaltene fractions of a broader distribution are more stable than those with narrow distributions. Resins stabilize asphaltenes analogous to broadening the distribution of asphaltene components. The effect of resins is greater than accounted for by changes in solvent properties [214A436, 214A439, 214A442, 214A447].

Hydrotreated products become unstable during severe hydrotreating above approximately 715°F (380°C) where cracking reactions become dominant and product stability drops rapidly. As the reactor temperature is increased, the asphaltene H/C ratio is reduced. This change is also indicated by the critical solubility parameter for the onset of asphaltene precipitation. With Arabian Heavy atmospheric residue, product instability mainly results from a significant change in oil solvent properties [214A444].

The plugging of a fixed bed hydrotreater resulted from the incompatibility of the mixture of hydrocarbon feeds. Insoluble asphaltenes coked an upstream heat exchanger. Coke flaked off the exchanger and plugged the catalyst bed. Maintaining the feed composition within compatibility limits predicted by Wiehe's Oil Compatibility model avoided plugging [214A433].

## Particles

Asphaltene self-aggregation is believed to be initiated above a critical concentration, the critical micelle concentration (CMC). Self-aggregation is believed to be the first step in particle formation. Charge transfer between molecules may be the significant mechanism leading to self-aggregation. The precipitation onset point as a function of concentration measured by titration and near-infrared spectroscopy can be used to estimate the CMC. The CMC values depend upon the type of asphaltenes and the solvent used. Two asphaltenes with different characteristics could have the same CMC values. CMC is not the only factor that determines asphaltenes precipitation and aggregation [214A440].

Sediment or sludge is soft coke-like substances that usually deposit on the catalyst surface, reactor and downstream equipment and cause both operability and catalyst deactivation problems. Sediment formation is the product of asphaltene instability or incompatibility between components of the residual oil producing precipitation.

Solids content of gas oils is typically determined by filtration. A bitumen coker gas oil may contain significant amounts of toluene-insolubles not measured by conventional filtration. A low speed centrifugation technique separated a highly polar organic phase containing high amounts of nitrogen and oxygen. This material most likely originates from a low molecular weight pyrrolic compound present in heavy gas oil. The material is easily oxidized to produce insoluble, gummy polymers that can interact with inorganic minerals and metals and bind filters [214A326].

Fine particles found in feed streams are another source of particles in the reactor and effluent. Clays, a concern especially for tar sand bitumen distillates, are entrained during distillation, coke particles originate in upstream delayed cokers and corrosion products come from upstream processing and oil field piping. Fine particles can deposit and clog the catalyst beds causing premature shutdown due to high pressure drop. The surface composition and charge determine the behavior of fine particles. For example, mineral solids from Athabasca bitumen that appear in hydrotreater feedstocks are coated with toluene-insoluble organic material that strongly adheres to the particle. The coated particles are "practically impossible to physically separate" from the bitumen [214A450]. Laboratory experiments show the asphaltene coating is

progressively removed from kaolin clay by active hydrotreating catalyst, destabilizing the suspension and increasing deposition in the packed bed.

Iron oxide and iron salts are commonly found in most crude oils and flow directly to residue hydrotreaters where  $H_2S$  produces iron sulfide. Iron sulfide has some hydrogenation activity, but is inferior to NiS catalysts. At hydrotreating conditions, asphaltene coated iron sulfide deposited more readily in the bed than asphaltene-coated kaolin. Low concentrations of water at supercritical conditions produced by hydrodeoxygenation may displace a portion of the asphaltene molecules from the kaolin particle surface. The exposed hydrophilic surface areas likely caused the increased tendency of the particles to adhere to the catalyst bed. The presence of polar compounds such as ammonia and quinoline has no significant effect on the deposition of fine particles [214A450].

## Thermodynamics

The hydrotreating of heavy oils simultaneously involves several reaction classes, especially aromatic hydrogenation, hydrodesulfurization and hydrodenitrogenation. Thermodynamics of simultaneous liquid phase reactions in the presence of a multitude of reactive compounds is extremely complex and requires experimentally determined properties. HDS and HDN reactions are generally not severely limited by thermodynamics, however, aromatic hydrogenation reactions are difficult to drive to completion at normal hydrotreating process conditions. The kinetics, catalyst activity and thermodynamics of aromatic hydrogenation limit the operating temperature to a narrow range of about 572 to 662°F (300 to 350°C). To maximize aromatic hydrogenation, an active catalyst, low temperatures and moderate pressure (3 to 5 MPa) are required. However, almost all hydrotreating reactions are thermodynamically favored at about 392 to 482°F (200 to 250°C) and moderate pressure, so highly active catalysts are needed.

A comprehensive review of available experimental thermodynamic data and methods for estimating the data includes tabulations of the equilibrium constants and standard enthalpies of reaction for representative single and multi-ring aromatic hydrogenations, hydrodesulfurization (of mercaptans, thiophenes and benzothiophenes) and selected hydrogenation, hydrogenolysis and overall hydrodenitrogenation [214A539].

## Kinetics

The kinetics of hydrotreating reactions (HDS, HDN and HDA) for petroleum feedstocks exhibits many "peculiarities". For example, the overall HDS or HDN reaction order is higher than for individual organosulfur or organonitrogen compounds. Furthermore, high activity catalysts show lower overall order than low activity catalysts. Difficult feedstocks have higher overall order than easy feeds. The overall HDS order decreases with increasing temperature. The overall order depends upon the reactor type. A continuum theory that treats the large number of reacting compounds of the feedstock as a continuous mixture. The kinetics are both feed and reactor dependent, which can account for pore diffusion limitations and nonlinear kinetics. As a result, in many cases characterization of only the most refractory feed fraction and running the reaction at an intermediate conversion level may be sufficient [214A523].

Kinetics and networks for hydroprocessing reactions (hydrogenation of aromatics, HDS, HDN, HDO) for model compounds, binary and multicomponent mixtures at high pressure were thoroughly reviewed up to 1991 by Girgis and Gates. They also include the effects of sulfur, nitrogen and oxygen compounds on these reactions [214A452]. Thermodynamics limit the hydrogenation of aromatics at high temperatures and lower hydrogen pressures [214A043]. The reactions and kinetics of mild hydrocracking (the once-through conversion of heavier materials in



the fee into lighter products at mild reaction conditions using a combination of hydrotreating and hydrocracking catalyst) are reviewed by Valavarasu et al. [214A161].

In general, the kinetic order of hydrodesulfurization ranges from one to two while the order of hydrodenitrogenation is first order [214A305]. Nickel removal is first order for the liquid-limited reaction [214A388].

Analysis of a small pilot scale continuous trickle bed reactor using a commercial NiMo/alumina catalyst showed hydrodynamic effects (holdup and catalyst wetting) need to be accounted for when determining the kinetics of HDS and HDM of petroleum residue [214A388].

### Hydrodesulfurization

Hougen-Watson kinetic models for HDS of model compounds (thiophene, benzothiophenes and dibenzothiophene) are reviewed in [214A039]. A methodology for kinetic modeling of HDS of oil fractions is presented based upon Hougen-Watson kinetics using a structural contribution approach.

The pre-exponential factor, activation energy and first order rate constant at 536°F (280°C) for 23 members of the benzothiophenes family and 12 dibenzothiophenes at 608°F (320°C) are tabulated in [214A403]. Substituents next to the sulfur atom reduce the reactivity compared to the unsubstituted molecule. Substituents in other positions either increase or decrease the reactivity.

The relative activities of transition metal sulfides for HDS of dibenzothiophene are listed in Table 5.29. The activity is calculated as the zero-order rate constant relative to MoS<sub>2</sub> normalized to 1 mole of metal for unsupported metal sulfides. For supported catalysts, the relative activity is dependent on the support. For example, unsupported Rh, Ru, Os and Ir sulfides are more active than Pt and Pd sulfides. For the platinum group metal sulfides supported on alumina, Pt is substantially more active than Ru and Ir for the HDS of dibenzothiophene. Conditions with the supported catalysts were much different than in the unsupported case [214A035].

**Table 5.29**  
**RELATIVE ACTIVITIES OF TRANSITION METAL SULFIDES IN THE HDS OF**  
**DIBENZOTHIOPHENE<sup>a</sup>**

<u>Metal</u>	<u>Relative Activity</u>	<u>Metal</u>	<u>Relative Activity</u>	<u>Metal</u>	<u>Relative Activity</u>
Ti	0.2	Zr	0.2	W	0.4
V	0.1	Nb	0.2	Re	4.9
Cr	0.6	<b>Mo</b>	<b>1.0</b>	Os	27
Mn	0.1	Ru	47	Ir	22
Fe	0.1	Rh	13	Pt	2.0
Co	0.2	Pd	1.6		
Ni	0.2	Ta	0.1		

Source: 214A035

<sup>a</sup> The relative activities are zero-order rate constants relative to that of MoS<sub>2</sub>, normalized to 1 mole of metal; unsupported metal sulfides.

The surface of HDS catalysts are generally believed to contain two types of adsorption sites: one site competitively adsorbs the sulfur molecule such as dibenzothiophene (DBT) and its products, the other site adsorbs H<sub>2</sub>. For HDS of DBT over either CoMo/MCM-41 or NiMo/MCM-

41 catalysts, the Langmuir-Hinshelwood kinetic model does not fit the kinetic data for either of these catalysts. A pseudo-first-order kinetic model fit the data well [214A042].

Heavy gas oil derived from oil sands bitumen (410-1211°F, 210-655°C) hydrodesulfurized in a micro trickle bed reactor over a commercial NiMo/alumina, trilobe catalyst (about 1.5 mm diameter) at the following conditions: 725°F (385°C), 88 bar reactor pressure, 0.5h<sup>-1</sup> LHSV and H<sub>2</sub>/feed ratio of 800ml/ml. The HDS followed a power law model with a reaction order of 2.0 (R<sup>2</sup> = 0.958):

$$k = [S_p^{-1} - S_f^{-1}]LHSV$$

where

k = apparent rate constant for sulfur removal, h<sup>-1</sup>(wt%)<sup>-1</sup>

S<sub>p</sub> = sulfur in hydrotreated product, wt%

S<sub>f</sub> = sulfur in feed heavy gas oil, wt%

LHSV = liquid hourly space velocity, h<sup>-1</sup>

The activation energy of the HDS reaction was 28 kcal/mol [214A284].

The addition of a solvent can promote the HDS catalytic activity and suppress catalyst deactivation during the hydrotreatment of atmospheric residue. Solvents increase hydrodesulfurization activity in the order of water > light cycle oil (LCO) > tetralin > no solvent > phenol. Coke deposition is reduced by all the solvents. The solvents are hydrogenated but also contribute to the inhibition of hydrodesulfurization when remaining on the active sites for long time. Water enhances desorption of asphaltenes and desulfurized products from the catalyst compared to the other solvents because it remains on the active sites for short periods [214A235]. A kinetic study of hydrodesulfurization of 4,6 dimethyldibenzothiophene in either n-dodecane or decaline over a commercial NiMoP/alumina catalyst shows catalyst activity is greater when n-dodecane is the solvent, but activity decreases at pressures below 34.7 bar (503 psi). The N-dodecane, the solvent with the higher hydrogen solubility, has a larger selectivity to products of the pathway of hydrogenation prior to C-S bond cleavage rather than to products of the direct pathway of C-S cleavage and then hydrogenation [214A548].

### Hydrodenitrogenation

HDN reactions usually involve multiple intermediate aromatic ring hydrogenation steps before C-N cleavage. Hydrogenation reactions sometimes are controlled by thermodynamic equilibrium with an intricate interaction between the thermodynamic equilibrium and kinetically controlled steps. Industrially, H<sub>2</sub>S appears to significantly affect HDN. HDN kinetics are further complicated by the effects of sulfur in the feedstock that vary depending upon the rate-controlling step(s). HDN kinetics including HDN in mixtures with different heteroatoms are reviewed in [214A038]. The reaction between a chemisorbed nitrogen compound and hydrogen is usually considered to be the rate limiting step.

Analysis of petroleum and Syncrude oils identified two main types of aromatic nitrogen compounds: nonbasic pyrrole benzologues (with a five-membered heterocyclic ring) and basic pyridine benzologues (with a six membered heterocyclic ring) [214A268]. Nitriles present in shale oil are hydrodenitrogenated at mild operating conditions much faster than five- or six-membered nitrogen heterocyclic compounds. Basic nitrogen compounds in heavy oils, for example pyridine, are more readily saturated than nonbasic compounds such as indole and pyrrole. For example, saturation of the nitrogen ring is always faster than saturation of the phenyl ring of quinoline or acridine. HDN reaction mechanism and kinetics are complicated by the generation of nonbasic

nitrogen compounds during the hydrotreating process [214A218, 214A245, 214A292]. Kinetic models of pyridine and piperidine are discussed by Pille and Froment [214A407].

Under constant process conditions in a trickle bed reactor with a commercial NiMo/alumina catalyst, the HDN rate of conversion of nonbasic nitrogen compounds in heavy gas oil is much lower than that of basic nitrogen compounds. For example, at 779°F (415°C), 88 bar, 600 volumetric H<sub>2</sub>/oil ratio and 1 LHSV, basic nitrogen is 92 % converted compared to 67% conversion of nonbasic nitrogen. Conversion of both types of nitrogen compounds increases with increasing temperature, but the rate of increase of basic nitrogen compounds is lower at higher temperatures (752-775°F, 400-415°C) than at lower temperatures (689-734°F, 365-390°C). This may be caused by the generation of basic nitrogen compounds by hydrogenation of nonbasic compounds. The effect of residence time is similar: conversion increases with increasing space time for both types of nitrogen compounds. At high space times (1.5-2 H), the conversion of nonbasic nitrogen compounds increases sharply compared to basic compounds, which is possibly due to the generation of more basic compounds from nonbasic compounds. This indicates the nonbasic compounds require more reaction time for conversion [214A245].

Pressure and the ratio of H<sub>2</sub>-to-oil more significantly effect the conversion of nonbasic nitrogen compounds than basic compounds. Conversion of both nitrogen types increases with increasing reaction pressure. The difference in relative rates of conversion between the easier to convert basic compounds and the nonbasic compounds decreases with increasing pressure. At lower pressures, the conversion of the basic compounds is faster than the nonbasic compounds due to competitive adsorption. At higher pressures, the HDN of basic compounds becomes relatively slow due to the increase in hydrogenation of nonbasic compounds to basic compounds. Conversion exhibits a maximum with the H<sub>2</sub>-to-oil ratio. As the ratio is increased, the H<sub>2</sub> partial pressure also increases, which promotes the hydrogenation of the heterocyclic ring. The rate of conversion increase of nonbasic nitrogen compounds with the H<sub>2</sub>-to-oil ratio is greater than that of basic compounds. When H<sub>2</sub> is in large excess, the reaction is pseudo first order with respect to H<sub>2</sub>. H<sub>2</sub> partial pressure affects nonbasic compounds more significantly than basic compounds. The rate limiting step in the HDN of heavy gas oil is the hydrogenation of nonbasic nitrogen compounds [214A245].

The HDN reactivity of gas oil fractions decreases exponentially as the boiling point (molecular weight) increases. A recent study of quinoline HDN demonstrates that for Athabasca coker gas oil fractions the reactivity decrease of a NiMo/ $\gamma$ -alumina catalyst is caused by the organonitrogen compounds. For this oil, the lightest fraction (649-739°F, 343-393°C) exhibits the highest extent of deactivation, but a nitrogen-rich extract from this fraction does not deactivate the catalyst and causes significantly less reversible inhibition. The primary species causing catalyst HDN deactivation are alkyl-carbazoles and tetrahydrobenzocarbozoles. This gas oil contains higher concentrations of polyaromatics than conventional gas oils. However, the non-nitrogen species are insignificant contributors to the deactivation. Additionally, the HDN activity varies with hydrogen partial pressure independent of the molecular weight [214A375]. Kinetic modeling of ortho-propylaniline, a major intermediate in the HDN of quinoline, is discussed in [214A408].

A study of three model compounds present in heavy gas oils compared the effect of trickle bed operating conditions using a commercial NiMo/alumina catalyst. The basic compound hydrogenated easier than the nonbasic compounds studied. The HDN of acridine, a basic compound, was higher at all H<sub>2</sub>S levels tested than that of the nonbasic compounds carbazole and 9-ethylcarbazole. The HDN conversion of acridine was 98-99% from 671 to 752°F (355-400°C). Conversion of carbazole increased from 92 to 95% as temperature increased over the same temperature range and the conversion of 9-ethylcarbazole similarly increased from 94 to 97%. Pressure over the range of 1120-1420 psig had no significant effect. Conversion of acridine and 9-ethylcarbazole was independent of liquid hourly space velocity (LHSV) whereas

conversion of carbazole increased from 92 to 99% as LHSV decreased from 2 to 0.5 h<sup>-1</sup>. Increasing the volumetric H<sub>2</sub>/feed ratio from 200 to 800 caused conversion of carbazole to significantly increase from 90 to 98%. The alkyl group of 9-ethylcarbazole had no steric hindrance effect on the HDN but caused an increase in HDN reactivity [214A318].

HDN conversion of mixtures of acridine and carbazole increased with increasing basic nitrogen (acridine) feed concentration. Basic nitrogen compounds adsorb faster on the catalyst surface than nonbasic compounds and occupy a greater fraction of the active sites. Conversion of feed containing only nonbasic nitrogen compounds is higher than feed containing low concentrations of both basic and nonbasic compounds [214A318].

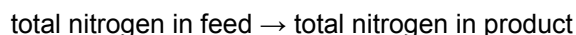
The HDN of indole is mainly controlled by the catalyst's relative strengths of hydrogenation and hydrogenolysis functions and not a single rate determining step. The effect of the presence of sulfur compounds on HDN activity varies significantly depending upon whether the hydrogenation of the aromatic ring is kinetically or thermodynamically controlled as well as which sites and steps are dominant in the overall reaction network. More H<sub>2</sub>S is needed at high temperatures and high H<sub>2</sub> partial pressures to maintain the proper balance between hydrogenation and hydrogenolysis [214A404].

It is well known that nitrogen-containing compounds inhibit HDS. However, the presence of H<sub>2</sub>S significantly increases the HDN reaction rate of heavy gas oil and quinoline. An increase in H<sub>2</sub>S (from added butanethiol) decreases the conversion of both basic and nonbasic nitrogen compounds present in heavy gas oil obtained from oil sands bitumen. Sulfur containing compounds also significantly increase the rate of HDN of pyridine at temperatures greater than 617°F (325°C) but reduce the rate at lower temperatures, probably due to competition for the catalyst site. At high partial pressure ratios of H<sub>2</sub>S to H<sub>2</sub>, hydrogenation is rate limiting while ring opening occurs readily by elimination or substitution. At still higher ratios, H<sub>2</sub>S negatively effects hydrogenation and lowers HDN activity. At lower ratios, C-N bond scission is rate limiting and H<sub>2</sub>S promotes elimination or substitution reactions [214A245, 214A375].

According to Bej et al., the kinetics of HDN of a heavy gas oil can be represented by the consecutive reaction scheme:



where  $k_1$  is the apparent rate constant of the first step and  $k_2$  is the apparent rate constant of the second step. A simplified reaction can represent the removal of total nitrogen from the heavy gas oil feed:



where  $k_3$  is the apparent rate constant for the overall HDN reaction. The conversion of nonbasic nitrogen compounds from heavy gas oil (first reaction) can be modeled by a simple power law with the rate constant values calculated:

$$k = \frac{1}{n-1} \left[ \frac{1}{N_p^{n-1}} - \frac{1}{N_f^{n-1}} \right] \text{LHSV}$$

where  $k$  is the apparent rate constant for conversion of total or nonbasic nitrogen compounds, h<sup>-1</sup>(wt%)<sup>1-n</sup>,  $n$  is the order of reaction,  $N_p$  is the total or nonbasic nitrogen in the product, wt%,  $N_f$  is the total or nonbasic nitrogen in the feed wt% and LHSV is the liquid hourly space velocity, h<sup>-1</sup>.

For heavy gas oil from oil sand bitumen, the 1.5 order of reaction was a better fit of the data for nonbasic ( $R_2 = 0.989$ ) and total nitrogen ( $R_2 = 0.995$ ) than the first or second order. This agreed with literature value of 1.7 for HDN of a bitumen derived feedstock.

The rate of disappearance of the intermediate, basic nitrogen compounds (second reaction) can be modeled assuming 1.5 order:

$$-dN_{\text{basic}}/dt = k_1 N_{\text{nonbasic}}^{1.5} - k_2 N_{\text{basic}}^{1.5}$$

where  $N_{\text{basic}}$  and  $N_{\text{nonbasic}}$  are the concentrations of basic and nonbasic nitrogen compounds at time  $t$ .

The values of the rate constants are tabulated in Table 5.30. The values of the apparent rate constants for the nonbasic nitrogen compounds are much lower than the values for the basic compounds. The values for the nonbasic compounds are mostly equal to the values for the total nitrogen removal. This indicates the rate of initial hydrogenation of the nonbasic nitrogen compounds to basic nitrogen compounds is the rate controlling step. The activation energies calculated from the Arrhenius plot are [214A245]:

nonbasic in feed → basic nitrogen compounds	80 kJ/mol
basic nitrogen → ammonia + hydrocarbons	74
Total feed nitrogen → product nitrogen	80

**Table 5.30**  
**VALUES OF APPARENT RATE CONSTANTS FOR CONVERSION OF NITROGEN COMPOUNDS IN HEAVY BITUMEN GAS OIL**

Apparent rate constants, $H^{-1}(\text{wt}\%)^{-0.5}$	Temperature, °F (°C)			
	689 (365)	725 (385)	752 (400)	779 (415)
$k_1$	1.16	1.84	2.64	3.41
$K_2$	2.98	4.58	6.53	8.15
$K_3$	1.26	2.06	2.92	3.75

Source: 214A245

### Hydrodeasphalting

Under typical hydroprocessing conditions, asphaltenes are highly reactive undergoing a multitude of reactions, including readily undergo radical bond fission, leading to high percentages of deasphalting. The order of deasphalting reaction experimentally is half order for a simple cracking model,  $C_0 - C = KC^{0.5}/\text{WHSV}$  where  $C_0$  is the initial concentration and  $K$  is an intrinsic rate constant (all gradients are absent) that follows the Arrhenius equation, with an activation energy of 41.5 kcal/mol [214A454].

### Aromatic Hydrogenation

A kinetic study of aromatic hydrogenation of light gas oil derived from Athabasca bitumen was conducted in single and two-stage hydrotreating processes. A NiMo/alumina catalyst was used in the first stage for heteroatom removal while NiW/alumina catalyst, which deactivates rapidly in the presence of sulfur and nitrogen, saturated aromatic rings in the second stage.  $\text{H}_2\text{S}$  was removed before the second stage. Hydrogenation of aromatic rings is an equilibrium reaction that shifts toward aromatics with increasing temperature. Kinetics were modeled using a Langmuir-Hinshelwood rate expression including the effect of  $\text{H}_2\text{S}$ . The apparent kinetic parameters were determined and reported. Since the rate constants for the single stage process are lower than those from the two-stage process, the two-stage process is favored by the faster

reaction rate. Equilibrium adsorption constants of the aromatics were lower than those of H<sub>2</sub>S in the single stage process, but were higher than those of H<sub>2</sub>S in the two-stage process. H<sub>2</sub>S from the HDS reaction inhibits both the hydrogenation of aromatics and HDS reactions. The inhibition is reduced by the inter-stage removal of H<sub>2</sub>S [214A300, 214A381].

### Feedstock Effects

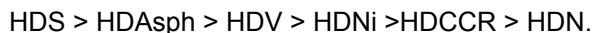
The effect of the various residue components on the performance of hydroprocessing catalysts used in fixed or ebullating bed processes is discussed by Lopez-Salinas et al [214A543].

A set of narrow fractions obtained by supercritical fluid extraction and fractionation (SFEF), a new separation method developed by the State Key Laboratory of Heavy Oil Processing (University of Petroleum, Dongying, China) increase in molecular weight and polarity. Eight narrow extracted fractions plus an unextractable end-cut obtained from three residue oils (atmospheric residue from Dagang crude, a paraffinic low sulfur crude; vacuum residue from Saudi light and medium crudes, both are naphthenic high sulfur crudes) show as the molecular weight and/or aromaticity of residue fractions increases, the decrease in the intrinsic HDN activity is more than that for HDS. The HDS order rate constant (assumed to be first order) gradually decreases while the HDN constant (also assumed first order) decreases substantially and then levels off. The decreased HDS and HDN reactivities of the heavier fractions result from increased diffusion resistance and decreased intrinsic reactivity, respectively. Further more, deep HDS of the lighter fractions is equally difficult as that for HDS and HDN of the heavier fractions. The heavier fractions contain end-cut residues that are difficult to hydroprocess and contain high concentrations of contaminants that cause rapid catalyst deactivation. Removing the end-cuts from residue before hydroprocessing is suggested [214A344].

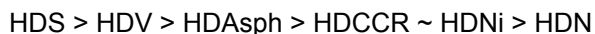
Heavy oils are generally upgraded using multiple reactors loaded with a HDM catalyst (such as Mo/alumina) followed by HDS (NiMo/alumina) and HDN (NiMoP/alumina) catalysts with the catalysts chosen on the basis of activity, selectivity and life. Evaluating mid section HDS and tail-end HDS/HDN catalysts with straight run residue (feed to the HDM reactor) will provide erroneous data. The reactivity pattern of tail-end catalysts towards different reactions will be in error as will the kinetic reaction orders and rate constants. HDS catalysts should be evaluated with the hydrodemetallized oil from the first reactor. Similarly, tail end HDS/HDN catalysts should be evaluated with the hydrodesulfurized oil from the second reactor. The activity of a NiMo catalyst evaluated with straight run atmospheric residue at low LHSV gave the following order of activities:



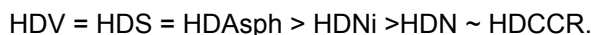
with demetalized feed, the order becomes:



similarly with a NiMoP catalyst with straight run feed, the order activities are:



compared to the order with demetallized and desulfurized feed:



The reaction order for HDS changes for the HDS/HDN catalyst from 2 obtained with the straight run feed changes to 1.5 with the demetallized/desulfurized feed since a narrower range of sulfur containing molecules are in the demetallized/desulfurized feed. Similarly for this catalyst, the order of the HDN reaction changes from 1.5 to 1.

For the HDS catalyst, the rate constants for HDS, HDV, HDAsph and to some extent HDN with the demetallized feed are generally higher than those using straight run atmospheric residue. The ratios of the rate constant for the demetallized feed to the rate constant for the straight run feed are in the order:

$$\text{HDAsph} > \text{HDS} \sim \text{HDV} > \text{HDCCR} \sim \text{HDN} > \text{HDNi}$$

similarly for the HDS/HDN catalyst, the ratios of HDS feed to straight run rate constants are:

$$\text{HDAsph} > \text{HDS} \sim \text{HDV} > \text{HDCCR} \sim \text{HDNi} > \text{HCN} \text{ [214A270, 214A288].}$$

### Asphaltene Conversion

The asphaltene content of hydrotreated products declined as pressure and temperature increased and the liquid hourly space-velocity decreased. The kinetics of asphaltene conversion of Maya heavy crude oil over a commercial NiMo/alumina catalyst in a pilot plant integral trickle-bed reactor were described well by a power law model:

$$-r_{\text{Asphaltene}} = 5.65 \times 10^5 e^{-10350/RT} C_{\text{Asphaltene}}^{2.1} C_{\text{Hydrogen}}^{1.28}$$

where

$C_{\text{Asphaltene}}$  is the concentration of asphaltenes

$C_{\text{Hydrogen}}$  is the concentration of hydrogen, which is in gas-liquid equilibrium.

The activation energy was 10.35 kcal/mol. The low value was attributed to the complexity of the asphaltenes and to the change in selectivity at the reaction conditions used [214A432].

### Aging Effects

A sulfided NiMo/alumina catalyst was deactivated by coke (40 wt% of fresh catalyst) and metal (1.1 wt% Ni, 2.7 wt% V) deposits over one year of continuous hydroprocessing of Arabian Light and Arabian Heavy residua. In this case, severity was not high so the catalyst accumulated only a relatively low amount of metal sulfide deposits that corresponded to a second stage reactor and not a guard bed reactor. Pseudo first order rate constants for naphthalene hydrogenation, dibenzothiophene HDS and quinoline HDN were determined experimentally in a basket equipped batch reactor for each separate reactant and for a mixture of all three reactants. Catalysts used were the fresh, spent, combustion regenerated spent catalyst and a model catalyst consisting of the fresh catalyst impregnated with nickel and vanadium concentrations equal to the spent catalyst. Since the metals on the spent catalyst were relatively low, the regenerated catalyst performed nearly the same as the model catalyst showing the model catalyst to be a good approximation for the performance of the regenerated catalyst. The regenerated catalyst was almost as active for naphthalene hydrogenation as the fresh catalyst, but was not as active as the model catalyst. The relative activities for HDS and HDN between the catalysts were similar to the hydrogenation activity. The rate constants for the primary forward reaction steps (naphthalene to tetralin; dibenzothiophene to biphenyl and quinoline to 1,2,3,4 tetrahydroquinoline) of the mixture (plus  $\text{H}_2$ ) relative to the single reactant (plus  $\text{H}_2$ ) are summarized in Table 5.31. This data suggests the model catalyst may be better for correlating relative activities than absolute activities. The model catalyst is not expected to perform identical to the regenerated catalyst because of nonuniformity of vanadium deposits in the regenerated catalyst and the near uniformity of deposits in the model catalyst [214A227].

**Table 5.31**  
**RATE CONSTANTS FOR MIXTURE RELATIVE TO THOSE FOR SINGLE COMPONENTS**

<b>Catalyst</b>	<b>Rate constant ratio</b>		
	<b>Naphthalene hydrogenation <math>(k_1)_{\text{mixture}}/k_1</math></b>	<b>Dibenzothiophene hydrodesulfurization <math>(k_1)_{\text{mixture}}/k_1</math></b>	<b>Quinoline hydrodenitrogenation <math>(k_1)_{\text{mixture}}/k_1</math></b>
Fresh	0.40	0.55	0.81
Spent	0.48	0.74	0.91
Regenerated	0.47	0.67	---
Model <sup>a</sup>	0.39	0.69	0.90

Source: 214A227

<sup>a</sup> Ni and V contents equal those of spent and regenerated catalysts (1.1 wt% Ni, 2.7% V).

## CATALYSIS

With the commercialization of active hydrotreating catalysts for middle distillates to meet near zero sulfur diesel fuel specifications, environmental attention and catalysis research interests are being directed to heavy oils. The heavy oil catalysts are entirely different than those used for selective hydrogenation of light oils or for desulfurization of middle distillates. Since heavy feedstocks vary extensively, depending on source and prior treatment, there does not appear to be a universal catalyst for these feedstocks. Typically a series of catalysts sequentially process heavy oil feeds usually starting with demetallization catalyst in a guard reactor. The oil is then subject to HDS and HDS/HDN catalysts. The hydrotreating catalyst's bimetallic main active metals, usually nickel or cobalt and molybdenum, are promoted by a third element, usually phosphorous. In hydrotreating, the catalyst support is important. Special attention is given the particle size and shape, pore volume and pore size distribution. For optimum catalyst life, an optimum balance is necessary between metals capacity and hydrotreating activity [214A155, 214A469, 214A487].

Molybdenum based sulfides are widely used industrially to hydrotreat heavy oils. It is well known that mixed CoMo sulfide and mixed NiMo sulfide catalysts are significantly more active than corresponding Mo, cobalt or nickel sulfide catalysts. The maximum activity of CoMo or NiMo catalysts is obtained at an approximately 0.3 ratio of promoter Co or Ni to promoter plus Mo, i.e. (Co or Ni)/(Co or Ni + Mo). Conventional CoMo catalysts are better than NiMo catalysts for hydrodesulfurization via the direct or hydrogenolysis pathway (see mechanisms) since the hydrogenation activity is relatively low. NiMo/alumina catalysts have high hydrogenation activity and are best for hydrodesulfurization via the hydrogenation route and for nitrogen removal [214A292, 214A455, 214A490].

Molybdenum catalysts exist as MoS<sub>2</sub> clusters having a layered structure where molybdenum atoms are in a plane located between two planes of sulfur atoms for each S-Mo-S layer. The catalysts contain small particles of MoS<sub>2</sub> with an average length of 3 to 4 nm with 1 to 3 layers deposited on the surface of the alumina support. The active sites are located at the edge surfaces of the MoS<sub>2</sub> crystallites. Promoter Ni or Co atoms are accepted to be located at MoS<sub>2</sub> edges. The exact location of the promoter atoms and the mechanism of the promotional effect are subjects of debate. The equilibrium sulfur coverage effects whether cobalt substitutes at the S-edge or at the Mo-edge. Different models of MoS<sub>2</sub> may be the cause of opposite conclusions on the most stable location of Co atoms in MoS<sub>2</sub> [214A049, 214A490].



The catalytic performance of sulfided CoMo or NiMo catalysts is strongly dependent on the catalyst preparation method and its activation conditions. Alumina can be prepared by four methods: ammonia hydrolysis, urea hydrolysis, ammonium carbonate hydrolysis or pH swing. Carbonate hydrolysis produces wide range of pores after calcination. Alumina-mixed oxide supports can be prepared by ammonia hydrolysis or urea hydrolysis methods. After the material is prepared, it is kneaded with additives and peptizing agent ( $\text{HNO}_3$ ) and shaped and sized such as by extrusion. The catalytic metals are impregnated onto the support, typically Mo or W first and then Co or Ni, to form the catalyst. Coprecipitation can be used when an additive such as phosphorus or a chelating agent is used [214A542].

Characterization of a hydrotreating catalyst entails measuring a number of properties that describe its physical, chemical and catalytic properties. With a large number of properties, many of which may be determined by several analytical techniques, a large number of methods are available. Analytical techniques used for characterizing hydrotreating catalysts are summarized by Ramirez et al [214A541]. Characteristics of various alumina and alumina metal oxide supports and Co/Mo catalysts prepared by different methods are tabulated by Rana et al [214A542]. They also discuss characterization of spent catalysts.

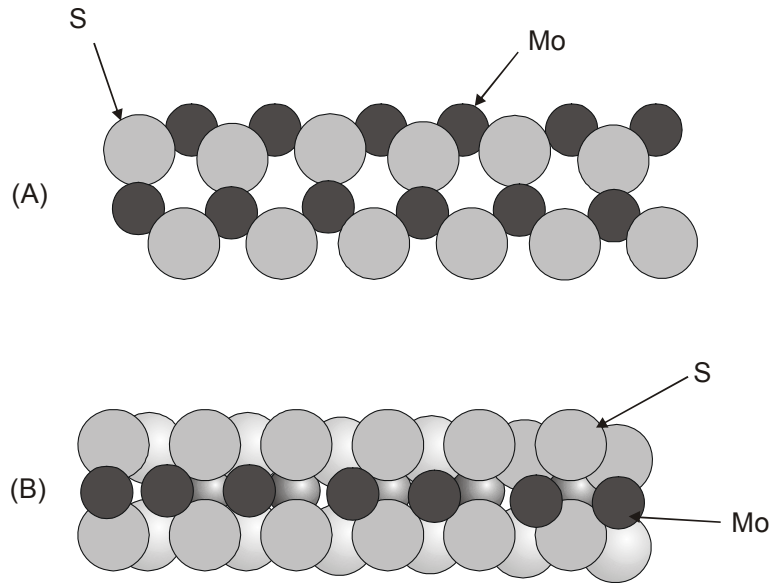
We first review theoretical results providing insights into Mo-sulfided catalysts. Catalyst supports are discussed next since they strongly influence the sulfided molybdenum active phases. Commercial catalysts are briefly discussed before reviewing catalyst deactivation, catalyst regeneration and metals recovery. Selected patents pertaining to hydrotreating catalysis of heavy oils are summarized in Table A.1 of Appendix A.

## Theoretical Results

Theoretical calculations produced insights into the structures and properties of Mo-sulfided catalysts that were not achievable experimentally. Sun et al. reviewed published theoretical results and conclusions. They generally concluded “the single slab  $\text{MoS}_2$  model containing two rows of molybdenum atoms (Figure 5.4) is adequate for discussing general energetic trends when sulfur coverage changes on the edge surface (Figure 5.5), however more substantive models were required to obtain accurate energetic and structural data. The stable structures at reaction conditions also had to be considered when discussing the locations of promoter atoms, the dissociation of hydrogen, and the adsorption of molecules on the edge surface” [214A490].

**Figure 5.4**  
**STOICHIOMETRIC  $\text{MoS}_2$  MODEL INCLUDING TWO ROWS OF  $\text{MoS}_2$  UNITS:**

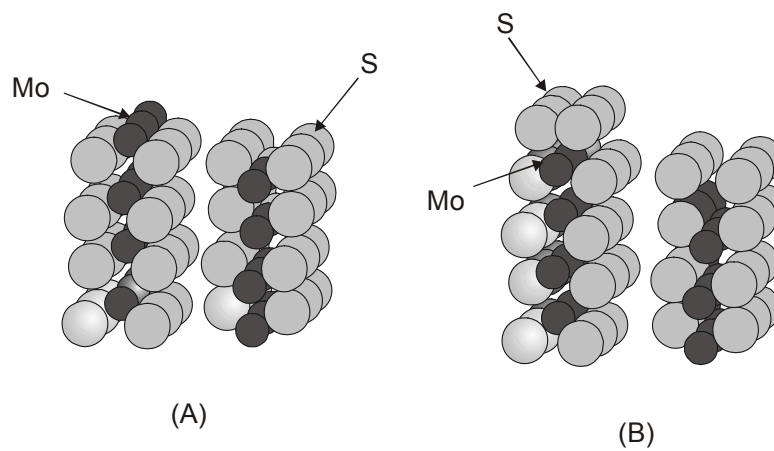
(A) SIDE VIEW;  
 (B) TOP VIEW [214490]



Source: 214A490

**Figure 5.5**  
**OPTIMIZED  $\text{MoS}_2$  EDGE SURFACES:**

(A) WITH BARE MO-EDGE AND FULLY SATURATED S-EDGE;  
 (B) WITH FULLY SULFIDED MO- AND S-EDGES

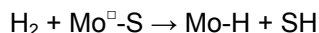


Source:214A490

The formation of vacancies on stable MoS<sub>2</sub> edges is thermodynamically unfavorable, but this endothermic process can be separated on the basis of kinetics into several elementary steps having mild activation energies. At hydrotreating reaction conditions, the MoS<sub>2</sub> surfaces are in dynamic equilibrium between the formation and saturation of vacancies. In the presence of H<sub>2</sub>S, the vacancies “displace towards the fully saturated stable edge surface”. This dynamic equilibrium allows for the existence of a small number of vacancies with a short lifetime. Vacancies are favored by low H<sub>2</sub>S partial pressure and high temperature. Conversely, high H<sub>2</sub>S partial pressure and low temperature decreases the number of vacancies on the edge. Vacancies can be created by hydrogen reacting with surface sulfur thereby activating the MoS<sub>2</sub> edge surfaces [214A490].

Experimentally, a study of unsupported MoS<sub>2</sub> showed the number of active sites increases with decreasing number of slabs in each MoS<sub>2</sub> particle. Single slab catalysts are known to be more active than multi-layer slabs [214A401].

Molecular hydrogen can dissociate on the catalyst in two ways depending upon the reaction location on the structure of the surface of MoS<sub>2</sub>. The heterolytic route involves an unsaturated metal site such as molybdenum with a sulfur vacancy (Mo<sup>□</sup>) and a sulfur atom and thus is possible only on a partially sulfided edge surface:



The homolytic route involves sulfur couples and is preferred on a fully sulfided S-edge or on a fully sulfided Mo-edge:

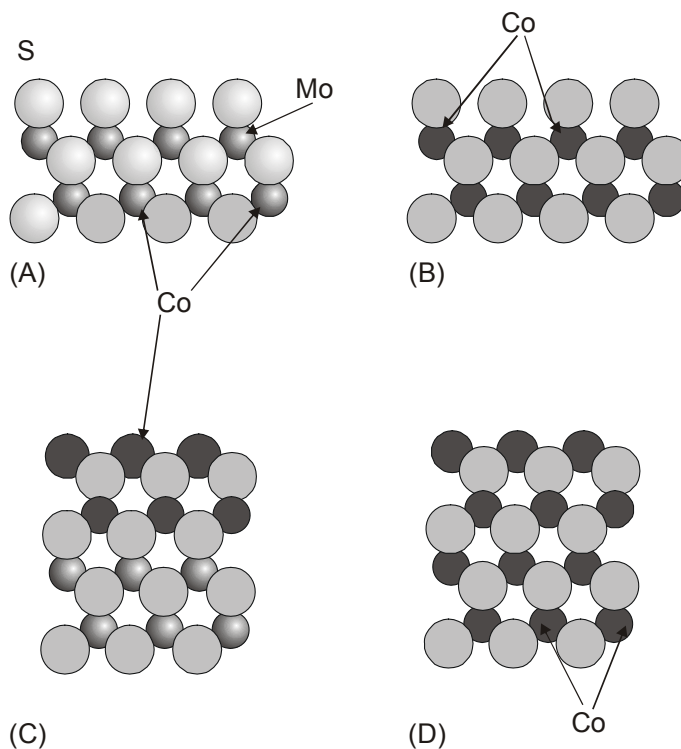


The heterolytic route is more energetically favorable than the homolytic route on a S-edge surface half covered by sulfur atoms.

The activity of molybdenum catalyst is significantly increased when promoter metals cobalt or nickel are present. The Ni or Co atoms are accepted to be located at MoS<sub>2</sub> edges. The exact location of the promoter atoms and the mechanism of the promotional effect are subjects of debate. Figure 5.6 shows four models for sulfided CoMo catalysts.

**Figure 5.6**  
**SULFIDED CO-MO CATALYST MODELS SHOWING COBALT ATOMS AT DIFFERENT**  
**LOCATIONS:**

- (A) TWO MO ATOMS ARE SUBSTITUTED BY CO ATOMS AT THE FULLY SULFIDED S-EDGE;  
 (B) TWO MO ATOMS ARE SUBSTITUTED BY CO ATOMS AT THE FULLY SULFIDED MO-EDGE;  
 (C) THREE MO ATOMS ARE SUBSTITUTED BY CO ATOMS AT THE BARE MO-EDGE;  
 (D) THREE MO ATOMS ARE SUBSTITUTED BY CO ATOMS AT THE FULLY SULFIDED S-EDGE.



Source: 214A490

The addition of a promoter atom such as cobalt or nickel has a number of affects, including:

- The binding energy of sulfur atoms on the catalyst edge surfaces and hence the degree of surface coverage by sulfur thereby adjusting the catalyst properties
- The electronic structure
- The activation of hydrogen.

The binding energy of sulfur atoms on the catalyst edge surfaces are changed by substitution of molybdenum by cobalt or nickel. In contrast to the removal of sulfur atoms from molybdenum, the removal of sulfur from cobalt substituted edges is an exothermic process, which implies a decrease in the sulfur binding energy. The lower binding energy leads to lower equilibrium sulfur coverage on the cobalt edges and more unsaturated metal sites that are believed to be the active sites for the hydrotreating reactions. Substitution of nickel atoms has a similar effect as cobalt, but the sulfur binding energy is weaker on nickel promoted edges than on cobalt edges. At the same condition the sulfur coverage on the edges decreases in the order:  $\text{MoS}_2 > \text{CoMoS} > \text{NiMoS}$ . Furthermore, the presence of cobalt or nickel in the edge surfaces

decreases the binding energy of sulfur on the catalyst surface, which allows the stable edge to contain more sulfur vacancies, the active sites for hydrotreating reactions. Other calculations confirm an increase in basicity of certain sulfur atoms bonded between the Mo and the Co or Ni atoms [214A417, 214A490].

The electronic structure is changed by the promoter atoms. This results in increased catalytic activity.

The activation of hydrogen is changed on the modified edge surface. Cobalt strongly enhances hydrogen activation, increasing the ability of the sulfur atoms to bind protons. The acidity of the cobalt sites is weaker than that of the molybdenum sites with the same sulfur coordination. The basicity of the sulfur atoms binding to cobalt is stronger than sulfur binding to molybdenum atoms. On a nickel promoted edge surface, the sulfur binding a nickel atom is unstable, meaning no S-Ni pair is available for hydrogen activation [214A490].

### Effect of Second Promoters

A large number of elements in addition to cobalt and nickel can be used as additives to further promote or modify CoMo and NiMo hydrotreating catalysts including halogens, phosphorous, boron, arsenic, alkalis, alkaline earths, gallium, rubidium, titanium, silicon and zinc. The addition of magnesium or zinc increases the structure of sulfided CoMo catalyst. Zinc added to CoMo/alumina depresses the formation of  $\text{CoAl}_2\text{O}_3$ , which allows more metals to be dispersed.

In commercial catalysts, phosphorus is mostly used as a third element. The role of phosphorus depends upon the support and upon the catalyst preparation methods. Reported effects are numerous including:

1. enhanced hydrodenitrogenation activity by modifying Lewis acid sites on alumina
2. increased hydrocracking activity with NiMo/alumina through an indirect effect on Bronsted acidity
3. increased size of  $\text{MoS}_2$  slab (clusters) and the number of  $\text{MoS}_2$  stacking
4. changing the electronic structure of sulfided NiMo while decreasing the dispersion of Ni-Mo-S phase
5. decreasing metal-support interactions
6. inhibiting the formation of  $\text{NiAl}_2\text{O}_4$  increasing the amount of P-Ni-Mo heteropoly compound
7. increasing dispersion of Co and Mo species
8. increasing the sulfidability of molybdenum [214A481].

The laboratory hydrotreating of a 50:50 weight blend of Maya crude oil and naphtha shows a laboratory prepared sulfided P(0.8 wt%)-Co(3 wt%)Mo(10 wt%)/alumina catalyst to be more active and to deactivate less for hydrodemetallization and asphaltene conversion than a commercial Ni(2.88 wt%)Mo(10.66 wt%) catalyst containing 3.73 wt% titania. The commercial catalyst is a little better for hydrodesulfurization; the hydrodenitrogenation activity of these catalysts is about equal. The commercial catalyst maintained activity for HDS; both are deactivated equally for HDN [214A481].

In other studies, the addition of phosphorus or boron to NiMo on alumina catalyst created extremely strong acid sites that enhanced HDN activity. No significant effect on sulfur conversion resulted. HDN and HDS activity are comparable to commercial catalysts [214A330]. Boron gave higher nitrogen conversion than a phosphorus catalyst, but at the same temperature, phosphorus

had higher sulfur removal. Phosphorus also promoted excellent hydrocracking at all operating conditions [214A331]. Phosphorus increased the stacking degree of MoS<sub>2</sub> on the catalyst surface, which increased activity by decreasing the average slab length and increasing dispersion of MoS<sub>2</sub> edge and corner atoms. Modeling showed maximum activity was obtained at minimum MoS<sub>2</sub> slab length of 10Å. Boron increased dispersion of MoS<sub>2</sub> increasing HDN activity [214A303].

A kinetics study of NiMo on boron-modified alumina catalysts showed an interactive effect of temperature and space velocity on HDN and HDS of heavy gas oil exists. Catalysts containing 9.1 and 11.7 wt% boron had HDN activities considerably higher than NiMo catalyst. Optimum conditions were 748°F (398°C) 7.9 MPa and 0.53 h<sup>-1</sup> for maximum nitrogen conversion and 774°F (412°C), 7.1 MPa and 0.82 h<sup>-1</sup> for maximum sulfur conversion. A power law model of HDN gave first order kinetics while HDS followed a 1.5 order kinetics. Comparison of the power law and Langmuir-Hinshelwood models indicated nitrogen and H<sub>2</sub>S adsorption significantly affected HDN and HDS reactions [214A312].

Trace amounts of noble metals (Rh, Pd, Pt) impregnated onto Co saponite (dry basis: 58.3% SiO<sub>2</sub>, 32.9% MgO, 5.6% Al<sub>2</sub>O<sub>3</sub> and 3.2% Na<sub>2</sub>O) produced higher catalytic activity and reduced carbon deposition on the catalyst when hydrotreating heavy oils than unpromoted Co saponite catalyst. Noble metals, especially rhenium, increase cobalt dispersion and the amount of active cobalt. The noble metals also more active than cobalt in creating reactive hydrogen species that enhance hydrogenation and reduce coke and prolong catalyst life. The energy of activation for hydrogen adsorption is reduced in the presence of the noble metals. Rhenium was more active a promoter than platinum or palladium [214A373]. Another study showed both rhenium and palladium significantly improved the reducibility of the Co on high porous saponite, rhenium more than palladium. A trace amount of rhenium along with palladium significantly enhanced the catalytic activity, comparable to that of a higher amount of rhenium alone, and further reduced the coke deposition [214A337].

The addition of fluorine to NiMo/alumina catalyst increases metal dispersion and catalyst acidity. Adding excessive fluorine decreases the surface area. The catalyst activity for hydrodesulfurization (HDS) of dibenzothiophene increases up to 0.5 wt% added fluorine and then decreases. Fluorine increases the amount of hydrogenated products compared to directly desulfurization. Activity for HDS of 4,6-dimethyldibenzothiophene increases up to 5.0 wt% F due to enhanced migration of the methyl groups to other positions in the ring while on the acidic sites. The amount of hydrogenated products decreases due to the acidic sites [214A415].

Alkali metals added to NiMo/γ-alumina catalysts neutralize surface acidity resulting in reduced coking and enhanced activity. The addition of 0.26 to 28 mmol alkali metal hydroxide/g of commercial Ni(3.5 wt% NiO)Mo(12.5 wt% MoO<sub>3</sub>) catalyst reduced the concentration of very acid sites. In laboratory hydroprocessing of Athabasca bitumen, Li and Na were similar in activity (80% S removal compared to 63% for the un-neutralized catalyst) and carbon deposition (14.4% compared to 17.3% for the untreated catalyst). The sodium treated catalyst increased the HDS rate constant by 40% compared to the untreated catalyst. Asphaltene removal also improved. HDN, microcarbon residue conversion and residue conversion were not affected. Doping with KOH resulted in a small change in coke deposition and activity at low concentrations [214A488].

## Catalyst Supports

In the hydrotreating of heavy oils, the catalyst support is very important since it is intimately involved with the performance of the catalyst. Because of its importance, catalyst supports are an ongoing research area with efforts to improve catalyst performance through support composition and preparation to provide adequate surface area, pore volume, pore diameter and mechanical

strength. Ramirez et al review these support properties and their effects [214A541]. Alumina is without question the most widely used support material since it has almost all the properties of an ideal support material, which include:

1. Stabilization of the active metal (Groups VI and VIII) oxides in highly dispersed or microcrystalline phases without detrimental interactions.
2. Stabilization of highly dispersed catalytic metal sulfides.
3. Available in high purity or at least without any negative interferences with the catalytically active phase by mobile impurities.
4. Cause no adverse reactions with the feedstock or products.
5. The active sites of the support positively contribute to the performance of the catalyst.
6. Easily controlled pore structure and specific area.
7. Be thermally stable under both reaction and regeneration conditions.
8. Easily be formed into the desired particle shape (pellets or extrudates for example) and size while having good mechanical strength.
9. Be low cost.
10. Not be adversely affected by metal recovery from spent catalysts [214A541].

The nature of the support strongly influences the sulfided molybdenum active phases through differences in interactions between the support and catalytic metals. For heavy oils, HDS, HDM, HDN and HDAs are affected by pore diameter and its effect on diffusion of the feedstock and the effects of the supports on the active phases. Catalysts with small pores are deactivated by metals and carbon deposits at the pore mouth whereas large pores deactivate by core poisoning. Large pore size supports, which have high metals capacity, are used for demetalization catalysts. The pore size gets smaller in the second and then in third beds. The optimum pore size for the catalyst depends upon the feedstock properties. For heavy feedstocks, too large pore size decreases the active surface area reducing catalytic activity [214A342, 214A384, 214A469, 214A480, 214A482, 214A541].

### **Pore Size Effect**

The effect of catalyst pore size when processing Kuwait vacuum residue is significantly different depending upon the hydrotreating reaction. For HDS, a unimodal pore size distribution with maximum pore volume in the medium mesopore range of 10-25 nm diameter yields the highest activity. Large pore size catalysts with a major portion of their pore volume in the 100-300 nm diameter pores are more effective for HDM and HDN. A greater proportion of large macropores (>300 nm) does not offer any advantage. Catalysts having bimodal pore size distributions with large portions of narrow pores deactivate at a higher rate than unimodal catalysts with a maximum amount of medium mesopores [214A426].

With a feedstock of Maya heavy crude oil diluted 50:50 by weight with hydrodesulfurized naphtha, conversion of the HDM reactions increased linearly (from about 67% to 90%) with average pore diameter above 44 Å up to 105 Å. Since a reference catalyst having the largest average pore diameter, but less total pore volume, was less active for HDM than the linear correlation indicated, the total pore volume is also an important parameter for HDM and HDAsp. The hydrodeasphalting (HDAsp) conversion increased slightly. HDS conversion first decreased with increasing average pore diameter and then increases. HDN conversion first increased and then decreased with increasing average pore diameter. The different relationship between

conversion and pore size indicates HDS and HDN occur on different active sites. The larger pore diameter catalysts experienced larger coke deposits [214A479].

### **Oxide Incorporated Aluminas**

The interaction of catalytic metals and the support is altered by incorporating magnesium oxide (MgO), silica (SiO<sub>2</sub>) or titania (TiO<sub>2</sub>) into  $\gamma$ -alumina. Delayed precipitation yielded high specific surface area (213-246 m<sup>2</sup>/g) catalysts comparable in specific area to pure alumina catalyst (242 m<sup>2</sup>/g), but less than pure silica (381 m<sup>2</sup>/g). The support is important for the reduction of Mo species. Molybdenum oxide is well dispersed on high surface area alumina-zirconia up to 12 wt% Mo loading. This indicates the amount of anionic vacancies increases. At higher Mo loadings, the rate remains essentially constant even though the surface area decreases as bulk metal oxide forms on the support surface [214A342]. However, on an alumina-titania (5.6 wt% Ti) support hydrotreating a heavy gas oil FCC feed, Mo loading of 6 wt% shows better results than a 10.5 wt% Mo catalyst for HDM and hydrodearomatization but not for hydrodesulfurization. The atomic ratio Ni/(Ni+Mo) of 0.45 is important in HDM especially at low temperature (626°F, 330°C). The low metal loading shows selectivity to saturating di-aromatic compounds. With polyaromatics, differences between metal loadings are negligible [214A053].

The nature of the support mainly depends upon the oxide incorporated. The Lewis acidity decreases in the order: alumina-titania ~ alumina-silica > pure alumina > alumina-zirconia > alumina magnesia. Basic supports enhance the promotional effect of Co or Ni on Mo more than acidic supports due to stronger metal support interaction. Alumina-zirconia (90:10 by weight) support provides better HDM selectivity with time on stream due to the basic nature of the support. The number of active sites on MoS<sub>2</sub> or Co or Ni promoted MoS<sub>2</sub> is changed by the presence of zirconia in the alumina [214A342].

### **Alumina-Zirconia**

The behavior of active sites was different for model compounds such as thiophene and real feed such as hydrotreated Maya crude (diluted 50:50 wt% with diesel). Treating thiophene, the HDS activity of CoMo or NiMo on alumina-zirconia was better than when the support was pure alumina or a CoMo reference catalyst. However, the HDS activity and stability of HDM activity of an alumina-zirconia supported sulfided CoMo catalyst were less than those of a NiMo reference catalyst of larger pore volume (0.358 cm<sup>3</sup>/g versus 0.328 cm<sup>3</sup>/g for the alumina-titania catalyst). These activity differences were attributed largely to the effect of pore volume. Coke or metal sulfides preferentially deposit at the pore entrance causing a 60-80% decrease in specific surface area and total pore volume. Thiophene gave higher activity with hybrid Ti-MCM-41 NiMo and NiW catalysts than with vacuum gas oil derived from Maya crude oil [214A342, 214A386].

### **Alumina-Silica**

Pilot plant evaluation of NiMo/alumina-silica catalyst hydrodesulfurizing heavy gas oil showed higher activity than NiMo/alumina catalyst. The rate of hydrodearomatization was also better. The surface area of the alumina-silica catalyst was larger than the alumina catalyst (241 m<sup>2</sup>/g vs. 207 m<sup>2</sup>/g), the pore volume larger (0.50 cc/g vs. 0.33 cc/g) and the mean pore diameter (8.3 nm vs. 6.5 nm) [214A050].

Alumina-silica binary oxide supported CoMo, PCoMo or PNiMo catalysts were less active for HDM, HDS, HDN and HDA<sub>sp</sub> of Maya heavy oil diluted with hydrodesulfurized naphtha (50 wt%) than a NiMo/ $\gamma$ -alumina reference catalyst that contained 3.73 wt% TiO<sub>2</sub>. Molybdenum atoms were



well dispersed on the CoMo catalyst but both phosphorous promoted catalysts contained crystalline  $\text{MoO}_3$  phases. The presence of the crystalline phases lowered the activity [214A480].

### **Alumina-Titania**

The favorable acid-base properties of alumina-titania make this a widely used support for hydrotreating catalysts. This material is prepared by the coprecipitation method using different precipitating agents, urea and ammonia. Using sodium aluminate and titanium chloride salts is reported to produce a support having higher pore volume and larger pore diameter than other methods [214A542].

The nature of the active sites is changed by the incorporation of  $\text{TiO}_2$  into  $\gamma$ -alumina by altering the metal-support interaction as demonstrated by HDT of diluted Maya crude oil (50 wt% diesel). The dispersion of active metals on the support may increase. Of four preparation methods of alumina-titania supported catalysts: urea hydrolysis, ammonia hydrolysis, incipient wetness impregnation and delay precipitation, urea hydrolysis produces increased initial activity for HDS, HDN and HDM. Delayed precipitation reduces activity due to a lower average pore diameter. Differences in activity may be related to variation in the pore size distribution with each preparation method. The specific surface areas of the two types of supports are comparable (200-250  $\text{m}^2/\text{g}$ ) [214A384]. In another study, this one using hydrodemetallized Maya crude diluted with diesel, concludes incorporation of titania into the alumina support of a NiMo catalyst increases the number of active sites as well as the acidity of the support. The increased acidity increases the cracking of hydrogenated asphaltenes. However, the effect of pore diameter appears more important than the number of catalytic sites [214A285].

The HDS activity for thiophene was highest for an alumina-titania weight ratio of 1:1 compared to other ratios.  $\text{MoO}_3$  on this support was five times as active as alumina supported catalyst and twice as active as titania supported catalyst. The alumina-titania oxide supports are amorphous or very poor crystalline nature. The binary oxide support resulted in more reducible  $\text{MoO}_3$  species. Other work hydrotreated Maya heavy oil diluted 50:50 by weight with hydrodesulfurized naphtha. CoMo/Alumina-titania catalyst (10 wt%  $\text{MoO}_3$ , 3 wt% CoO) with a support prepared by a combination method of urea hydrolysis and pH variation was most active for HDM, HDS and hydrodeasphalting (HDAsp) compared to supports prepared from aluminum sulfate and either titania chloride or titania isopropoxide. HDN activity was highest for the CoMo catalyst with the support prepared using titania isopropoxide. Adding 0.8 wt% phosphorous to the catalyst with the support prepared by the combination method further increased the activity for HDM, HDS and HDAsp [214A479].

Highly dispersed  $\text{TiO}_2$  (monolayer) supported on  $\gamma$ -alumina was prepared by chemical vapor deposition. Under mild operating conditions (573°K, 3 MPa), Mo/alumina-titania (10 wt%  $\text{TiO}_3$ ) was more active for 4,6-dimethylbenzothiophene hydrodesulfurization than Mo/alumina or Mo/titania. The ratio of product 1,3-dimethyl-cyclohexylbenzene to 3,3'-dimethyl-biphenyl indicated the alumina-titania support promoted the hydrogenation of the benzene ring adjacent to the sulfur atom reduced the steric hindrance of the two methyl groups. The interaction of Mo and alumina was stronger than the interaction between Mo and alumina-titania. The  $\text{TiO}_2$  coated alumina facilitated the reducibility of the Mo from the oxide to the sulfide. The number of HDS active sites probably increased with the alumina-titania support [214A416].

### **Molecular Sieves**

Saponites with only Co, Ni or Zn as octahedral ions are not stable when treated with  $\text{H}_2\text{S}$  due to the formation of bulk metal sulfides. However, saponites with only magnesium or combinations of magnesium and Co or Ni incorporated into the octahedral layer are stable. For

mixed Co-Mg saponite, the cobalt atoms at the edges of the platelets are sulfided as part of the lattice cobalt. This catalyst is highly active for HDS of thiophene, comparable to conventional alumina catalyst. Impregnating bare Mg-saponites with active HDS metals such as Co/Mo gives similar results [214A404].

Ni-Mo sulfide catalysts supported on mixtures of various ratios of  $\gamma$ -alumina and HY zeolite to vary the acidity and hence the ratio of hydrogenation to hydrocracking. The optimum balance of hydrogenation to hydrocracking activity depended upon feedstock properties. Hydrogenation activity solely functioned for HDS and hydrodearomatization of high nitrogen heavy feedstocks, typically oil sand bitumen and coal-derived oils. The dual-functional mechanism was important for hydrodenitrogenation as well as hydrocracking [214A066].

Grafting  $\text{Ti}^{+4}$  into the aluminosilicate (MCM-41) structure up to 20 wt%  $\text{TiO}_2$  maintained the hexagonal symmetry of the MCM-41 pores. With 20 wt%  $\text{TiO}_2$ , the surface area increased from 1040  $\text{m}^2/\text{g}$  up to 1138  $\text{m}^2/\text{g}$ . At greater  $\text{Ti}^{+4}$  concentrations, the hybrid supports showed loss of pore ordering and the support area decreased. With 50% Ti, surface area decreased to 948  $\text{m}^2/\text{g}$ . Adding Ti increased the surface acidity. Acidity increased further upon co-impregnation of NiMo or NiW and the surface area decreased to 174  $\text{m}^2/\text{g}$  and 67  $\text{m}^2/\text{g}$  respectively. Hydrothermal stability of the hybrid catalysts increased from about 932°F (500°C) to 1112°F (600°C) under 100% water vapor. Sulfided NiMo/Ti-MCM-41 and NiW/Ti-MCM-41 showed the highest HDS activity for heavy vacuum gas oil derived from Maya crude oil; activity was comparable to the reference catalysts. Ti-MCM-41 supported catalysts showed increased thiophene conversion. This different behavior with different types of sulfur compounds (dibenzothiophene, 2,4-dimethyldibenzothiophene) found in the vacuum gas oil compared to thiophene suggests distinct surface sites might be involved for the dibenzothiophene type compounds and thiophene. The high conversion of the 50% Ti catalysts for thiophene did not correlate with mesoporosity nor with enhanced surface acidity, but a combination of surface sites and their distribution seemed to be involved with the complex sulfur compounds of the vacuum gas oil [214A386].

Both CoMo and NiMo on siliceous MCM-41 supports showed very high activity for the HDS of dibenzothiophene (DBT). Contrary to an alumina support, the highest activity was obtained at a Co/Mo or Ni/Mo atomic ratio of 0.75. The high activity and high optimum ratio were attributed to the high surface area (685 and 660  $\text{m}^2/\text{g}$  BET surface area respectively) of this support leading to the observed high dispersion of the metals. The direct (hydrogenolysis) mechanistic pathway dominated for the CoMo while for the NiMo the hydrogenation pathway dominated. Ni accelerated the hydrogenation of a phenyl ring in the DBT. Temperature programmed reduction indicated a strong Ni-Mo interaction. The interaction between Co/MCM-41 and Mo/MCM-41 are quite different from the interactions observed with Co/alumina and Mo/alumina respectively [214A042].

### Other Supports

A catalyst composed of a composite support of alumina with 8-18 wt% carbon black impregnated with nickel (3.5 wt% NiO) and molybdenum (15 wt%  $\text{MoO}_3$ ) produced fewer sediments and less Conradson carbon formation. Yields of naphtha and kerosene increased. Pyrolysis of the alumina-carbon support in an almost inert atmosphere resulted in shaped strong particles suitable for an ebullated bed reactor. With appropriate mixing and extrusion conditions, the pore size distribution was bimodal with 11-20% of total pore volume as macropores (>1000 Å). Macropores are beneficial in removing heavy metals as demonstrated against alumina-carbon black having no macropores. The feedstock was about 80% vacuum residue (mixture of 60% Isthmus and 40% Maya crude oils) and about 20% vacuum gas oil. The Conradson carbon residue was 20.78 wt%; the metals were 346 ppm vanadium and 69 ppm nickel. The sulfur

content was 5.68 wt% while the nitrogen was 5136 ppmw. The carbon black may be promoting the relative abundance of a NiMoS species that is more active than another [214A314].

Sulfided phosphorus NiMo on alumina catalyst was found to be superior to the corresponding carbide or nitride catalysts. NiMo carbide and NiMo nitride phases gradually transformed into the NiMo sulfide phase during the precooking period [214A310]. In earlier work, Mo<sub>2</sub>N and W<sub>2</sub>N ceramic phases were more active for HDN and less active for HDS of a heavy vacuum gas oil from Maya crude oil than a sulfided CoMo on alumina catalyst under similar operating conditions. Hydrogenation activity and stability of the mixtures was superior to the CoMo catalyst [214A248].

Microwave radiation used to intercalate Al- and Ti- polyoxocations to form pillared interlayered clays from natural Durango, Mexico, montmorillonite significantly reduced preparation aging time by about a 100 fold decrease and increased the total yield per batch compared to conventional preparation methods. The shorter contact time with the acidic solution limits the migration of structural aluminum and titanium species from the clay and should lead to less blockage of pores. Surface sites were primarily medium to strong Lewis acid sites. CoMo/ $\gamma$ -alumina prepared by the microwave method showed HDS activity at least comparable, and sometimes superior to, conventionally prepared pillared clays and particularly to a reference CoMo/ $\gamma$ -alumina catalyst [214A280].

## HDM Catalysis

Nickel and vanadium in heavy oils typically deposit on hydrotreating catalysts as sulfides (Ni<sub>3</sub>S<sub>2</sub>, V<sub>3</sub>S<sub>2</sub> and V<sub>3</sub>S<sub>4</sub>) typically having crystal size of 2-30 nm and poison the catalyst. Calcium, magnesium and iron also may deposit on the exterior surface of the catalyst [214A487]. Model simulation indicates maximum metal capacity of a HDM catalyst is highly influenced by the processing conditions and feedstock [214A352]. It is well known that HDM is diffusion controlled. An optimum balance exists between hydrodemetallization activity and diffusion properties. A high ratio of the intrinsic hydrodemetallization activity to the asphaltene diffusion into and through the catalyst pore indicates the metals will be removed at the pore mouth, over time restricting diffusion of feed into the pore and plugging it. Operation at too hot a temperature during the initial, high activity phase of the catalyst cycle can cause excessive pore mouth blockage as can a too high acidity catalyst or a feedstock with highly reactive metal contaminants. The high activity main HDS and HDN catalysts have smaller average pore diameters than hydrodemetallization catalysts and a sharper pore size distribution and high surface area. These catalysts are more susceptible to pore mouth plugging but are protected by the guard bed catalyst, which has a large pore diameter. The laboratory hydrodemetallization (HDM) of a 50:50 weight blend of Maya crude oil and naphtha showed the following HDM activity for sulfided alumina catalysts: CoMo > CoW > NiMo > NiW [214A155, 214A481, 214A487].

A search for cheaper HDM guard bed catalysts identified two candidate catalyst-adsorbents: reduced 7.4% Co/silica and sulfided Co(3.4%)Ni(4.1%)/alumina. Their advantage is they do not contain expensive molybdenum [214A069].

In the HDM by a CoMo/alumina-titania catalyst of Maya heavy crude oil diluted 50:50 by weight with hydrotreated naphtha, the rate of vanadium removal is much higher than nickel removal. Vanadium atoms are linked to an oxygen atom that extends perpendicularly above the asphaltene plane. This oxygen atom forms a strong bond with the catalyst surface that increases the rate of vanadium removal. Nickel does not have this oxygen atom [214A479].

A HDM catalyst prepared with a smaller amount of effective metals and lower catalytic activity than conventional catalysts resulted in prolonged life under deep desulfurization of atmospheric residue (product sulfur content below 0.3 wt%) when followed by a bed of HDS

catalyst. Life was prolonged by the preferential decomposition of maltenes on the low activity HDM catalyst provided the guard bed temperature was maintained low (680-716°F, 360-380°C) and continuously controlled from the inlet of the guard bed reactor to the outlet of the main reactor. Rapid coking resulted when the guard bed reactor temperature was a constant 770°F (410°C) to rapidly decompose the maltenes and asphaltenes to increase the rate of metals removal in the guard bed. Separate decomposition of the maltenes and asphaltenes was concluded to be important for continuous hydrotreating of atmospheric residue [214A477].

The deactivation of the low activity HDM catalyst (25 vol% of total HDM and HDS catalyst) in a guard reactor and HDM catalyst (15%) followed by HDS catalyst (60%) in the main reactor is reduced by operating the guard reactor at a constant low temperature. The maltenes preferentially decompose and deposit metals (about half the feed metals) on the HDM catalyst in the guard reactor. Asphaltenes did not react in the guard reactor at low temperature. The main reactor operated with increasing axial temperature gradient sufficient to produce 0.1 wt% sulfur product up to 4200 H and then to produce 0.2 wt% sulfur until the end of run (7000 H). In the main reactor, asphaltenes gradually decompose and deposit metals (and coke) on both the HDM and HDS catalysts. With only HDS catalyst, the 770°F (410°C) maximum temperature was reached after 1400 H [214A320]. Catalyst deactivation is further discussed later in this section.

### **Hydrodesulfurization**

The laboratory hydrodesulfurization (HDS) of a 50:50 weight blend of Maya crude oil and naphtha showed the following HDS activity for sulfided alumina catalysts: NiMo > NiW > CoMo = CoW [214A481].

### **Hydrodenitrogenation**

In the HDN of nitrogen heterocycles, nickel associated sulfur vacancies in the Ni-Mo-S phase are the active sites for hydrogenation of the aromatic rings while Mo sites promote the C-N cleavage reactions. Bronsted acid sites are reversibly generated by adsorption and dissociation of H<sub>2</sub>S on Mo-associated sulfur vacancies. The generation of the Bronsted acid sites from Mo-S vacancies strongly depends upon temperature and H<sub>2</sub>S-to-H<sub>2</sub> ratios [214A404].

The laboratory hydrodenitrogenation (HDN) of a 50:50 weight blend of Maya crude oil and naphtha showed the following HDN activity for sulfided alumina catalysts: NiMo > NiW = CoMo > CoW [214A481].

### **Commercial Catalysts**

Demand for hydrotreating catalysts is forecast to grow at 4.9%/y to \$1.2 billion/y in 2011, faster than the growth in FCC catalysts, 2.6-2.7%/y to \$1.0 billion/y in 2011 [214A526]. Demand is driven by three major factors:

1. The final phase-in of low sulfur fuel regulations in developed countries plus stricter regulations in developing countries like China, India and Mexico.
2. The refining of increasingly higher sulfur crude oil is raising the consumption of hydroprocessing catalyst per barrel to compensate for the higher levels of impurities. Upgrading tar sands in an ebullating bed HDT requires up to 20-30 times more catalyst to produce ultra low sulfur diesel fuel than conventional HDT of lower sulfur crude oils [214A528]. Development of higher activity catalysts counters this trend and allows a larger percentage of heavier feedstocks to be HDT without decreasing unit throughput.
3. The higher consumption of fuels.

Growth will be heterogeneous with gains primarily in Asia-Pacific region, mainly China, and the Middle East as new refining capacity is brought online. In response, catalyst manufacturers announced capacity expansions in the U.S. and planned additional capacity in Asia and Europe [214A527, 214528].

Commercial hydrotreating catalysts are included in the biannual Oil Gas Journal's "OGJ international refining catalyst compilation". The recent compilation lists over 100 catalysts applicable for VGO and heavier feedstocks. The listing includes the primary differentiating characteristics of the catalyst, type of feedstock and product applications and usually the form. For some catalysts, the compacted bulk density, support and active agents are also provided. The catalyst vendors offering catalysts applicable for heavy oils are listed in Table 5.32 [214A580]. Recent developments in the catalyst industry are summarized in "PTQ Catalysis roundtable" discussions published in PTQ Catalysis (supplement to PTQ) [214A529].

**Table 5.32**  
**HEAVY OIL HYDROTREATING CATALYST VENDORS**

Advanced Refining Technologies LLC	Criterion Catalysts & Technologies
Albemarle Catalysts & Nippon Ketjen Co. Ltd.	Haldor Topsoe AS
Axens	Ripp-Sinopec, Sinopec Catalyst Co.
Catalysts & Chemicals Industries Co. Ltd.	UOP LLC
Chevron Lummus Global LLC	

Source: 214A580

The selection of hydrotreating catalysts for heavy oils, a more viscous and higher boiling feed with lower H/C ratio than lighter feedstocks, requires special attention to the pore size and distribution, pore volume and size and shape of the particles for maximum utilization of the catalyst as discussed earlier in this section. Meso- and macropores increase catalyst utilization. Diffusion of large metal-containing molecules through the catalyst pores is the rate limiting factor in HDM. There is an optimum pore size for heavy feeds. With too small pores, the metal deposits at the pore mouth, blocking further diffusion to the interior active sites. With too large pores, metal deposition is highest at the mouth (which remains open) and decreases along the pore length. The activity decreases due to the decrease in surface area. There is an optimal combination of average pore diameter, surface area and activity for HDS, which depends upon the properties of the heavy feed. Bimodal pore size catalysts have improved metals penetration compared to unimodal catalysts. The higher the pore volume provides higher the metal storage capacity [214A469].

The type of reactor as well as the feed properties affect the optimal particle size and shape. The size and shape of catalyst particles (Table 5.33) is important, especially size in ebullating bed reactors. Spheres are more abrasion resistant than cylinders. Ebullating beds are designed with ample free space between particles for entrained solids to pass through the bed without increasing the pressure drop. This enables smaller catalyst particles to be used, for example 1/32 in. extrudates, which decreases diffusion limitations and considerably increases the reaction rate. In fixed bed reactors, proper size and shape of the catalyst can overcome pressure drop limitations and to some extent improve the catalyst stability. Rings are favored for greater surface area and improved diffusion. Trilobe and pentalobe extrudates provide higher external surface area to improve accessibility to the catalyst interior and also have lower pressure drop than cylinders [214A469, 214A487].

**Table 5.33**  
**COMMERCIAL CATALYST SHAPE CHARACTERISTICS**

<u>Shape</u>	<u>Size (diameter, inches)</u>	<u>Use</u>
Cylinder	1/8, 1/10, 1/16, 1/20	General use.
Cylinder ring	3/16, 3/32, 1/8 x 1/16	Lower pressure drop and less plugging. Used as top layer of beds or for entire bed.
Trilobe and pentalobe	1/8, 1/10, 1/16, 1/20	Overcome diffusion limitations by reducing diffusion path without increasing pressure drop. Since they pack less densely, the total mass of catalyst charged is reduced, which must be balanced by improved activity.
Extrudate	1/25, 1/32	For ebullating bed.

Source: 214A525

Hydrotreating is often conducted with a series of catalysts, each chosen for a particular role. As discussed above, guard bed catalysts have large pore diameter, large voidage and, of course, excellent ability to promote demetallization. HDS, HDN and HDA catalysts are evaluated mostly on the basis of performance for the particular feedstock in meeting the most critical specification of the HDT product. In fixed bed hydrotreaters, the first stage (guard bed) is typically followed by a catalyst with good HDS activity along with fair to good HDN activity. The catalyst contains some large pores to handle residual metals from the first stage but more small pores than the guard catalyst. As a result, surface area is higher (180 m<sup>2</sup>/g versus 150 m<sup>2</sup>/g). Activity of the third stage is similar to the second stage with further HDS and HDN activity. Ebullating bed reactors can use large pore demetallization catalyst followed by second stage high activity HDS and HDN catalysts. In general, CoMo/alumina catalysts are preferred for HDS, NiMo/alumina catalysts are better HDN and HDM catalysts, and NiW/alumina hydrogenate aromatics [214A525].

The most likely cause of guard reactor fouling is by precipitated asphaltenes or tramp iron in the feed. To reduce fouling of the guard bed catalyst, the catalyst at the top section of the bed is graded. Criterion achieves significant improvements over the standard grading scheme by tailoring the grading scheme to the characteristics of the feedstock. Grading layers spread the fines over a larger depth of packed bed as occurs in deep-bed filtration [214A020].

### **New Catalysts**

A new catalyst with prolonged life for the hydrodemetallization of atmospheric residue prior to deep hydrodesulfurization (sulfur less than 0.3 wt%) is characterized by its low catalytic activity. The catalyst contains 0.7 wt% nickel, 3.3 wt% MoO<sub>3</sub> and 4.0 wt% vanadium on a 1.15 mm trilobe shaped support with a pore diameter of 14.0 nm. Vanadium has weak hydrotreating activity for atmospheric residue. The HDS catalyst is a 1.0 wt% cobalt, 1.5 wt% nickel, 12.0 wt% MoO<sub>3</sub>, 1.15 mm trilobe alumina catalyst with medium pores (10.4 nm).

Mo carbide/alumina catalysts activity for HDN of carbazole was reported [214A406].

### **CATALYST DEACTIVATION**

Rapid catalyst deactivation is a major operational and economic problem in hydrotreating of heavy oils. Under favorable reaction conditions coking occurs at relatively low overall rates. The main mechanisms for catalyst deactivation of hydrotreating catalysts are the formation of coke and metal deposits on the catalyst. Deactivation by poisoning (Table 5.34), fouling, aging or

sintering can occur but are relatively infrequent. These general mechanisms of catalyst deactivation are reviewed by Bartholomew [214A456]. A general discussion of catalyst decay by Birtill tells how to use plant performance data and spent catalyst characterizations to construct simple decay models. A holistic approach from laboratory to plant scale is required. Although a detailed study of decay kinetics usually requires using gradient less reactors, single tube, plug flow reactors can provide approximate data useful for insight into decay kinetics [214A457].

**Table 5.34**  
**ORIGIN AND CONSEQUENCES OF IMPURITIES IN HEAVY OILS AND THEIR EFFECTS ON**  
**HYDROTREATING CATALYSTS**

<u>Impurity</u>	<u>Source</u>	<u>Main Cut</u>	<u>Catalyst Poison</u>	<u>Maximum Spent Catalyst Content, wt%</u>
Ni, V	Crude	Distillates, Residues	Strong, deposit inside catalyst and plugging	10 30-40
As	Crude	All	Strong, deposit at top of reactor	0.2-2
NaCl	Crude	Residues	Strong, deposit at top of reactor, generates pressure loss	1.0
Fe	Crude and corrosion	All	Slight, deposit at top of reactor, generates pressure drop	1
Cl	Solvents and slops	---	Very slight, promotes coking and corrosion	0.1-0.5
CO/CO <sub>2</sub>	Hydrogen makeup	All	Very slight, formation of carbonyl Ni, Co, Fe at low temperature	<0.05% vol

Source: 214A044

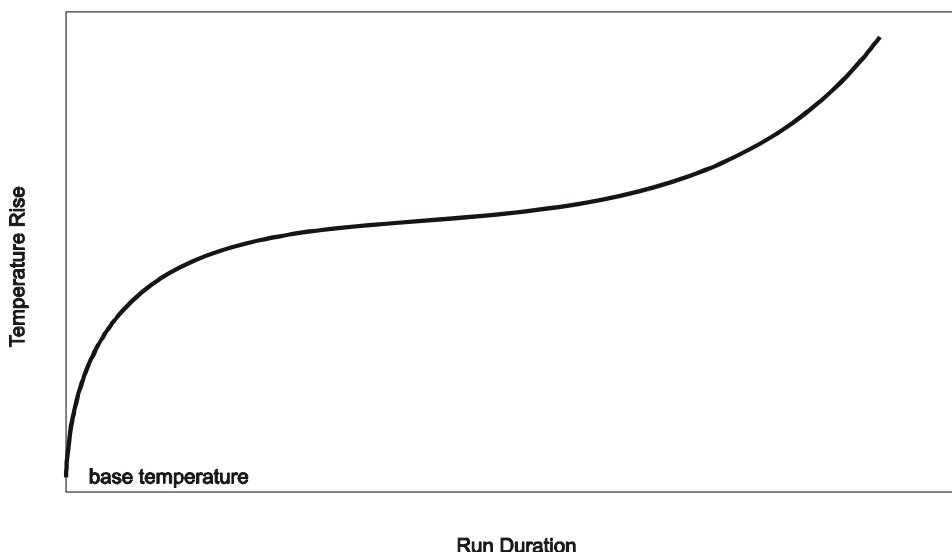
The yield of coke during hydrotreating is a function of the feedstock, catalyst and operating conditions. Heavy feedstocks deactivate by coke and metals deposition to a greater extent than light oil feedstocks and follow a different trend [214A541]. Catalysts for heavy oils need sufficient active hydrogen on the catalyst surface to prevent aromatics and heterocyclic compounds from forming higher molecular weight species. High hydrogen pressure in the presence of a catalyst with good hydrogenation activity reduces coke formation by suppressing polymerization and by hydrogenating adsorbed species. Deactivation is compensated by gradually raising the reaction temperature. Catalyst activity with time on stream typically follows an S-shaped curve (Figure 5.7). This temperature-time plot shows deactivation occurs in three stages:

1. An initial rapid activity decline necessitates a sharp temperature rise.
2. A relatively long period of quasi-steady state is characterized by a slow and gradual temperature increase (activity decline) leading gradually to the third stage.
3. Near the end of run, rapid deactivation again occurs. The temperature is risen linearly to the maximum operating temperature (a complete loss of activity).

The mechanism of the first stage, initial rapid activity decrease, is the formation of coke. The gradual accumulation of metal deposited at the pore mouth causes the further loss in activity

during the second stage. In the third stage, enough catalyst is already deactivated that still hotter temperature is required to maintain conversion. These high temperatures accelerate both coke formation and metals deposition. Diffusion limits caused by constricted or blocked pores due to metal deposition finally stop catalytic activity [214A241, 214A447, 214A460, 214A461, 214A465]. A simple one dimensional homogeneous plug flow model for ARDS unit includes the three stages of catalyst deactivation. The model parameters are: temperature, fluid velocity, reaction rate constant, catalyst combination, catalyst bed length and the feed concentrations for sulfur, metals and asphaltenes [214A343].

**Figure 5.7**  
**TYPICAL S-SHAPED HYDROTREATER DEACTIVATION CURVE [214A460]**



Source: 214A460

Hydrothermal noncatalytic deactivation reactions are important after catalytic activity has been substantially reduced or at hotter reaction temperatures. When both conditions occur, hydrothermal noncatalytic reactions are more pronounced. The most important thermal reactions include breakage of C-C and C-H bonds, breakage of bonds with metals and heteroatoms, aromatization, alkylation, condensation and hydrogenation-dehydrogenation. A model of hydrotreater performance that incorporates the hydrothermal noncatalytic reactions shows an extended period of substantial sulfur removal arises due to the hydrothermal noncatalytic reactions under conditions of constant sulfur operation [214A352, 214A432].

Detailed characterization of the spent catalysts from an industrial fixed-bed residue hydroprocessing unit showed the concentration of nickel plus vanadium on catalysts from the four reactor fixed bed unit decreased from the first reactor to the last reactor. The concentration of coke showed the opposite trend. The front-end reactors had more metals than coke. Losses of surface area and pore volume were higher for the front-end reactors and caused by metal deposits. Vanadium distribution across catalyst pellets was higher and more uniform in the first reactor than the others. Pellet nickel distribution was more uniform than that of vanadium for all four reactors. Coke deposits were more aromatic, and the dominant cause of deactivation, in the back-end reactors [214A276].



Spent NiMo catalysts from an industrial ebullating bed reactor contained a mixture of highly fouled and partly fouled particles. The heavily fouled catalyst had substantially more vanadium (14 wt%) than the lightly fouled particles (4.4 wt%) but the carbon content did not differ appreciably between the two types of particles. The particle length, which affects the bed uniformity and mixing pattern, was considerably altered. The mixed spent particles contained considerably more small particles (25 wt% < 1.5 mm in length) than the fresh catalyst (1%); the heavily fouled particles had the highest concentration (40 wt%) and the lightly fouled, the least (14%). Changes in the ebullated bed catalyst physical and mechanical properties caused by the stress and attrition of the process along with coke and metal deposits caused the catalyst deactivation [214A276].

The influence of multiphase (high and low density liquids and vapor phases) in trickle bed reactors on coke deposition is an important factor that is beginning to be researched. The second liquid phase originates either from dilution oil or as a product of hydrotreating. For Athabasca vacuum bottoms the liquid-liquid region extends from approximately 20% to 50% vacuum bottoms. Phase behavior is complex. Within a multiphase region, the absolute and relative amounts of the phases changes with pressure at fixed composition. Coke deposition is greater with the high density liquid phase than with the low density liquid. Hydrogen solubility is greater in the light liquid phase, which reduces the coke formation. Dense phase gas phase feed is preferential over liquid phases for reducing coke formation. Transfer of feed to the vapor phase as pressure is increased has a greater impact on coke reduction than shifting the feed from the dense liquid to the light liquid phase or the impact of pressure on hydrogen solubility in the liquid phases. Over dilution of feeds with lighter oils or significant production of light oil can lead to the whole bed or the lower part of the bed being subject to dense liquid phase coking. The formation of only the dense liquid phase region, although not likely in industrial hydrotreaters, would require significant dilution. The presence of even a small fraction of dense liquid phase affects the flow regime and raises the coke deposition, shortening catalyst life. The common practice of diluting heavy feeds during operating problems may exacerbate coke deposition [214A354].

### Catalyst Effects

The rate limiting step of HDM is the diffusion of large molecules into and out of the catalyst pores. Bulk diffusion occurs in macropores (mean pore radius larger than 100 Å). Knudsen diffusion predominates in the micropores (less than 100 Å mean radius). Diffusion becomes increasingly restricted by pore mouth blocking by metal deposits accumulating with catalyst age. A mathematical model of catalyst deactivation during heavy oil hydrotreating has been applied to catalysts of different pore structures. Simulations of the HDM reaction predicts catalyst life times of 5 to 15 months when comparing three pore structure distributions: macropore, random pore and micropore. (The macropore and micropore cases are extremes of the random pore case.) Activity decays linearly for both the macropore and random pore cases but nonlinearly for the micropore case. Large pore diameters appear to be more promising for long life heavy oil hydrotreating catalysts since the large molecules encounter less diffusion resistance than in smaller pores [214A378]. However, large diameter pores have less specific surface area than small pores. Comparison of pilot plant spent and fresh tetralobe commercial NiMo catalyst (Table 5.35) shows an 88% reduction in pores greater than 500 Å and a 70% reduction in 250-500 Å pores. The pores of 100 to 250 Å are little changed (8% reduction) while pores less than 100 Å have increased over 3 times due to the creation of pores of this size by coke reducing the radius of larger pores [214A241].

**Table 5.35**  
**PROPERTIES OF FRESH AND SPENT HYDROTREATING CATALYST (PILOT PLANT)**

	<u>Fresh Catalyst</u>	<u>Spent Catalyst</u>
Specific surface area, m <sup>2</sup> /g	175	88
Pore volume, cm <sup>3</sup> /g	0.56	0.33
Bulk density, g/cm <sup>3</sup>	0.72	1.041
Mean pore diameter, Å	127	152
Pore size distribution, vol%		
>500 Å	6.1	0.7
250-500 Å	15.0	4.5
100-250 Å	69.1	63.7
<100 Å	9.8	31.1
Composition, wt%		
Molybdenum	10.66	5.56
Nickel	2.88	2.64
Sodium	0.041	0.13
Vanadium	0	4.41
Iron	0	0.082
Carbon	0	18.3
Sulfur	0	8.56

Source: 214A241

Coked catalyst pellets appear to contain narrower pores than when fresh due to preferential coke deposition in larger pores than the smaller ones. Adsorption hysteresis curves suggest the coked pellets retain the shape similar to the fresh pellets and that pore narrowing rather than pore mouth plugging occurs from coke deposition [214A354].

Coke produced by a back-end HDN catalyst was higher than the upstream HDM (Mo/alumina) and HDS (NiMo/alumina) catalysts. The HDN catalyst contained Ni, Mo and an additional promoter on alumina. The higher coke production was attributed to the catalyst's high acidity, small pores and high concentration of promoters [214A325].

### Initial Deactivation

Rapid coke buildup on the catalyst starts as soon as feed is introduced, reaching as high as 10 wt% within 3 hours in a fixed bed laboratory reactor hydrotreating vacuum gas oil. The coke levels off, reaching an equilibrium within 24 hours. During the first three hours, coke predominately deposits in the narrow pores (<50 Å) of a commercial NiMo/γ-alumina catalyst decreasing the surface area 40%. The HDN activity is more rapidly deactivated by the initial coke than the HDS function [214A472]. An analysis shows the initial coke is deposited on the support surface and not on the active metal surface phase since no carbon was deposited on the metal. Part of the nitrogen is associated with the active metal sulfide phase [214A428].

A NiMo/γ-alumina bimodal macroporous, spherical hydrodemetallization catalyst similarly rapidly coked (11 wt% carbon after 6 hours and 14 wt% at almost steady state after 240 hours) at

low pressure (8 MPa) to favor coking over demetallization. Carbon and vanadium from hydrotreating Safanyia atmospheric residue feed were well distributed inside the catalyst grain. Three-dimensional amorphous carbon was the major type of carbon deposit [214A462].

Conversion decreased in the order: HDAs > HDV  $\geq$  HDS > HDN > HDRe  $\geq$  HDNi showing deasphaltenization, HDV and HDS were easier than HDN and HDNi. The deactivation of HDS appeared exponential with time-on-stream. The other reactions deactivated similarly. Some carbon species deactivated both the hydrogenation and HDS functions, changing the selectivity with carbon content of vanadium free catalyst, suggesting some species are on the active surface phase. Deactivation by vanadium was attributed to destruction of the NiMoS phase and the loss of the promoter effect of the nickel on the MoS<sub>2</sub> phase. A small amount of vanadium well dispersed inside the catalyst grain was found to be more deactivating than a large amount of carbon [214A462].

Comparing deactivation of a HDM catalyst with a HDS catalyst, another study showed the HDS catalyst lost more surface area and pore volume than the HDM catalyst due to the narrower pore volume of the HDS catalyst. Metals and coke were more uniformly distributed in the HDM catalyst. The initial coke on the HDM catalyst became more aromatic and condensed with increasing operating severity. The higher hydrogenation activity of the HDS catalyst formed less aromatic coke having a lower condensation, especially above 752°F (400°C), than the unpromoted HDM catalyst [214A324].

A further study of initial coke deposition with unpromoted Mo/alumina HDM catalyst treating a Kuwaiti atmospheric residue feedstock showed initial coke formation occurred in three phases. (1.) During the first hour the catalyst experienced fast buildup of coke (33% carbon on catalyst) consisting of few condensed ring aromatics having shorter but heavily branched alkyl groups. (2.) From 1-12 hours, carbon deposition slowed (33-39%). Aromatic carbon and dealkylation/hydrogenation of aromatic rings occurred. (3.) Steady state carbon deposition was obtained (12-240 hours, 39-50%). The existing coke transformed into hydrogen rich aromatics and CH<sub>3</sub> deficient aliphatics. HDM was still high and prevented the coke from becoming hydrogen depleted. During the remainder of the catalyst run, the coke converts into hydrogen deficient, highly condensed polyaromatics coke containing a high percentage of heteroatoms [214A120]. Initial catalyst deactivation was caused by asphaltenes adsorbed on acidic sites of the support, plugging small pores with considerable loss of surface area. Simultaneously, NH<sub>x</sub> species were adsorbed on and poisoned co-ordinatively unsaturated catalytic sites of the active metal phase. From the start of the run, the initial coke exclusively deposited on the support. Refractory coke strongly adsorbed on the support surface. A more reactive soft coke also formed on the support. The active metal sulfide phase initially remained coke-free, but nitrogen compounds adsorbed on the active metal sulfide sites. Heteroatoms tended to concentrate in the refractory coke rather than in the soft coke. After 120 hours, most of the coke had converted into tetrahydrofuran insoluble coke that still contained a considerable amount of aliphatic hydrocarbons [214A473].

### Feedstock Effects

The distribution of the metals between porphyrin and non-porphyrin type structures and the nature of the coke deposits depend upon the origin of the feedstock. Each feed is expected to show different deactivation patterns [214A241].

In an industrial system consisting of a series of catalysts in the order HDM, HDM/HDS and HDS/HDN treating a straight run atmospheric residue feedstock, the hydrotreated feeds generated significantly more coke than the straight run feed. This coke is less aromatic than that from atmospheric residue. These effects of hydrogenated or partially hydrogenated feeds are due to the bulky aromatic structure of the asphaltenes following HDM along with a high H/C ratio of

the feed promoting phase separation-precipitation-coke formation. A relationship between the degree of condensation or degree of alkyl substitution of the coke and feedstock is not found [214A325].

Asphaltenes of residue feedstocks cause the rapid initial coke deposition as shown in tests with Athabasca bitumen vacuum residue and its narrow fractions using a commercial NiMo/γ-alumina catalyst. A high tendency of asphaltenes is to adsorb onto the catalyst surface blocking the pores and preventing other molecules from contacting the active sites. Asphaltenes interact with the catalyst through the basic nitrogen. Both on the catalyst and in the reactor, the asphaltene-rich fraction produced higher coke yields and coke with a lower H/C ratio than the lighter fractions. HDS activity of the spent catalyst decreased monotonically with increasing carbon on the catalyst. A portion of the coke on catalyst was mobile and reactive at the condition used (824°F, 440°C; 1500 psig, 10.3 MPa). The mobile carbon significantly impacted the observed activity [214A447, 214A461]. Other work later suggested nitrogen containing asphaltene fractions concentrate on the catalyst during the initial period and the nitrogen content decreases at longer times on stream [214A199].

Petroleum resid contains high concentrations of natural hydrogen donors (Table 5.36) and more are generated during thermolysis from substituted naphthenes in the resid. Gould and Wiehe discovered the asphaltene portion of petroleum resid contains approximately the same concentration of natural donor hydrogen as the whole resid, but the asphaltene fraction contains the most reactive donors (Table 5.36). Of the hydrogens in Arabian Heavy asphaltenes, 25% are on saturated rings fused to aromatic rings (a typical structure of hydrogen donors). For Hondo resid, 32% of the hydrogens are in natural hydrogen donors. The significance of natural hydrogen donors during thermal conversion is described by Gould and Wiehe: "Since the hydrogen donors in asphaltenes are more active than those in the other resid fractions, the fast depletion of donor hydrogen in asphaltenes is likely the cause of asphaltenes forming higher molecular weight coke when in a separate phase than the other resid fractions. Not only does hydrogen donation terminate free radicals but it can increase the ring size of the aromatic core in the asphaltene. Since the asphaltene core cannot be converted in thermal conversion, one would have preferred asphaltenes to have the least donor hydrogen of all the fractions." [214A555].

**Table 5.36**  
**CONCENTRATION AND RELATIVE REACTIVITY OF MODEL COMPOUNDS AND RESIDUES**

	<b>Donor H<sup>a</sup>, g/100 g sample</b>	<b>Donor H, % of Total H</b>	<b>Hydrogen Donor Relative activity</b>
Tetralin	3.0	33	1.0
1,2,3,4-Tetrahydroquinoline	3.0	33	50
9,10-Dihydroanthracene	1.1	17	28
9,10-Dihydrophenanthrene	1.1	17	0.63
Deaclin	0	0	0
Brent Atmospheric Resid	1.2	11	---
Brent Vacuum Resid	1.4	13	5.7
Dan-Gorm Atmospheric Resid	1.6	14	6.0
Hondo Vacuum Resid	2.9	30	7.9
Hondo Asphaltenes	2.7	32	---

**Table 5.36 (Concluded)**  
**CONCENTRATION AND RELATIVE REACTIVITY OF MODEL COMPOUNDS AND RESIDUES**

	<b>Donor H<sup>a</sup>, g/100 g sample</b>	<b>Donor H, % of Total H</b>	<b>Hydrogen Donor Relative activity</b>
Arabian Heavy Vacuum Resid	1.9	19	2.7
Saturates	1.1	9.6	1.2
Aromatics	2.1	19	2.0
Resins	2.0	21	2.9
Asphaltenes	1.9	25	4.2
Arabian Light Resid	1.6	16	5.4

Source: 214A555

<sup>a</sup> By dehydrogenation by 2-3-dichloro-5,6-dicyano-p-benzoquinone.

The asphaltene quality appears to be more important in catalyst deactivation than the asphaltene content of the feed. The H/C molar ratio of the coke on spent catalysts is strongly related to the quality of the asphaltenes in the product oil as measured by aromatic character. The feed asphaltene content does not correlate well with coke deposition. Increased aromaticity and ring condensation increases coke formation. Each feed asphaltene sub-fraction yields different amounts of coke. The polar fractions show a high propensity to adsorb on the catalyst surface, producing increasing yields of coke: acids < bases < amphoteric. The solvent power of the oil media surrounding the asphaltene micelle is also an important factor in coke formation. Partial hydrogenation of maltenes reduces their solubility power during heavy oil hydrotreating. One relative solubility index is defined as the ratio of the H/C ratio of the asphaltenes to the H/C ratio of the product oil (maltenes). The trends of the relative solubility index and coke quality are independent of the type of catalyst and the operating severity. The index can be used to select better catalysts for atmospheric residue hydrotreating. The scission of alkyl chains decreases steric hindrance, facilitating asphaltene adsorption. Thermal cracking decreases asphaltene size, allowing more asphaltene to penetrate the pores, react and potentially deactivate the metal sites. As discussed above, large pores facilitate the diffusion of large molecules for hydrotreating [214A447, 214A451].

### Aging

Reacting a Maya heavy fraction (81.5% over 650°F, 343°C, and 18.5% light gas oil, 383-650°F, 195-343°C) over a commercial NiMo/γ-alumina hydrotreating catalyst (tested as a guard bed catalyst in a composite bed) at high pressure (about 1450 psig, 10 MPa) in a fixed bed reactor for 308 days showed initial rapid carbon deposition (as high as 16 wt% of fresh catalyst within 100 hours). The coke tended to level off at an equilibrium value of 23.8 wt% carbon based on fresh catalyst between 46 and 88 days. Carbon decreased to 15 wt% from days 88 through 129 and did not significantly change further, indicating complete deactivation. Aromaticity increased with time on stream as reversible aliphatic carbon is removed from the aged catalyst [214A199].

Hydrotreating Maya crude oil with a commercial tetralobe (2.54 mm diameter) NiMo catalyst at isothermal conditions (752°F, 400°C; 70 kg/cm<sup>2</sup> total pressure, 1.0 h<sup>-1</sup> LHSV) in a down flow reactor showed different time on stream rates of deposition of vanadium and nickel. After about 200 hours, nickel content of the catalyst reached a constant value while the vanadium

concentration continued to rise. This was attributed to different porphyrin type structures between the nickel and vanadium: the vanadium has a perpendicularly linked oxygen atom that forms a strong bond with the catalyst while the nickel does not have this oxygen link. An alternative explanation was the rate of nickel deposition was strongly influenced by the formation of vanadium deposits since the initial vanadium content was more than 5 times higher than the nickel (299 wppm and 55 wppm respectively). The vanadium profile across the tetralobe catalyst showed higher vanadium content on the external surface especially on the lobes of the catalyst [214A241].

A study of a commercial NiMo/ $\gamma$ -alumina catalyst specially developed for HDM pretreatment with low HDS activity of residual oils to reduce metals, asphaltenes and Conradson carbon showed deactivation by metals throughout the 120 days on stream. Metal retention capacity was high (57 wt% of the fresh catalyst). The metals were deposited as sulfides, the crystalline phases identified as  $V_{5.45}S_8$ ,  $V_{2.14}Fe_{0.75}S_4$  and  $V_2NiS_4$ . High concentrations of vanadium were found at the edges while nickel was more uniformly deposited. Removing vanadium from the oil becomes diffusion rate limited, which results in less deep vanadium penetration into the catalyst pellet. Vanadium removing guard bed catalysts should have wide pore diameters [214A458].

Coke and metals also deposited rather rapidly on bimodal CoMo/ $\gamma$ -alumina catalyst in a three-stage ebullating bed unit reactor hydrotreating vacuum residue. The mesopores of catalyst from the first stage initially filled with carbon and metals, but after the first day, coke increased only slowly. Coke levels of the third-stage catalyst were higher than in the first-stage and increased logarithmically with age, picking up relatively little metals over the first 21 days. End-of-run samples (120 days) showed an extensive network of mesoporous channels associated with the equilibrium coke. With increasing time on stream, coke of both the first and third stage catalysts became more hydrogen (decreasing H:C molar ratios, increasing aromaticity) and sulfur deficient. Sulfur in the coke appeared associated with the upper coke layers. Nitrogen may adsorb preferentially during the initial coke laydown, presumably on the acid sites, since the initial coke N:C ratios were high compared to the feedstock in both the first and third stage samples. With age, the N:C ratios decreased in the third-stage samples but remained relatively constant in the first-stage samples. Two types of adsorbed nitrogen species were detected in the coke:  $NH_x$  species associated with the CoMoS phase and a more strongly adsorbed nitrogen associated with the coke. HDS activity was less sensitive to coke than HDN and hydrogenation activities. Initial metal deposits more strongly affected the loss of HDS activity than HDN and hydrogenation activities, indicating different sites are involved in these reactions [214A478].

Following an initial 11.7 day deactivation period when treating Maya crude oil over a commercial NiMo catalyst, step changes in reactor temperature, the first from 752°F (400°C) to 788°F (420°C); the second after 29 days from 788°F (420°C) to 806°F (430°C), did not result in another period of carbon deposition as occurred during the first hours of the run. Instead, the deposited carbon on the catalyst was essentially constant (18.3 and 18.5 wt% respectively) following the step increases in temperature. This demonstrated that coke was only deposited during the first hours of operation. Following each step change, throughout the run metals deposited on the catalyst continued the same linear increase with time on stream established during the first period. Immediately after both step changes, the product oil's sulfur, vanadium, nickel, Ramsbottom carbon and asphaltene content all decreased. However, within 50 hours of the second step change the sulfur, vanadium and Ramsbottom carbon increased to levels occurring just before the step change and proceeded to increase more rapidly than over the proceeding period. Nickel and asphaltene content also quickly returned to previous concentrations but then continued to increase. The nickel in the oil increased during the third period at about the same rate as the second period. The asphaltene content increased a lesser rate. The higher amounts of contaminants remaining in the product oil during the third stage indicated first the 18°F (10°C) temperature increase was not high enough to compensate for the

deactivation of the catalyst. Secondly, deactivation by metals was becoming more significant. Deactivation rates also increased due to the exothermality of the reactions at the hotter temperature. The longer the time on stream, the higher the loss of the catalyst's specific surface area and pore volume [214A257].

Aging tests of catalysts in a two-stage residue desulfurization process (HDM followed by HDS) treating Arabian Light atmospheric residue feedstock showed the HDS catalyst was deactivated by coke deposition rather than metals passing through the HDM stage. Asphaltene aromaticity of the feed was found to be a good index for HDS catalyst deactivation. The catalyst fouling rate was strongly affected by the combination of asphaltene aromaticity of the HDS feed and the HDS reaction temperature [214A476].

The coke deposits can be characterized by solubility into soft coke and hard coke. Soft coke is extracted by dichloromethane whereas the hard coke is insoluble. The soft coke extracted from spent NiMo/ $\gamma$ -alumina and CoMo/ $\gamma$ -alumina hydrotreating catalysts is mostly alkylated mono-aromatics, di-aromatics and small amounts of polyaromatics. The hard coke from the hydrotreating catalysts is relatively high in aliphatics [214A321].

On atmospheric residue desulfurization catalysts, the yield of soluble coke depends upon the type of feed, type of catalyst and decreases with increasing time-on-stream [214A428].

In a continuous flow reactor, both carbon and metals deposit on the catalyst with carbon quickly reaching steady state but in higher amounts than in a batch reactor [214A462].

### **Life Extension**

Pt-Rh promoted Co/high porous saponite catalyst showed lower coking that resulted in higher activity for hydrocracking and hydrodesulfurization of vacuum gas oil, which was sustained for a longer period of time than the unpromoted Co catalyst. Reactive hydrogen spilled over from the noble metal sites to both the acid sites (and the Co sites) and then hydrogenated cracked intermediates to prevent their deposition. The Pt-Rh combination was more effective than either only Pt or the Rh promoted Co catalysts [214A372].

The life of residue hydrodesulfurization catalyst can be extended by the intermittent injection of oil soluble metal catalyst precursors to the feed oil. In a test, 310 ppm of molybdenum naphthenate (or MOLYVAN L containing 8 wt% Mo) and 60 ppm of cobalt naphthenate in atmospheric residual oil feedstock charged to a flow through test unit. Mo and Co deposited on spent commercial vacuum residue hydrodesulfurization catalyst, a NiMo/alumina catalyst (3.16 wt% Ni, 9.41 wt% Mo) containing 18.6 wt% vanadium, 14.1 wt% sulfur and 5 wt% carbon. The HDS activity was enhanced and required a less severe temperature increase, which will further extend the catalyst life. Increased conversion of asphaltenes after injection of the metal precursors suggested the deposited metals were located primarily on the outer surface of the catalyst [214A208].

### **CATALYST REGENERATION AND METALS RECOVERY**

Spent hydrotreating and hydroprocessing catalysts are classified as hazardous wastes by the U.S. Environmental Protection Agency. Spent catalyst from heavy oil hydrotreating after deoiling contains coke and metals removed from the feedstock. Spent catalysts are potentially self heating or pyrophoric when dry and exposed to air. The catalysts are unloaded under nitrogen and transported in airtight sealed, small containers. The catalysts can ignite organic vapors. Catalyst manufacture's unloading and handling procedures should be followed. Since the spent catalysts also contain toxic metals that can be leached from the catalysts and pollute

ground water, proper disposal procedures need to be followed [214A040, 214A499; 214A500, 214A501, 214A522, 214A524].

Hydrotreating catalyst life time varies from 1 to 4 years [214A336]. Catalyst in gas oil hydrotreaters can run for 1 to 2 years with a total lifetime of 2 to 6 years. Residue units processing metal containing feeds under very severe conditions can have a lifetime as short as 0.25 to 1 year [214A044, 214A522]. A major portion of the spent catalyst in most refineries is from the hydrotreating and hydroprocessing of residue and heavy oils. The volume of spent heavy oil hydrotreating catalyst produced annually has increased substantially in recent years as the processing of heavier feedstocks containing higher levels of sulfur, nitrogen and metals increased [214A468].

Depending upon the state of the catalyst, the spent catalyst can be regenerated and recycled to the same unit or to a less demanding service or disposed. Spent catalysts contain the original molybdenum, cobalt or nickel along with metals accumulated during hydrotreating, mainly vanadium and nickel. Catalysts containing large amounts of metals or many segregated  $\text{NiS}_x$  crystals usually can not be regenerated. Unfortunately, these metals can be leached by water after land filling and pollute the environment. Although typically used in the past, land filling is becoming more and more environmentally restricted. Recycling the metals and restoration of catalytic activity are therefore more attractive options [214A522].

Restoring spent catalyst activity through regeneration and rejuvenation is not an easy option. Carbon deposits can be removed completely by *in situ* or *ex situ* conventional regeneration via controlled combustion with air-steam or air-nitrogen. The accumulated metals remain. The main one, vanadium, is usually concentrated near the outer surface of the catalyst particle, blocking the pore mouths, significantly reducing the available surface area within the inner pores. Regenerated catalyst processes are mainly evaluated based upon the regenerated catalyst activity, physical quality (mainly extrudate length-to-diameter ratio and fines content) and yield of regenerated product [214A085]. Rejuvenation is the process of removing accumulated metals and restoring the catalyst to near its original activity and selectivity.

## Regeneration

Reusing regenerated catalyst for at least two cycles reduces catalyst waste disposal by at least one-half. Regenerated catalyst can be reused:

1. In the same unit for a second or third cycle,
2. In a less severe service (from gas oil hydrotreating to naphtha or straight run distillate hydrotreating for example),
3. By cascading to a higher metals service such as a guard bed or the first main bed,
4. By cascading to a high silicon service (Silicon contamination, originating from anti-foam injection into a delayed coker, causes excessive carbon deposition, reducing the cycle length due to silicon breakthrough or a high reactor pressure drop.)
5. Or as make-up catalyst after frequent reactor skimming of the top of the bed to restore low pressure drop.

Problems with *in-situ* catalyst regeneration include temperature excursions that lead to irreversible loss of catalyst activity from sintering and metals agglomeration and regeneration gas channeling that results in incomplete regeneration and poor activity recovery. *Ex-situ* regeneration minimizes these problems and also allows screening to remove the fines and chips that contribute to increased bed pressure drop [214A085].



## TRICAT Regeneration Process

The TRICAT Regeneration Process (TRP) is a proprietary commercial *ex-situ* hydroprocessing catalyst regeneration process developed by TRICAT, Inc. The process uses an ebullating bed regenerator, which allows better regenerator heat release control, improved catalyst activity retention in a single-pass and reduced catalyst handling minimizes catalyst losses.

Their regeneration services include pretreatment inert gas (mainly nitrogen and carbon dioxide) stripping of excessive hydrocarbons and water from downflowing spent catalyst. Whether to strip the catalyst prior to regeneration is determined after analyzing a representative composite sample of the catalyst. Catalyst containing up to 40% volatiles can be regenerated in a single pass. Stripping produces a uniform hydrocarbon content (spent catalyst stripped in the reactor is often uneven due to uneven gas flow) and reduces the amount of hydrocarbons to be burned in the regenerator. The regenerator temperature rise is restricted since the hydrocarbons burn hotter than the coke and can contribute to erratic regeneration. Higher regeneration rates and reduced residence time are permitted. Stripping also improves the catalyst flow properties since excessive hydrocarbons and water make the catalyst cohesive.

Spent catalyst (after pre-stripping) is first screened in a vibrating feed screener to remove support material and catalyst fines prior to regeneration. Support material can be washed, reclassified and reused. Except for precious metal catalyst fines that must be first decarbonized, fines are typically sent directly to metals reclamation. Screened catalyst then enters the first of two ebullating bed regeneration reactors operated in series. Fluidizing air passes through a bottom distributor plate of each reactor at independently controlled rates. Reactor temperature (typically maintained between 850 and 950°F, 454 and 510°C) is controlled by controlling the catalyst feed rate, inlet air temperature (800°F, 427°C at startup; ambient air at steady state to the first reactor), cooling coils and regenerator catalyst level (increasing level increases the catalyst residence time and temperature). Regenerated catalyst is cooled in a water-jacketed cooler prior to screening and packaging. Fines are sent to metals recovery. This screener can also separate a mixture of extrudate sizes. It is common to load larger size catalyst extrudate on the top (or occasionally bottom) of a bed of 1/16 or 1/20 in extrudates.

Regenerator flue gas is cooled and filtered in a bag house to recover catalyst dust. The gas is then scrubbed to remove SO<sub>x</sub> and discharged to the atmosphere. Scrubber solution is neutralized and discharged [214A085].

## Developmental Rejuvenation Processes

Recent research shows commercial spent NiMo/alumina catalyst (4.0 wt% Ni, 4.5 wt% Mo, 9.7 wt% V and 15.3 wt% C) can be recycled into an active, new hydrodemetallization catalyst for residual oils. The recycled spent catalyst is mixed with boehmite, an aluminum oxide hydroxide mineral, AlO (OH), peptized and extruded. The hydrodemetallization catalyst is prepared according to the following steps:

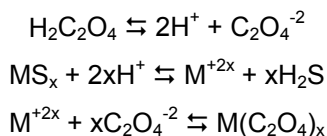
1. Spent catalyst is deoiled by washing with naphtha and extracted with toluene.
2. Deoiled spent catalyst is ground and sieved to obtain particles in the range of 25-90 microns, similar to the boehmite powder.
3. To the boehmite powder, 2% dilute nitric acid is added at a constant rate.
4. The spent catalyst and boehmite are mixed, peptized and kneaded for 20 to 30 min. into an extrudable paste in a kneading and extrusion machine.
5. The paste is extruded through 1.5 mm diameter die holes into extrudates.

6. The extrudates are dried at 230°F (110°C) for 24 H.
7. The dried extrudates are calcined at 698°F (370°C) for 2 hours, increased to 842°F (450°C) for 3 H and finally to 932°F (500°C) for 2 H.
8. The calcined extrudates are cooled in a desiccator.

The prepared catalyst containing up to 40 wt% spent catalyst to boehmite contained large pores, a fairly high surface area (>120 m<sup>2</sup>/g) and pore volume (>0.5 ml/g). A catalyst prepared with 40 wt% spent catalyst is more active for HDM and HDS reactions than a reference commercial catalyst when hydrotreating residual oil. The increased activity may result from new kind(s) of active sites from different combinations of vanadium, molybdenum and nickel obtained from the spent catalyst. Literature indicates vanadium alone or combined with nickel or molybdenum exhibit some hydrotreating activity. NiV and VMo on alumina both show fairly high HDM and HDS catalytic activity [214A468].

A recent hydroprocessing catalyst rejuvenation process demonstrated 95% recovery of fresh catalyst activity in the laboratory. The commercial CoMo atmospheric residue hydrodesulfurization catalyst (cylindrical extrudates 1 and 4.3 mm in average diameter and average length, respectively) contained sulfur (5.3 wt%) and acquired nickel (3.1 wt%), iron (0.8 wt%) and carbon (15.6 wt%). The catalyst was deoiled by washing with naphtha and then toluene. Vanadium (14.9 wt% of the spent catalyst) was first continuously extracted with oxalic acid promoted by ferric nitrate. The extraction recovered 85% of the fresh catalyst activity. Only about 40% of the vanadium was leached from the catalyst, yet 85% of the original activity was restored by this step. The remaining 10% of the activity was restored in the second stage, removal of the coke. Coke deposition apparently had less effect on activity than metals deposition in deactivating the catalyst [214A266].

In another rejuvenation process, oxalic acid leaches metals from the spent catalyst. In spent catalyst, the metals (M) are primarily sulfides in low oxidation states due to the presence of carbon. Leaching with oxalic acid likely proceeds in three reaction steps:



The oxidation state of the metal largely affects the ease of formation of the metal ion, the reaction with oxalic acid and the dissolution of the product. Oxalic acid by itself shows very little leaching activity. Additives such as ferric nitrate, a good oxidizing agent, oxidize the metals to higher oxidation states. Since oxidized vanadium is complexed more easily by the oxalate ion and maintained in solution, the promoter concentration largely affects the leaching rate. The manner of addition of the ferric nitrate affects the surface area and pore volume; the improvement is in the order: continuous addition > batch addition > successive extraction.

During the leaching process, the unleached vanadium remaining in the treated catalyst is likely redistributed within the catalyst pellet. The rejuvenated catalyst's surface area and pore volume both increased substantially upon removal of the vanadium and coke from the pores. During the leaching process, molybdenum, cobalt and nickel are also redistributed on the catalyst surface. A part of the original inactive cobalt and nickel atoms present in the tetrahedral sites of the alumina support may be leached and redistributed over the molybdenum layer. Close proximity of nickel promoters with the molybdenum allows better interaction and promotes the formation of precursors of active Co-Mo-S and Ni-Mo-S phase structures in the rejuvenated catalyst. Hydrodesulfurization can also be promoted by well dispersed vanadium along with the molybdenum and nickel [214A266].

Laboratory tests suggest NiMo/alumina spent catalysts can be reactivated by treatment with cobalt phenyl siloxane and ferro phenyl siloxane. 0.25-0.5 wt% siloxanes added to the catalyst surface gave maximum conversion of thiophene. The organometallic siloxanes can increase and/or retain the activity of both fresh and spent catalysts at high temperatures [214A405].

## Metals Reclamation

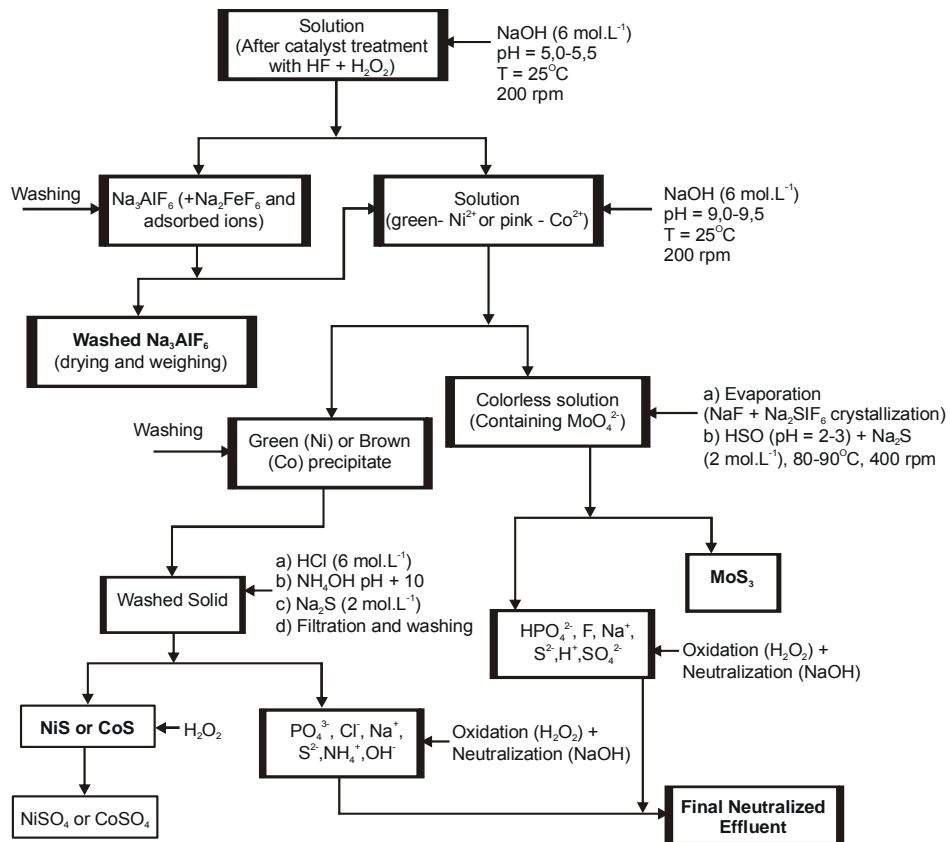
The concentration of metals is usually greater than their occurrence in natural ores. Drawbacks of metals recovery from the spent catalyst include the low purity of the metals recovered, fluctuations in metals prices and the high cost of shipping spent catalyst. The Basel Convention (on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal) places restrictions on the international shipping of hazardous wastes from developed countries to less developed countries [214A502, 214A503].

A variety of proposed methods for metals recovery from HDT catalysts may be classified as solubilization in acidic medium, high temperature chlorination and pyro- or hydrometallurgical processes. Pyro- or hydrometallurgical methods were dominant until the 1980s but require severe operating conditions and are very energy intensive. Acid digestion methods under mild conditions were the most proposed type the last 20 years. Generally thermal treatment to eliminate carbon and most sulfur precedes acid digestion. Sulfuric acid with or without additives, particularly hydrogen peroxide is most commonly used. After adjusting acid concentration, time, temperature and other conditions, high solubilization yields may be obtained for metals such as vanadium, iron and arsenic. Recoveries of Co, Ni, Mo and Al are usually below 95% due to insoluble/refractory compounds (silicates, phosphates and spinels), which can be decomposed by fusion with  $\text{Na}_2\text{CO}_3$  and NaOH but dissolve in HF under mild conditions. Sulfuric acid is also used for selectively extracting metals with organic solvents as well as classical precipitation methods [214A336].

In a new, laboratory demonstrated process, spent commercial NiMo/alumina or CoMo/silica-alumina catalysts are dissolved in aqueous solutions containing fluoride ions under mild conditions. HF plus hydrogen peroxide (1:1 volume ratio) leachants fully solubilized the spent catalysts in less than 1 h at 112-140°F (50-60°C) and 400 rpm regardless of composition. Excess HF (1.5:1 volumetric ratio) decreased the dissolution rate. Excess hydrogen peroxide should be avoided due to the loss of  $\text{F}^-$  as HF reduces the yield. Silica containing catalysts require longer solubilization time than silica-free catalysts. HF is best for dissolving silica and phosphate-containing catalysts. NaF can also be used but only in low amounts due to its limited solubility in water and acids and requires more time.

Metals from the leach solution can be recovered very efficiently with low residue generation by the general process scheme shown in Figure 5.8. There are two effluents from the process: a NiS or CoS precipitate and a molybdenum precipitate. Both are oxidized with hydrogen peroxide at room temperature to convert excess sulfide ions to sulfates before the solutions are neutralized with NaOH. Further treatment with CaO and sodium carbonate produces a precipitate of calcium fluoride, phosphate and sulfate that can meet water discharge requirements [214A336].

**Figure 5.8**  
**LEACH SOLUTION RECOVERY PROCESS**



Source: 214A336

## 6 PROCESS REVIEW

Hydrotreating of heavy oil is a relatively new refining process. Hydrodesulfurization of atmospheric residue was introduced in 1969 in Japan for fuel oil desulfurization. Hydrotreating of atmospheric resid for RFCC's followed in the early 1980's. Hydrodesulfurization of vacuum residues followed in 1977. Although further development is required, pilot plant exploration suggests heavy crude oils such as Maya can be directly hydrotreated under severe conditions to synthetic crude oil with very low contaminants and high distillates yields [214A071, 214A267]. Hydrocracking of heavy oils is older than hydrotreating. Hydrocracking of vacuum gas oils began in 1962 followed closely by hydrocracking of vacuum residues by the H-oil process one year later. High conversion hydrocracking of vacuum residues is newer, introduced in 1984 [214A168]. Despite its relatively young age, considerable development of the hydrotreating process has occurred.

Advances in residue hydrotreating are a combination of development of catalysts, discussed in Section 5, and reactor development. This Section focuses on the common processes, operation and design of heavy oil hydrotreaters. The application of hydrotreating of FCC and RFCC feedstocks is then briefly reviewed as background for the economic evaluation of the hydrotreating of catalytic cracking feedstocks in Sections 7 and 8.

### REACTOR TYPES

The method of feed introduction, the arrangement of the catalyst beds and the design and manner of operation of the reactors are important factors in residue hydrotreating. Hydrotreating is performed with a series of reactors, each with catalyst optimized for a different purpose. Depending upon the residue properties, the reactors in a hydrotreating unit may be fixed bed, moving bed, ebullated bed or a combination. A guard reactor protects downstream reactors from metals. Fixed bed catalysts important physical properties include particle size, pore size and pore size distribution. Fixed bed reactor pressure drop and proper fluid distribution over the catalyst bed depends on the particle size and shape. Ring-shaped particles provide increased bed voidage. Polylobe particles increase the external surface area to improve accessibility to the catalyst interior. Optimum HDM and HDS depend upon pore size and pore size distribution [214A469, 214A479].

Hydrotreating reactors may be fixed bed with periodic off-line catalyst replacement or a type that allows essentially continuous on-line catalyst replacement: moving bed, ebullating bed or slurry (entrained) reactors. Of the 73 hydroprocessing units identified as operating in March, 2003, 60 (82%) had fixed bed reactors, 12 (16%) were moving beds (believed to include ebullated bed reactors) and one (1%) was a slurry reactor [214A541]. Characteristics of these types of reactors are summarized in Table 6.1. The catalyst activity, selectivity, particle size and shape, pore size and deactivation rate, along with the type of reactor, have to be optimized with the properties of the heavy feedstock for optimum performance.

**Table 6.1**  
**COMPARISON OF DIFFERENT HYDROTREATER REACTOR TYPES**

	<u>Fixed Bed</u>	<u>Moving Bed</u>	<u>Ebullating Bed</u>	<u>Slurry</u>
Maximum (Ni+V) in feed, ppmw	120-400 <sup>a</sup>	500-700	>700	>700
Tolerance for impurities	Low	Low	Average	High
Max. conversion of 1022°F (550°C), wt%	60-70	60-70	80	90
Unit operability	Good	Difficult	Difficult	Difficult

Source: 214A037

<sup>a</sup> swing reactors

These types of reactors and their characteristics are described in great detail by Ancheyta [214A540].

### **Fixed Bed**

The down-flow fixed bed reactor (trickle bed reactor) is the most common hydrotreater reactor type for residue feedstocks. Temperature of these adiabatic reactors is controlled with quench hydrogen. A major limitation of this type of reactor is deactivation with time due to coke and metals buildup on the catalyst as discussed in Section 5. For this reason, atmospheric residues can generally be reliably processed in fixed bed units but not difficult vacuum residues. Moving bed and ebullating bed reactors are reliably used with the heaviest oil feedstocks, especially vacuum residues [214A469, 214A487].

High performance fixed bed internals are required for maximizing catalyst utilization. Internals include inlet liquid distributors, grading materials, uniform bed catalyst density, quench boxes, placement of thermal couples.

Particle filtering or scale catching with appropriate grading significantly impacts catalyst run length, especially units with a 6-12 month cycle life that shut down routinely due to pressure drop buildup. The upper bed layer of the first fixed bed reactor traditionally consists of guard material to retain particles in the feed. The particles often are iron but may be salt, coke from furnace tubes, sediments, catalyst fines, solids formed by reaction of additives. Particle diameters range up to over 100 microns. If not retained, the particles would deposit on the outer surface of the catalyst or between catalyst particles and raise the bed pressure drop. The guard material (<5 wt% of the bed) is porous solids such as activated bauxite and alumina that have no or little catalytic activity and macropores of about 100 micron diameter. Capacity for iron is about 20 times that of hydrotreating catalyst [214A037, 214A045, 214A480, 214A546, 214A577].

Packing of catalyst beds in the order of large to small pores enhances the catalyst activity for HDM and HDS. The molecular weight distributions of product oil asphaltenes and maltenes are affected by pore order. Large to small order most effectively cracks asphaltenes and reduces sludge formation since the solubility of both asphaltenes and maltenes is increased. The middle bed catalyst apparently controls catalyst life. Small pores in the middle catalyst enhance maltene cracking and reduce asphaltene cracking, thereby increasing sludge formation [214A269].

For the treating of heavy feedstocks, the upflow fixed bed reactor has benefits compared to downflow bed with graded catalyst as summarized in Table 6.2. Quench gas is injected into the upflow bed at two elevations. Upflow is said to be “much more economical in assuring that catalyst cycle life will be determined by catalyst deactivation rather than by fixed bed guard zones of reactors” [214A023].

**Table 6.2**  
**UPFLOW COMPARED TO DOWNFLOW FIXED BED REACTORS**

<u>Feature</u>	<u>Upflow</u>	<u>Downflow</u>
Catalyst bed condition	Slight expansion	Fixed
Catalyst contacting and wetting	Submerged in oil, very uniform	May not be uniform
Flow distribution	Good	Worse toward end of run
Conditions for good flow distribution	Low gas rate	High liquid and gas rate
Pressure drop	Very low	Moderate and increasing
Plugging potential	Low	Minimized with grading
Catalyst agglomeration	Less likely	Increasing with feed contaminants

Source: 214A023

The Fushun Research Institute of Petroleum and Petrochemicals (FRIPP), SINOPEC commercialized their SHIFT-G technology of inverse catalyst loading used to optimize the catalyst grading in residue hydrotreating of up flow fixed bed reactors. With a commercial upflow reactor and down flow reactor in series, the catalyst life of the upflow reactor was shorter than that of the downflow reactor. The SHIFT-G technology places less active catalysts in areas where coking can readily occur. This maintains the HDM activity of the catalyst. This distributes the reaction heat release to minimize hot spots, improves product quality and prolongs the operating cycle [214A579].

Hydrotreating Maya heavy crude oil in a fixed bed pilot plant study was better using a NiMo/alumina catalyst for HDM in a first stage and a CoMo/alumina catalyst for HDS in the second stage than single stage hydrotreating using a different NiMo catalyst. The two-stage system compared to the single stage process produced:

- Lower product sulfur and metals contents
- Low nitrogen and Ramsbottom carbon contents
- Higher API gravity, which implies more distillates are produced.

In both systems, asphaltenes were almost the same [214A262]

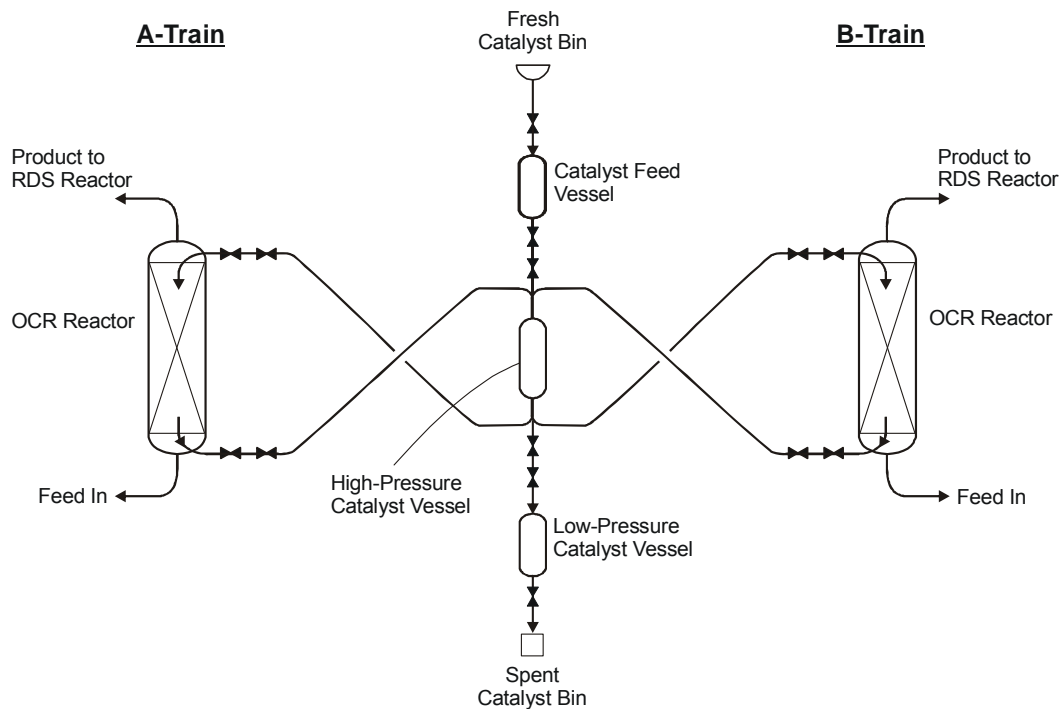
### **Moving Bed**

Moving bed processes, where the catalyst bed slowly moves down the reactor as catalyst is withdrawn from the bottom and make-up catalyst added at the top, are much like fixed bed processes. Moving bed catalysts are similar to fixed bed catalysts except catalyst shape is chosen to reduce abrasion and particle strength is greater. Fixed bed HDS and HDN reactor(s) can follow a moving bed guard reactor for HDM. Moving beds are most useful as HDM reactors processing high metals or other contaminants containing feedstocks.

Chevron Lummus Global developed On-Stream Catalyst Replacement (OCR) technology (shown schematically in Figure 6.1 for two reactor trains) to add fresh catalyst and withdraw metals laden spent catalyst from high pressure moving bed reactors without interrupting the operation of the hydrotreater. Catalyst is regularly added and withdrawn batch-wise to maintain the required catalyst activity. The basic steps in the transfer process are:

1. Fresh catalyst is transferred by gravity into the low pressure feed vessel.
  2. Flush oil, usually a heavy gas oil, is added to slurry the catalyst and transport it to the high pressure vessel.
  3. The low pressure catalyst feed vessel is isolated and the pressure equalized with the OCR reactor.
  4. Fresh catalyst slurry is transferred to the top of the reactor.
  5. After the transfer is complete, the double isolation valves are flushed to remove catalyst and the high pressure vessel is isolated from the system.
- A desired amount of spent catalyst is similarly transferred from the bottom of the reactor.

**Figure 6.1**  
**CHEVRON LUMMUS GLOBAL ON-STREAM CATALYST REPLACEMENT SYSTEM**

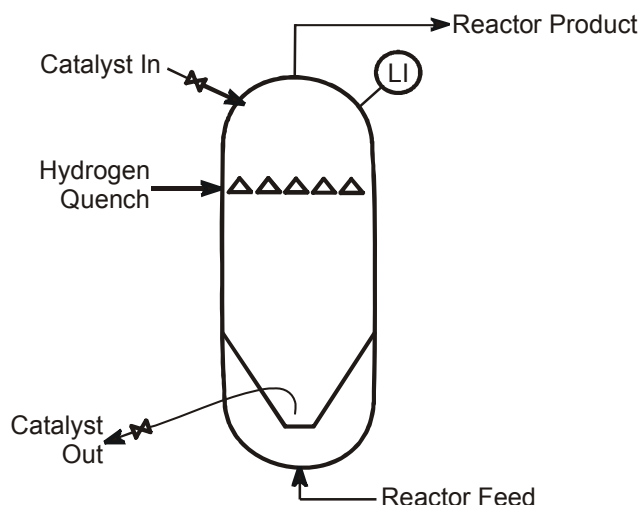


Source: 214A046

The OCR reactor (Figure 6.2) is essentially a fixed bed that intermittently moves down the reactor. A level detector at the top monitors the catalyst level. As fresh catalyst is added at the top, residuum is fed to the bottom, which expands the bed slightly. Meanwhile, fully spent catalyst is removed at the bottom. The special design of the cone at the bottom provides plug flow of the catalyst during removal [214A046].



**Figure 6.2**  
**CHEVRON LUMMUS GLOBAL ON-STREAM CATALYST REPLACEMENT REACTOR**



Source: 214A046

### **Ebullating Bed**

Ebullating bed reactors are three phase (liquid, gas and solid) fluidized bed reactors. Feedstock and  $H_2$  are fed through a distributor grid plate at the bottom along with recycle liquid. The bed is catalyst, typically 0.8 mm diameter extrudate. The feed expands and back mixes the catalyst bed as feed and hydrogen react and the mixture passes through the reactor. The mixing causes these reactors to be isothermal. The height of the bed is controlled by the recycle rate. The expanded bed minimizes bed plugging and lowers the pressure drop. At the top of the reactor, the oil and catalyst are separated with the catalyst recirculating to the reactor bottom to mix with the feedstock. In an external separator, gas and liquid are separated. Quench hydrogen is not used. Very high metals, asphaltene and sulfur containing feeds can be hydrotreated since fresh catalyst is added daily at the bed top and equilibrium catalyst is withdrawn from the bottom. On-line replacement of catalyst allows more severe operating conditions than fixed or moving bed reactors, ensures isothermal operation throughout long run lengths with constant product quality. Run lengths are typically determined by the refinery turnaround schedule, typically 2-3 years. Compared to fixed bed reactors, the ebullated bed reactor offers improved temperature control, flexibility in feedstocks, flexibility in reaction conditions and severity and lower investment cost for processing heavy, high metals feedstocks. Compared to slurry reactors (mostly hydrocrackers), the ebullated bed reactor can operate at lower severity since the slurry catalyst must be recovered from the residue oil, produce higher quality distillates since more active catalysts are used and more efficiently use hydrogen due to less light gas yield [214A487, 214A562, 214A563].

### **Slurry Reactors**

Slurry (entrained flow) reactors like ebullating bed reactors also are three phase (liquid, gas and solid), isothermal reactors. However, the slurry reactor catalyst particles are small enough so the particles are carried by upward flowing fluids of high enough linear velocity to entrain and circulate the catalyst without the catalyst accumulating in the reactor. Slurry reactors are being

designed to handle residue feeds with high impurities. General operating conditions are similar to ebullating bed reactors.

Examples of reactor types hydrotreating Safaniya vacuum residue is summarized in Table 6.3. Products in this example, especially the ebullating bed and slurry bed reactors, will require additional hydrotreating.

**Table 6.3**  
**EXAMPLE OF PRODUCT YIELDS AND QUALITY FOR PROCESSING IN DIFFERENT TYPES OF REACTOR**

<u>Type of Reactor</u>	<u>Fixed/Moving Bed</u>	<u>Ebullating Bed</u>	<u>Slurry</u>
<b>Feed</b>			
Crude yield, wt%	34.0		
Specific gravity	1.035		
Viscosity at 212°F (100°C), mm <sup>2</sup> /s	3,900		
Sulfur, wt%	5.28		
Conradson carbon, wt%	23.0		
C <sub>7</sub> Asphaltenes, wt%	11.5		
Ni + V, ppm	203		
<b>Gasoline</b>			
Yield, wt% of feed	1-5	3-10	10-15
Specific Gravity	0.720-0.740	0.710-0.720	0.720
Sulfur, wt%	<0.01	0.01-0.2	0.06
Nitrogen, ppm	<30	<50	200
<b>Gas Oil (Diesel)</b>			
Yield, wt%	10-25	20-35	40-45
Specific Gravity <sup>a</sup>	0.850-0.875	0.840-0.860	0.866
Sulfur, wt%	<0.05	<0.1	0.7
Nitrogen, ppm	<500	<1,000	1,800
Cetane Number	42-46	42-46	40
Aromatics, wt%	40-50	---	40-50
Viscosity at 122°F (50°C), mm <sup>2</sup> /s	2.5	---	3.5
<b>Vacuum Distillate</b>			
Yield, wt%	20-35	35-45	20-25
Specific Gravity	0.925-0.935	0.930-0.940	1.010
Sulfur, wt%	0.2-0.5	0.4-0.8	2.2
Nitrogen, ppm	<2,000	<2,500	4,300
Viscosity at 212°F (100°C), mm <sup>2</sup> /s	8-12	8-12	7
Conradson Carbon, wt%	<0.5	<1	<2

**Table 6.3 (Concluded)**  
**EXAMPLE OF PRODUCT YIELDS AND QUALITY FOR PROCESSING IN DIFFERENT TYPES**  
**OF REACTOR**

<u>Type of Reactor</u>	<u>Fixed/Moving Bed</u>	<u>Ebullating Bed</u>	<u>Slurry</u>
Vacuum residue			
Yield, wt%	35-60	20-40	5-20
Specific Gravity	0.980-1.010	1.010-1.050	1.160
Sulfur, wt%	0.5-1.0	1-2	2.7
Nitrogen, ppm	<4,000	<5,000	11,000
Viscosity at 212°F (100°C), mm <sup>2</sup> /s	150-1,200	1,000-2,000	60,000
Conradson Carbon, wt%	15-20	20-30	47
Ni + V, ppm	10-40	50-100	90

Source: 214037

<sup>a</sup> 15°C referenced to 4°C

Deep desulfurization (to near zero sulfur) occurs under severe operating conditions with conventional catalysts. Unfortunately, severe conditions also favor undesired coking, so the severity is limited in practice by the HDS unit design. Hydrotreating efficiency can be increased by using multiple beds within one reactor, new internals, new catalysts. Best results are obtained by a combination of approaches, i.e., appropriate catalysts with improved activity in an advanced reactor design. For a cycle length of 1 year, the guidelines shown in Table 6.4 relate the basic reactor types and catalyst systems that can generally tolerate the indicated feedstock metals levels [214A267, 214A455].

**Table 6.4**  
**REACTOR TYPE AND CATALYST SYSTEMS AS A FUNCTION OF FEEDSTOCK METALS**  
**CONTENT<sup>a</sup>**

<u>Metals Level, ppmw</u>	<u>Reactor Type</u>	<u>Catalyst System</u>
< 25	Fixed bed	Single tailor-made optimum catalyst
25-50	Fixed beds	Dual catalyst system: higher metal tolerant catalyst ahead of higher desulfurization catalyst
100-150	Fixed beds	Triple catalyst system: HDM catalyst, balanced HDM/HDS catalyst and HDS
>100-150	Swing, fixed guard beds followed by fixed beds	Swing guard beds: HDM catalyst Main reactors: HDS and other catalysts tailored to the feedstock and desired product
	Moving guard bed reactors followed by fixed beds	Moving guard beds: HDM catalyst Main reactors: HDS and other catalysts tailored to the feedstock and desired product
	Ebullating guard bed reactors followed by fixed or ebullating bed main reactors	Ebullating guard bed: HDM catalyst Main reactors: HDS and other catalysts tailored to the feedstock and desired product

Source: 214A429

<sup>a</sup> for 1 year catalyst cycle length

## HYDROTREATING PROCESSES

Fixed bed hydrotreating of atmospheric or vacuum residuum is basically the same in process flow and catalyst. These processes generally operate at 13-18 MPa and 662-806°F (350-430°C). The temperature is limited due to coke formation, which limits conversion. Hydrogen consumption ranges from about 700 to 1300 SCF H<sub>2</sub>/B of feedstock. Fixed bed reactors can be used for desulfurizing and demetallizing FCC feedstock such as gas oils.

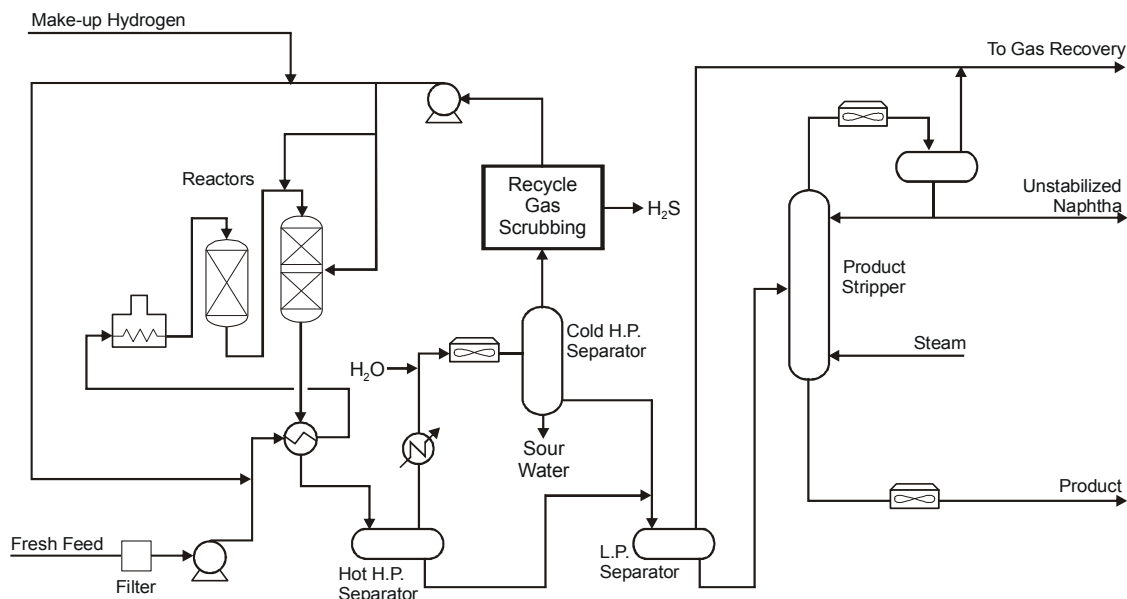
### Chevron Lummus Global RDS/VRDS

Commercialized in 1969, Chevron Lummus Global Residuum Desulfurization (RDS) process removes sulfur, nitrogen, metals from atmospheric residue from the crude unit with a TBP initial cut point of 698°F (700°C) along with other feeds such as cracked gas oils. The feed to the vacuum residuum desulfurization (VRDS), commercialized in 1977, is generally vacuum residue from a vacuum crude unit typically with an initial true boiling point of 1000°F (538°C) up to 1067°F (575°C). Other VRDS feeds include solvent deasphalted pitch and vacuum gas oils. Depending upon the feedstock heteroatom content, especially metals, and targeted product specifications, the reactors may be fixed bed or a moving bed reactor using On-Stream Catalyst Replacement technology. Over 26 RDS/VRDS units are in operation (2006); 6 with vacuum residue feeds. RFCCU feedstock is pretreated in 16 units. On-Stream Catalyst Replacement is used in four units with up to another six in engineering.

Fixed beds generally operate at moderately high pressures (150 to 200 atm, 2133 to 2850 psig) at 662-797°F (350-425°C) under 80 to 95 mol% hydrogen. Operation in “conversion mode” where the reactor temperature is raised fairly high early in the run to promote hydrocracking and held to the end of the run, minimizes the production of fuel oil at the expense of shorter catalyst life [214A530; 214A534].

Filtered feedstock in the Chevron Lummus Global RDS/VRDS process (Figure 6.3 GLS) is combined with makeup enriched recycle hydrogen and first heated by heat exchange with effluent from the last reactor. A fired heater brings the feedstock to reactor inlet temperature. Effluent from each reactor catalyst bed is quenched with cold recycle hydrogen to provide high hydrogen partial pressure and high gas velocity and to maintain the desired reactor inlet temperature. The reactor effluent is cooled by exchange with the feedstock and maintained at a constant temperature.

**Figure 6.3**  
**CHEVRON LUMMUS GLOBAL RDS/VRDS PROCESS**



Source:214530

Hydrogen is recovered from the cooled reactor product by flashing first in the hot high pressure separator (HHPS), which also roughly splits light and heavy reaction products. The vapor is cooled and water is injected to absorb hydrogen sulfide and ammonia. The mixture is further cooled in an air cooler and charged to the cold high pressure separator (CHPS). Hydrogen rich gas from the CHPS is amine treated to remove H<sub>2</sub>S. The purified recycle hydrogen gas is compressed and charged to the reactors as quench gas. Liquid water separated in the CHPS is sent to the sour water recovery unit for removal of the hydrogen sulfide and ammonia. Liquid hydrocarbon is decanted from the sour water in the CHPS and combined with liquid hydrocarbons from the HHPS, reduced in pressure and charged to the low pressure separator (LPS). Liquid hydrocarbons from the LPS are steam stripped and fractionated, removing unstabilized naphtha and heavy oil products. Overhead gas and gas from the LPS are sent to a gas recovery unit [214A530, 214A534].

The yields and product properties from hydrotreating a high quality RFCC atmospheric residue feedstock from Arabian Heavy crude oil are summarized in Tables 6.5 and 6.6 respectively.

**Table 6.5**  
**YIELDS FROM RDS HYDROTREATING ATMOSPHERIC RESIDUE FROM ARABIAN HEAVY**  
**CRUDE OIL**

	<u>Wt%</u>	<u>Vol%</u>
Feeds		
Raw oil	100.00	100.00
Chemical H <sub>2</sub> consumption	1.43	[930 SCFB ]
Products		
H <sub>2</sub> S	4.28	
NH <sub>3</sub>	0.22	
C <sub>1</sub> -C <sub>4</sub>	0.23	
C <sub>5</sub> -280°F (C <sub>5</sub> -138°C)	1.38	1.93
280-650°F (138-343°C)	12.51	14.49
650°F+ (343°C+)	82.81	87.23
Total	101.43	103.65

Source: 214A530

**Table 6.6**  
**PRODUCT PROPERTIES FROM RDS HYDROTREATING OF ATMOSPHERIC RESIDUE**  
**FROM ARABIAN HEAVY CRUDE OIL**

	<u>Feedstock</u>	<u>Naphtha</u>	<u>Middle Distillate</u>	<u>Residue</u>
Boiling range, °F (°C)	650+ (343+)	C <sub>5</sub> -280 (C <sub>5</sub> -138)	280-650 (138-343)	650+ (343+)
Gravity, API	11.8	68.2	34.5	19.4
Sulfur, wt%	4.37	0.004	0.034	0.40
Nitrogen, wt%	0.30	0.003	0.016	0.14
Carbon residue, wt%	13.6	---	---	5.5
Nickel, ppmw	34	---	---	5
Vanadium, ppmw	97	---	---	5
Viscosity, cSt at 122°F (50°C)	3240	---	---	160

Source: 214A530

### Hyvahl Process

The Hyvahl process, licensed by Axens (IFP), is a hydrotreating process for atmospheric or vacuum residuum feedstocks containing high concentrations of asphaltenes, maltenes and metals to produce naphtha or middle distillate respectively. Three choices of reactor are offered: fixed bed (Hyvahl F Process), moving bed (Hyvahl M process) and swing by-pass guard reactor (Hyvahl S process). The swing bed process operates at higher temperature, high hydrogen pressure and low contact time [214A471, 214A487]. For processing heavy feeds, Axens Permutable Reactor System (PRS) is an advanced guard bed reactor system that increases

hydrotreater time on stream by minimizing costly shutdowns while the FCCU is operating. Run length increases about 60% [214A547, 214A582].

In the Hyvahl process, residue feed and hydrogen are heated in a feed/effluent heat exchanger and then in a furnace. The reactor section normally has parallel guard bed reactors ahead of the main HDM and HDS reactors. For heavy feedstocks, the guard beds are permutable in operation (PRS technology), which allows catalyst reloading during the run as described below. The HDM section completes the demetallization and conversion continues. With most of the contaminants removed, the residue oil goes to the HDS section. Typical HDM and HDS rates are greater than 90%. Net diesel plus naphtha production is 12% to 25%. Six units (totaling 319,000 B/sD) are operating or licensed by the end of 2006; two treating combined atmospheric residue and vacuum residue feed and four feeding only vacuum residue feed [214A581].

The guard reactors are operated to maintain a constant low metals HDS feed. PRS provides special valving and safety features that allow the lead guard reactor to be changed out when the pressure drop exceeds a specified level. The lag reactor remains in operation during the 2-3 week turnaround. A low pressure catalyst conditioning section is independently connected to each reactor. The fresh reactor is returned to service as the lagging reactor. The steps are:

1. The spent reactor is isolated using special valves.
2. The bed is cooled.
3. Reactor is depressurized and inerted.
4. Catalyst is unloaded.
5. Reactor is reloaded.
6. Reactor is heated to the activation temperature for catalyst sulfiding.
7. Catalyst is sulfidized using the low pressure conditioning section.
8. Reactor is repressurized.
9. Reactor is connected as the lead reactor [214A547].

A model (THERMIDOR) simulates the HYVAHL process time on stream operation accounting for the associations of guard bed materials and catalysts including particle size, activity, pore size and shape grading effects. Two main deactivation mechanisms, coke and metals deposition, are realistically represented. Synergy between HDM and HDS catalysts are shown [214A395].

Properties of the catalyst system in use in the mid 1990's are summarized in Table 6.7. Table 6.8 shows the major properties and yields of four HYVAHL hydrotreated residua.

**Table 6.7**  
**PROPERTIES OF HYVAHL PROCESS CATALYST FOR RESIDUE HYDROTREATING**

<u>Characteristics</u>	<u>Guard Material</u>	<u>HDM catalyst</u>	<u>HDS catalyst</u>
Surface, m <sup>2</sup> /g	<0.1	120-170	180-220
Pore volume, cm <sup>3</sup> /g	<0.25	0.7-1.0	0.4-0.6
Active component	---	NiMo	CoMo
Wt% of total catalysts	<5	30-70	30-70

Source: 214A045

**Table 6.8**  
**PERFORMANCE OF HYVAHL PROCESS FOR RESIDUES HYDROTREATING**

	<b>Straight Run Residue</b>		<b>Vacuum Residue</b>	
	<u><b>Arabian</b></u>	<u><b>Cold Lake</b></u>	<u><b>Kirkuk</b></u>	<u><b>Safaniya</b></u>
<b>Feed</b>				
Density	0.988	1.024	1.021	1.035
Sulfur, wt%	3.95	5.05	5.14	5.28
Viscosity, cSt at 212°F (100°C)	95	1095	880	3900
Conradson carbon, wt%	13.8	18.3	18.2	25.0
Asphaltenes, wt%	5.7	10.5	7.5	13.2
Ni+V, ppm	104	325	189	203
<b>Hydrotreated residue</b>				
Density	0.934	0.958	0.950	0.970
Sulfur, wt%	0.50	0.80	0.47	0.70
Conradson carbon, wt%	4.0	8.9	6.4	10.0
Asphaltenes, wt%	0.3	2.5	0.8	5.3
Ni+V, ppm	1.5	24	1.5	20
<b>Yields, wt%</b>				
H <sub>2</sub> S + NH <sub>3</sub>	3.88	5.08	5.28	4.92
C <sub>1</sub> -C <sub>4</sub>	2.14	3.20	2.27	2.60
Gasoline	3.47	5.20	4.02	4.60
Gas oil (diesel)	21.55	27.50	22.20	32.80
Residue	70.50	61.02	68.01	70.26

Source: 214A045

### **T-Star Process**

The T-Star process is an ebullated-bed hydrotreating or hydrocracking process licensed by IFP for treating distillates and vacuum gas oils, especially hard to treat vacuum gas oils containing significant amounts of metals, carbon residue or solids. HRI developed the process as a milder extension of the well known commercial H-Oil hydrocracking process for residue feedstocks. Conversion in the T-Star process is generally in the 20-60 vol% range when producing diesel fuel and FCC feedstock. The lower end of the conversion range is within the range of hydrotreating; the upper end is in the range of mild hydrocracking. Hydrodesulfurization can be maintained in the 93-99% range. The desired product qualities determine the operating severity. Advantages of process with daily catalyst addition and withdrawal include isothermal operation without quench hydrogen, constant catalyst activity and product quality, flexibility in feedstocks and in product properties and long run lengths. In FCC feedstock pretreating, run length is usually determined by the turnaround schedule of the FCCU, typically three years or more [214A562, 214A563].

### **HYCON Process**

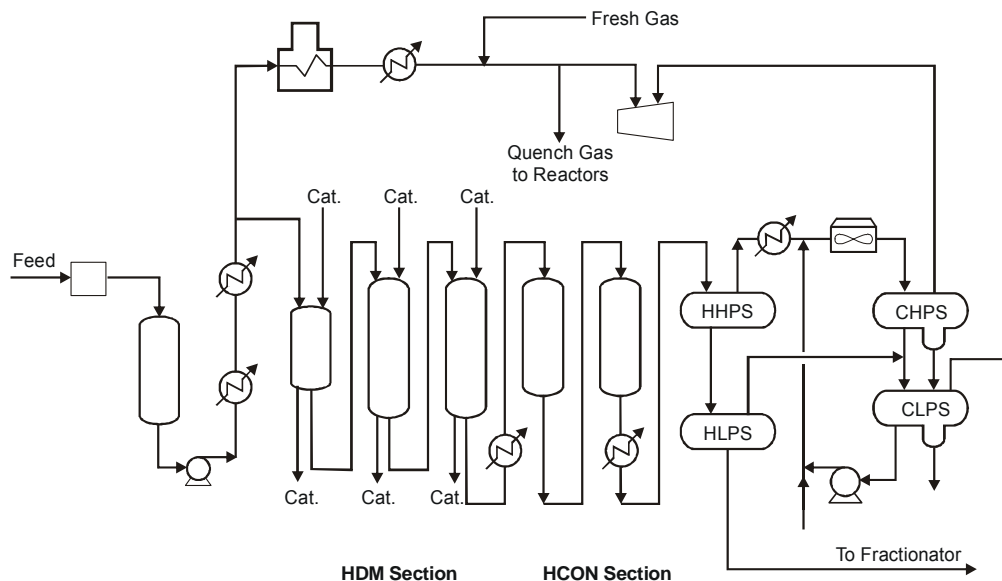
The Residue Hydroconversion Process (HYCON), licensed by Shell Global Solutions International B.V., is available with fixed or moving bed reactors. For heavy oil feeds, low sulfur



FCCU feedstock is the main product. All fixed bed reactors are used with relatively low metals feeds. As feed metals increase, one or more bunker demetalization reactors are added at the front end to ensure a catalyst life of at least one year. An all bunker reactor option eliminates the need for catalyst change-out. Bunker reactor catalyst replacement rate typically ranges from 0.5 to 2 vol% of inventory/day.

A simplified flow sheet of the HYCON process is shown in Figure 6.4 using three bunker demetalation reactors in series followed by two fixed bed reactors. Reactor pressure ranges from 1,450 to 3,000 psig (100-200 bar). Feedstock is filtered and preheated before combining with hot recycle hydrogen from the hydrogen furnace. The hydrogen and oil mixture enter the top of the first guard HDM bunker reactor. Effluent is charged serially directly to the top of the next two bunker reactors. The effluent from the last bunker reactor is heated and charged to the top of the first fixed bed reactor. The second fixed bed reactor directly follows the first. Each reactor is quenched with hydrogen. Effluent from the bottom of the last reactor is heated. The hot high pressure separator (HHPS) overhead vapor is condensed and combined with recycled cold low pressure liquid. The mixture is further cooled and separated from the recycle hydrogen in the cold high pressure separator (CHPS). The liquid from the HHPS flows to the hot low pressure separator (HLPS). HLPS overhead is combined with the CHPS light liquid and feed to the cold low pressure separator (CLPS) along with the heavy liquid from the CHPS. Vapor from the CHPS is vented. The liquid is combined with the HLPS liquid and fractionated [214A535].

**Figure 6.4**  
**SHELL GLOBAL SOLUTIONS HYCON PROCESS**



Source: 214A535

### UOP RCD Unionfining Process

The UOP RCD Unionfining Process hydrotreats heavy feedstocks such as atmospheric and vacuum residues and deasphalted oil most commonly to produce FCC or RFCC feedstock. Commonly about 90% of the sulfur and organo-metals are removed. The process is also used to produce low sulfur fuel oil and partial conversion of non-distillables in the feed to distillates. The



cooler. The partially condensed gas is then charged to the cold high pressure separator (CHPS). Gas from the CHPS is amine scrubbed to remove H<sub>2</sub>S and recycled to the reactors after combining with make-up hydrogen and compression. A portion of the recycle gas is purified by membrane separation that removes light hydrocarbons, mainly methane, to increase the reactor hydrogen partial pressure. Liquid from the HHPS is flashed in the hot low pressure flash drum (HLPF). The light hydrocarbon vapor is partially condensed and charged to the cold low pressure flash drum (CLPF). Liquid from the CHPS is also flashed in the CLPF to remove light hydrocarbons that are sent to the refinery fuel gas system. Liquids from the CLPF and the HLPF are separately fed to a fractionator to produce gas, naphtha, distillate and the hydrotreated residue oil [214A531, 214A532, 214A533].

The yield and product properties from an RCD Unionfining unit are shown in Tables 6.9 and 6.10 respectively. Feedstock is reduced crude (atmospheric residue) of Middle Eastern blended crude oils.

**Table 6.9**  
**YIELDS FROM HYDROTREATING A MIDDLE EASTERN BLEND REDUCED CRUDE OIL**

	<u>Wt%</u>	<u>Vol%</u>
<b>Feeds</b>		
Raw oil	100.00	100.00
Chemical H <sub>2</sub> consumption	1.29	[140m <sup>3</sup> /m <sup>3</sup> ]
<b>Products</b>		
H <sub>2</sub> S	3.91	
NH <sub>3</sub>	0.19	
C <sub>2</sub>	0.67	
C <sub>3</sub>	0.36	
C <sub>4</sub>	0.36	
C <sub>5</sub> -309°F (C <sub>5</sub> -154°C)	1.10	1.50
309-680°F (154-360°C)	14.70	16.70
680°F+ (360°C+)	80.00	84.20
<b>Total</b>	<b>101.29</b>	<b>102.40</b>

Source: 214A533

**Table 6.10**  
**PRODUCT PROPERTIES FROM HYDROTREATED MIDDLE EASTERN BLEND REDUCED CRUDE OIL**

	<u>Naphtha</u>	<u>Middle Distillate</u>	<u>Residue</u>
Boiling range, °F (°C)	C <sub>5</sub> -309 (C <sub>5</sub> -154)	309-680 (154-360)	680+ (360+)
Specific gravity	0.720	0.868	0.935
Sulfur, wt%	0.004	0.02	0.47
Nitrogen, vol%	0.004	0.02	0.17
V+Ni, ppm	---	---	18
Viscosity, cSt at 122°F (50°C)	---	2-3	151

Source: 214A533

## Eni Slurry Technology

Eni Slurry Technology (EST) integrates slurry hydrotreating at a relatively low temperature with solvent deasphalting (SDA). The heaviest residues or bitumen can be treated. Asphaltenes are converted by thermal decomposition into dealkylated and more aromatic intermediates. Hydrogen prevents recombination of the thermal produced free radicals, which avoids coke formation through condensation of aromatic clusters. The microcrystalline (micron sized) molybdenite ( $\text{MoS}_2$ ) highly dispersed catalyst is generated in-situ by thermal decomposition of an oil soluble precursor. The catalyst is very active in promoting hydrogenation reactions, which remove almost all the contaminants. The catalyst concentration is high (thousands of ppm) since the catalyst is recovered and recycled by solvent deasphalting.

Laboratory and continuous pilot plant of the whole process demonstrated overall hydrodemetallization of greater than 99%, hydrodesulfurization greater than 80% and Conradson carbon residue reduction greater than 96%. The reactor product is fractionated to remove the lighter products and the residue is sent to SDA. The SDA unit separates deasphalted oil for FCC or hydrocracker feedstock from the asphaltenes. The asphaltene product contains all the catalyst and is mixed with fresh feed and recycled to the hydrotreating reactor. The process is reviewed in PEP Review 99-2, *Eni Slurry hydroprocessing Technology for Diesel Fuel* (2003).

Stability determines the upper limit of thermal conversion processes such as visbreaking, delayed coking and hydrocracking. Above a certain level, asphaltenes become more aromatic and less soluble in the maltenes (as discussed in Section 5), which can create fouling problems and coke deposits. EST stops the hydrocracking reaction before the mixture becomes unstable. The asphaltenes are separated from the maltenes in the hydrotreating reactor effluent. The asphaltenes are blended with fresh feed, which restores stability [214A016, 214A246].

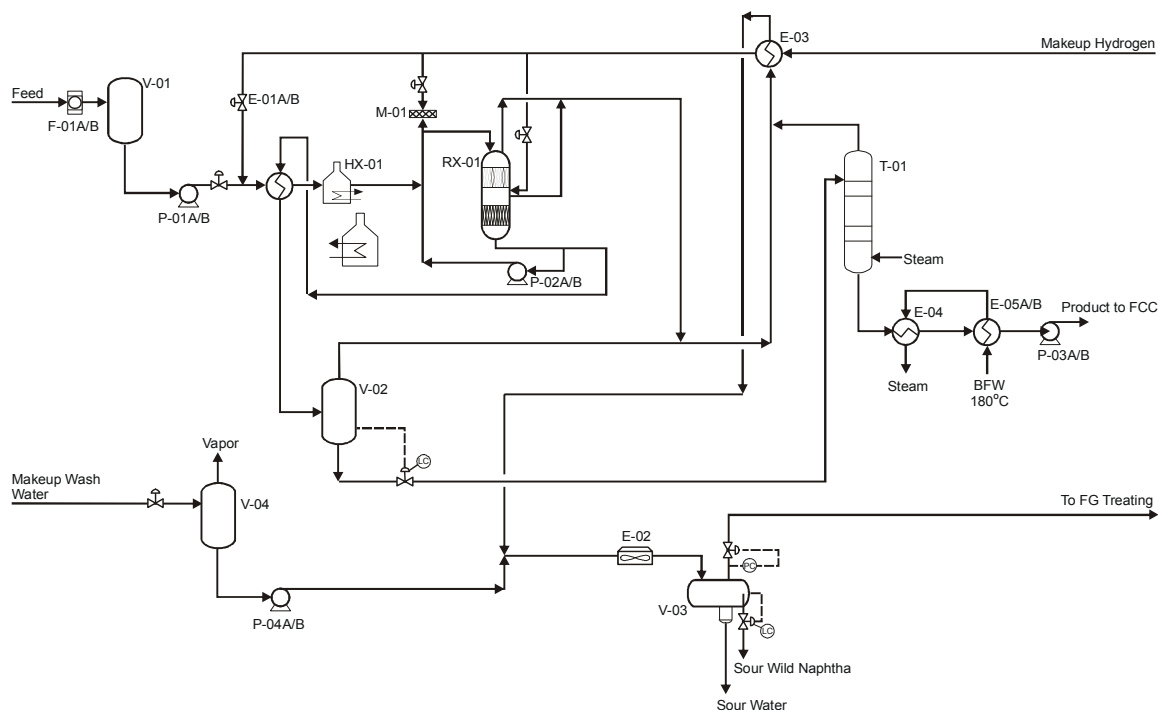
## IsoTherming™ Process

IsoTherming™ is a hydrotreating or mild hydrocracking process developed and commercialized by Process Dynamics, Inc. and acquired by DuPont. The process was first commercialized in a 2003 startup of revamped hydrotreater at the Giant Refinery in New Mexico to produce ultra low sulfur diesel fuel. Since then, three more middle distillate units and two mild hydrocrackers were contracted. Process Dynamics was awarded a contract in November, 2006 to revamp a 55,000 B/D gas oil hydrotreater to produce 800 ppm sulfur catalytic cracking feedstock.

The process, shown in Figure 6.6, is differentiated from other hydroprocesses by dissolving the hydrogen into the feed oil prior to the reactor rather than supplying the hydrogen as in a gas phase. This liquid feed allows higher reactor space velocities and hence smaller reactors than conventional reactors. Hydrogen recycle is eliminated. Liquid reactor effluent is recycled. The reactor operates more isothermally, which improves yields with less light ends made. The hydrogen mass transfer limitation is also removed so the reactor operates in a kinetically limited mode. An IsoTherming unit can be installed ahead of an existing hydrotreating reactor as at the Giant Refinery or be a stand-alone unit [214A029, US 6123835, US 6428686, US 6881326, US 2005 0082202].

Economics for the process hydrotreating vacuum gas oil for FCC feedstock are evaluated in Section 7.

**Figure 6.6**  
**ISOTHERMING™ PROCESS**



Source: 214A029

### Genoil Hydroconversion Upgrader

Genoil Inc. is developing the Genoil Hydroconversion Upgrader (GHU™) process for hydrotreating atmospheric or vacuum residues. The relatively simple and easy to operate process can be used as a field upgrader to produce a higher quality heavy oil product meeting pipeline specifications and avoid the need to ship costly diluents. Two key features of the process are low reactor pressure (1800 psi in one trial) and proprietary reactor liquid hydrocarbon mixing devices and other reactor internals. Feed and hydrogen are heated in a feed-effluent heat exchanger and process furnace (756°F (402°C) reactor temperature in one trial). The reactor typically has a guard HDM section and a HDS section. Reactor effluent is cooled as mentioned by exchange with the oil feed. Off gas and upgraded oil product are separated.

The process is designed to remove metals and maximize desulfurization (>90%), denitrogenation (>70%) and reduction of carbon residue (>90%) and produce a product of increased API gravity. Up to 90% conversion of the 663°F+ (350°C+) feed fraction is possible. Yields range from 0-10% naphtha, 1-20% kerosene and 21-47% diesel fuel [214A532, 214A553].

### Experimental Process

Bitumen is upgraded by a process using in situ generated hydrogen along with a dispersed Mo catalyst formed from phosphomolybdic acid. Emulsion breaking and upgrading occur in the same reactor. Hydrogenation is generated from water via the water gas shift reaction. A model compound, dibenzothiophene, was 84.6% converted at 716°F (380°C) and about 20 wt% water.

At an optimized water:CO mole ratio (1.35), HDS activity was higher with *in situ* H<sub>2</sub> compared to externally supplied hydrogen [214A261].

## RECYCLE H<sub>2</sub> PURIFICATION PROCESSES

Recycle H<sub>2</sub> gas has long been purified by removing H<sub>2</sub>S. The HPH<sup>SM</sup> Technology is being developed to remove methane, H<sub>2</sub>S and C<sub>2</sub>-C<sub>5</sub> hydrocarbons to provide much higher purity recycle H<sub>2</sub>. Hydrogen recovery using membrane separation is being practiced. Other H<sub>2</sub> purification processes have not met with commercial success in this application for the reasons summarized in Table 6.11.

**Table 6.11**  
**LIMITATIONS OF H<sub>2</sub> PURIFICATION PROCESSES AS APPLIED TO RECYCLE H<sub>2</sub>**  
**PURIFICATION**

<u>Hydrogen Purification Process</u>	<u>Significant Limitations &amp; Features</u>
Cryogenic	<ul style="list-style-type: none"> <li>Extremely cold temperatures, &lt;-250°F (&lt;-157°C)</li> <li>Operating pressure &lt; 1,000 psig</li> <li>Low flexibility for feed composition changes</li> </ul>
Pressure swing adsorption	<ul style="list-style-type: none"> <li>Low H<sub>2</sub> recovery (80 to 85%)</li> <li>Operating pressure &lt;600 psig</li> </ul>
Membrane Systems	<ul style="list-style-type: none"> <li>Extremely high pressure drop</li> <li>Lower purity and recovery (~90%)</li> </ul>
Sponge oil systems	<ul style="list-style-type: none"> <li>High circulation rate from high molecular weight oils</li> <li>Ineffective for methane absorption</li> <li>Limited purity improvement (~+2 mol% H<sub>2</sub>)</li> </ul>

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Source: 214A022

## Amine Treating

The inhibiting effects of H<sub>2</sub>S are minimized by amine scrubbing of the recycle H<sub>2</sub> gas stream. Amine treating is discussed in PEP Report 216, Acid Gas Treatment and Sulfur Recovery, (1997).

## HPH<sup>SM</sup> Technology

HPH<sup>SM</sup> Technology (Hydrogen Purification Hydroprocessing) is a process Saudi Aramco is developing for increasing the reactor's hydrogen partial pressure. Methane, H<sub>2</sub>S and C<sub>2</sub>-C<sub>5</sub> hydrocarbons contained in the flashed gas from the high pressure separator are chilled and absorbed in lean solvent in a counter-current absorber to produce a purified H<sub>2</sub> stream for recycling to the hydroprocessing reactor. The absorbed gases are released from the rich solvent by pressure reduction.

The sour flashed gas from the high pressure separator is first cooled by heat exchange with a colder, purified recycle H<sub>2</sub> stream and then chilled by propane refrigeration to about -4°F (-20°C). Any water in the gas is prevented from freezing by injecting ethylene glycol on the tube

(flashed gas) side of the exchangers and separating an ethylene glycol-water stream in a three-phase coalescer/separator before the chilled gas and condensed liquids enter the methane absorber column. Most of the  $\text{H}_2\text{S}$  in the flashed gas is also absorbed by the solvent. The rich solvent from the bottom of the absorber is reduced in pressure to separate the absorbed gases from the solvent. The lean solvent is the heaviest component. This flash regeneration of the solvent is essentially a heatless process. The regenerated lean solvent is pumped and cooled to remove the heat of pumping before entering near the top of the absorber. The recovered sour fuel gas ( $\text{C}_1\text{-C}_5$ ) is sent for further treating within the refinery. Alternatively, the fuel gas may be first sweetened by amine treatment to remove  $\text{H}_2\text{S}$ . The size of this amine treater is significantly smaller than the size required to treat the whole flash gas stream since the gas volume is less than 22% of the volume leaving the high pressure separator.

The flash regeneration process features include:

- Capability to operate at up to about 2,500 psig
- $\text{H}_2$  recovery of 96%+
- $\text{H}_2$  purity of 96%+
- Minimal pressure drop of less than 30 psig
- Very high feed gas composition change flexibility
- Uses standard low temperature carbon steel metallurgy
- Ethylene glycol dehydrogenation required

The recycle  $\text{H}_2$  purity may be increased to 96-98 mol%  $\text{H}_2$  from the 78-83 mol%  $\text{H}_2$  range leaving the high pressure separator. The pressure drop across the absorber system is less than 30 psig. Because the methane and heavier hydrocarbons are removed by the absorber, there is no need to purge a part of the  $\text{H}_2$  recycle stream, thus avoiding the purge loss. The overall recovery of  $\text{H}_2$  across the absorber is 96-98% [214A022, US 6740226].

## OPERATIONS

Process catalysts, yields and operating conditions are next briefly reviewed.

### Catalysts

Heavy oil containing high metals concentrations are typically hydrotreated using a series of catalysts that vary in activity, metals deposition capacity and pore volume as reviewed in Section 5. Metals (As, Si, Ni, V) deactivate HDT catalysts to varying degrees. Opportunity crudes can introduce arsenic or multiple (3-5) poisons with different metal removal mechanisms that significantly reduce cycle length due to quicker catalyst deactivation (see Section 5) [214A480, 214A546]. Hydrotreating catalysts, their properties and deactivation are reviewed in Section 5. Here, catalyst selection and the processes of catalyst loading, unloading and presulfiding are briefly addressed.

## Catalyst Selection

The guard bed catalyst is chosen for excellent HDM activity and high metals deposition capacity. Catalysts in the main reactors are also chosen to perform specific functions. For example, the catalyst system for a hydrotreater treating straight run atmospheric residue consists of the following sequence:

- Guard bed reactors: graded HDM catalyst
- First main reactor: transition reactor has both HDM and HDS graded catalyst
- Second main reactor: HDS and/or HDM and HDS activity catalyst
- Third main reactor: HDS catalyst having HDN activity [214A020]

Catalysts can be tailored for optimal performance with a particular feed. For example, a bed of NiMo consisting of four layers of different shapes and sizes (3/16 in. rings on top followed by layers of 1/8 and 1/16 cylinders with 1/8 in. cylinders at the bottom of the bed) greatly outperformed a bed of only 1/16 in. NiMo cylinders both in terms of activity and catalyst life. A catalyst bed arrangement common for a wide range of feeds does not exist. The use of mixed-bed, layered-bed and multiple catalyst-bed systems may reduce deactivation by metals [214A469].

Charging the optimum volumes of HDM catalyst and high activity catalyst required to achieve the hydrotreater product specifications is critical. Too little HDM catalyst results in premature deactivation of the high activity catalyst. Too much HDM catalyst does not enhance the process and often causes low hydrotreating activity and premature shutdown [214A155].

## Catalyst Loading and Unloading

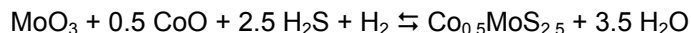
Catalyst loading is faster with supersacks instead of drums, reducing time by about 33%. This reduces the unit turnaround time by the days saved. Catalyst is available in super sacks of 700 kg, 600 kg and 500 kg per sack. Catalyst is either sock loaded or dense loaded. Sock loading gives loose packing while the dense method usually increases the packed catalyst density by 15%. Sock loading is conducted with close monitoring by the process engineers with checks including the type, proper leveling of each layer of catalyst and most importantly, the calculation of the loading density. According to one manufacturer, the maximum allowable variation of loading density compared to the estimated density is +2%. A higher loading density indicates the probability of catalyst breakage that will result in higher pressure drop. Lower density indicates a problem in leveling that will result in channeling during the run. Efficient loading practices have improved catalyst performance [214A020].

Effective dumping procedures are important for ensuring safety and reducing the turnaround time. The catalyst is dumped wet following soaking in soda solution normally from the 3<sup>rd</sup> and 4<sup>th</sup> reactors that normally are free flowing. Most of the catalyst from the guard and first reactors is very hard and not free flowing and must be jackhammered out. One contractor uses a 1 ft. diameter drilling machine to drill a hole from the top to the bottom before using jackhammers to breakup lumps, saving about one day compared to earlier practice [214A020]. The merits of wet versus dry dumping are summarized and inert entry discussed in a case study of the dumping of a C<sub>4</sub> selective hydrotreater's catalyst [214A060].



## Presulfiding

Presulfiding is a very important step in starting up a new catalyst charge. The metal oxides are exothermically converted to sulfides in the presence of hydrogen by a sulfur containing feed. Water is a reaction product. For CoMo catalysts, the reaction is:



Too severe sulfiding conditions can result in the formation of large sulfide particles. Three presulfiding methods are used: gas phase, liquid phase and ex-situ. The gas phase method generally uses a mixture of hydrogen and H<sub>2</sub>S or an organic sulfide such as methyl mercaptan. A disadvantage of this method is considerable temperature increases can develop. The catalyst temperature increase is limited by the liquid phase method. Under hydrogen pressure, an olefins free heavy naphtha or gas oil sometimes containing an organic sulfide is injected. Ex-situ presulfiding is conducted off site by a specialized company. Usually the catalyst is impregnated with a heavy sulfur compound and activated by heating. Only thermal activation is performed in the reactor. At least 40 hours of operating time can be gained by using ex-situ presulfided catalyst compared to in-situ presulfiding [214A044, 214A469].

Prior to the introduction of the sulfur feed to an ARDS unit, the reactor is pre-wetted, such as with a straight run light gas oil (about 1.3 wt% sulfur). The initial phase of presulfiding of a ARDS reactor is conducted with the light gas oil. The feed is then changed to heavy gas oil (about 2 wt% sulfur) from the crude unit for the remainder of the presulfiding. This method achieves stable reactor bed temperature and lower radial temperature differences, which extend catalyst life [214A020].

In liquid phase sulfiding of NiMo catalysts, feed and temperature are critical for achieving optimal hydrotreating catalyst activity. Straight run gas oil (1.70 wt%) spiked with 1 wt% dimethyl disulfide (DMDs) produced better commercial NiMo catalyst performance than the straight run gas oil alone, hydrodesulfurized straight run gas oil plus 1 wt% or 1.7 wt% DMS. Catalyst sulfided at 662°F (350°C) showed better activity than when sulfided at 608°F (320°C) or 556°F (290°C). Of the carbon on the catalyst following reaction, 50% is deposited during the sulfiding step [214A485].

## Yield and Selectivity

The major product of hydrotreating heavy oils is either low sulfur FCC or RFCC feedstock or low sulfur fuel oil. Hydrotreating conversion is about 33%, usually less. To reduce hydrogen consumption, conditions are chosen to minimize the production of naphtha and middle distillates. Yields obtained in hydrotreating at moderate pressure and temperature atmospheric and vacuum residues from Arabian Light and Arabian Heavy crude oils are presented in Table 6.12. The effect of hydrotreating severity on yields is shown in Tables 6.13 and 6.14 with two vacuum gas oils. The first is from a Kuwait crude oil; the second is from a Middle Eastern crude blend. Table 6.15 presents yields and properties obtained with an atmospheric residue feedstock.

**Table 6.12**  
**YIELDS AND SULFUR CONTENT OF HYDROTREATED ARABIAN LIGHT AND ARABIAN**  
**HEAVY ATMOSPHERIC AND VACUUM RESIDUE**

	<b>Arabian Light Residue</b>		<b>Arabian Heavy Residue</b>	
	<u>Atmospheric</u>	<u>Vacuum</u>	<u>Atmospheric</u>	<u>Vacuum</u>
<b>Feed Properties</b>				
Gravity, API	17.7	6.5	16.8	6.1
Sulfur, wt%	3.2	4.1	3.9	5.1
<b>Distillation, vol%</b>				
Boiling below 650°F (343°C)	5	---	16	---
Boiling below 1000°F (538°C)	67	1	60	10
H <sub>2</sub> chemical consumption, SCF/B	560	750	780	960
<b>Product Yields, vol%</b>				
C <sub>4</sub> -, wt%	3.5	---	4.7	---
C <sub>5</sub> -350°F (177°C)	1.4	5.7	1.4	6.4
350-650°F (177-343°C)	11.1	---	25.0	---
650-1000°F (343-538°C)	64.4	18.1	43.4	26.6
1000°F+ (538°C+)	24.3	78.4	31.4	69.9
<b>Sulfur Content, wt%</b>				
650°F+ (343°C+)	0.46	1.0	0.55	1.0
1000°F+ (538°C+)	0.97	1.2	0.88	1.25

Source: 214A557

**Table 6.13**  
**YIELDS OF TWO HYDROTREATED AND MILD HYDROCRACKED VACUUM GAS OILS**

<b><u>Feedstock</u></b>	<b><u>Iranian Light</u></b>	<b><u>Kuwait</u></b>
TBP cut point, °F (°C)	725-1058 (385-570)	725-1058 (385-570)
Specific gravity, 59°F/39°F (15°C/4°C)	0.927	0.926
Sulfur, wt%	1.80	3.02
Nitrogen, ppm	1400	950
Conradson Carbon Residue, wt%	0.5	0.5
Viscosity at 212°F (100°C), mm <sup>2</sup> /s	12	9
Aniline point, °F (°C)	187 (86)	178 (81)
Ni+V, ppm	3	3
Pour point, °F (°C)	111 (44)	90 (32)
ASTM D1160 distillation, °F (°C)		
IBP	572 (300)	572 (300)
10 vol%	743 (395)	743 (395)
30	783 (417)	783 (417)

**Table 6.13 (Concluded)**  
**YIELDS OF TWO HYDROTREATED AND MILD HYDROCRACKED VACUUM GAS OILS**

<u>Feedstock</u>	<u>Iranian Light</u>		<u>Kuwait</u>	
50	833 (445)		833 (445)	
70	898 (481)		898 (481)	
90	1000 (538)		1000 (538)	
EP	1085 (585)		1085 (585)	
725°F- (385°C-), vol%	8		8	
<u>Process</u>	<u>HDS</u>	<u>Mild HDCr</u>	<u>HDS</u>	<u>Mild HDCr</u>
Yields, wt%				
H <sub>2</sub> S	1.82	1.88	3.05	3.17
NH <sub>3</sub>	0.08	0.10	0.05	0.07
C <sub>1</sub>	0.10	0.24	0.05	0.20
C <sub>2</sub>	0.15	0.35	0.12	0.30
C <sub>3</sub>	0.17	0.40	0.15	0.40
iC <sub>4</sub>	0.07	0.30	0.03	0.26
nC <sub>4</sub>	0.11	0.40	0.09	0.34
C <sub>5</sub> -176°F (C <sub>5</sub> -80°C)	0.30	1.30	0.28	1.20
176-338°F (80-170°C)	0.90	3.80	0.81	3.60
338-725°F (170-385°C)	13.50	25.93	14.50	25.86
725°F+ (385°C+)	83.30	66.00	81.55	66.55
Total	100.50	100.70	100.75	100.95
H <sub>2</sub> consumption, wt%				
Chemical	0.50	0.70	0.75	0.95
Dissolution and losses	0.15	0.15	0.15	0.15
Total	0.65	0.85	0.90	1.10

Source: 214A044

**Table 6.14**  
**PRODUCT PROPERTIES FROM HYDROTREATING AND MILD HYDROCRACKING OF TWO**  
**VACUUM GAS OILS**

Process	Iranian Light		Kuwait	
	<u>HDS</u>	<u>Mild HDCr</u>	<u>HDS</u>	<u>Mild HDCr</u>
Naphtha, C <sub>5</sub> -176°F (C <sub>5</sub> -80°C)				
Specific gravity, 59°F/39°F (15°C/4°C)	0.730	0.730	0.730	0.730
Sulfur, wt%	<120	<50	<120	<50
Nitrogen, ppm	<20	<10	<20	<10
Bromine Number, g/100g	<2	<2	<2	<2
RON clear	58	60	58	60
Diesel, 338-725°F (170-385°C)				
Specific gravity, 59°F/39°F (15°C/4°C)	0.888	0.883	0.888	0.883
Sulfur, ppm	200	100	200	100
Bromine Number, g/100g	<2	<2	<2	<2
Cetane Number	40	43	40	43
Flash point, °F (°C)	149 (65)	149 (65)	149 (65)	149 (65)
Pour point, °F (°C)	16 (-9)	10 (-12)	16 (-9)	10 (-12)
Viscosity at 68°F (20°C)	6	5.6	6	5.6
Vacuum Distillate, 725°F+ (385°C+)				
Specific gravity, 59°F/39°F (15°C/4°C)	0.901	0.895	0.901	0.895
Sulfur, wt%	0.18	0.12	0.30	0.20
Nitrogen, ppm	840	600	560	400
Conradson Carbon Residue, wt%	0.1	0.1	0.1	0.1
Viscosity at 212°F (100°C), mm <sup>2</sup> /s	11	8.5	8	7.5
Aniline point, °F (°C)	198 (92)	207 (97)	194 (90)	205 (96)
Ni+V, ppm	0.5	0.5	0.5	0.5
Pour point, °F (°C)	113 (45)	207 (97)	97 (36)	205 (96)
Refractive index, 158°F (70°C)	1.483	1.478	1.484	1.478
ASTM D1160 distillation, °F (°C)				
IBP	608 (320)	608 (320)	608 (320)	608 (320)
5 vol%	716 (380)	707 (375)	716 (380)	707 (375)
10	743 (395)	743 (395)	743 (395)	743 (395)
30	779 (415)	770 (410)	779 (415)	770 (410)
50	824 (440)	815 (435)	824 (440)	815 (435)
70	894 (479)	887 (475)	894 (479)	887 (475)
90	995 (535)	986 (530)	995 (535)	986 (530)
95	1036 (558)	1022 (550)	1036 (558)	1022 (550)
EP	1085 (585)	1067 (575)	1085 (585)	1067 (575)

Source: 214A044

**Table 6.15**  
**YIELDS AND PROPERTIES FOR DESULFURIZATION OF KUWAIT CRUDE OIL**  
**ATMOSPHERE RESIDUUM**

<u>Yield, % of feed</u>	<u>Feed</u>	<u>1% Sulfur Fuel</u> <u>650°F+ (343°C+)</u>	<u>0.3% Sulfur Fuel</u> <u>375°F+ (191°C+)</u>	<u>0.1% Sulfur Fuel</u> <u>375°F+ (191°C+)</u>
H <sub>2</sub> S, wt%		3.07-3.14 {3.10} <sup>a</sup>	3.73-3.74 {3.73}	3.93-3.94 {3.93}
NH <sub>3</sub> , wt%		0.08-0.07 {0.08}	0.13-0.12 {0.12}	0.17-0.17 {0.17}
C <sub>1</sub> -C <sub>4</sub> , wt%		0.27-1.10 {0.62}	0.33-1.67 {0.89}	0.40-2.07 {1.14}
C <sub>5</sub> -375°F (191°C) naphtha, vol%		1.4-4.1 {2.6}	2.0-6.4 {3.8}	2.5-7.6 {4.6}
375-650°F (191-343°C) distillate, vol%		6.6-11.2 {8.5}	8.9-17.4 {12.5}	9.1-20.8 {14.0}
650°F+ (343°C+) residue, vol%		92.7-86.5 {90.1}	90.4-78.9 {85.6}	89.9-74.6 {83.5}
Chemical H <sub>2</sub> consumption, SCF/B		{497}	{650}	{725}
Residue product properties				
Gravity, API	16.6	20.5-22.1 {21.2}	22.0-23.9 {22.8}	22.5-24.4 {23.3}
Sulfur, wt%	3.8	1.0	0.32-0.35 {0.33}	0.10-0.11 {0.11}
Carbon residue, wt%	9.0	5.6-6.1 {5.8}	3.6-4.1 {3.8}	3.0-3.6 {3.2}
Nitrogen, wt%	0.22	0.17-0.19 {0.18}	0.13-0.15 {0.14}	0.09-0.11 {0.10}
Pour point, °F (°C)	60 (15.6)	65-55 (18-13)	70-20 (21- -7)	60-0 (16- -18)
		{60 (15.6)}	{35 (1.7)}	{15 (-9)}
Nickel, ppm	15	4.5-4.8 {4.6}	1.3-1.6 {1.5}	0.4-0.5 {0.5}
Vanadium, ppm	45	7.9-8.6 {8.2}	2.4-2.8 {2.6}	1.0-1.3 {1.2}
Viscosity, SUS at 210°F (99°C)	250	122-88 {108}	104-70 {90}	94-64 {81}

Source: 214A557

<sup>a</sup> Values in brackets, {}, indicate average values for cycle.

Fixed bed hydrotreating (ARDS/VRDS) converts 20% of the feed to distillates (diesel and gasoline). FCC feed hydrotreating reduces FCC catalyst aging and significantly increases the refinery profit margin when operated optimally. The order of sulfur and nitrogen concentrations in catalytically cracked liquid products corresponds to the order of the sulfur and nitrogen concentrations in the cracking feedstock. The better cracking selectivities for sulfur and nitrogen were obtained with a commercial octane enhancing FCC catalyst than for commercial bottoms cracking catalyst due to the former's higher hydrogen transfer ability [214A162, 214A547].

During HDN of heavy gas oil, the rate of removal of nonbasic nitrogen compounds is much lower than the removal of basic nitrogen compounds, resulting in the product containing mainly nonbasic nitrogen compounds even at severe conditions [214A245].

### Operating Conditions

The main operating variables for hydrotreating reactors are:

- Hydrogen partial pressure
- Weight average reactor temperature
- Liquid hourly space velocity

Important secondary variables are:

- Hydrogen purity and recycle ratio
- H<sub>2</sub>S partial pressure

For a grassroots unit, the design pressure and catalyst type are two important decisions. A higher pressure reduces reactor volume, reducing catalyst costs. Higher pressure also favors hydrogenation that improves HDS activity, aromatics saturation and conversion, which increases hydrogen consumption. The rate of catalyst deactivation is reduced. However, the operating pressure is limited due saturation of the catalyst and capital costs. Feed properties are important in setting the operating conditions [214A364, 214A529].

The effects of pressure, temperature, hydrogen-to-oil ratio and recycle gas rate and space velocity and fresh feed rate are described in [214A540].

Typical residuum trickle bed hydrotreating reactor temperatures range from 662-842°F (350-450°C) and pressures range from 725-2175 psi (5-15 MPa). One straight run atmospheric residue feed (12.8 API, 4.5 wt% S, 11.5 wt% Conradson carbon residue, 75-85 ppm (Ni+V) and 2500 ppm nitrogen) is preheated to about 536°F (280°C) by heat exchange. The feed then is filtered to remove sediments and carbonaceous material that could coke the fired feed heater and foul the catalyst. The feed is further preheated to 680°F (360°C) at the start-of-run by exchange and a finally a fired heater before entering the guard reactor. End-of-run WABT in this case is about 760°F (405°C). Excessive temperatures result in thermodynamic equilibrium constraints that reduce conversion. During a one year cycle life, the pressure drop across the guard reactor increased from less than 1 bar at startup through about 150 days to 13 bar at the end-of-run [214A020, 214A364, 214A487].

Typical operating conditions for heavy oil hydrotreating are summarized in Table 6.16. Operating conditions are becoming more severe as the product heteroatom specifications lower.

**Table 6.16**  
**TYPICAL OPERATING CONDITIONS AND PERFORMANCE RESULTS**

<b><u>Feedstock</u></b>	<b><u>VGO</u></b>	<b><u>Atmospheric Resid</u></b>	<b><u>Vacuum resid, Ebullating bed</u></b>
LHSV, h <sup>-1</sup>	1.0	0.25	1.0
Pressure, psig	1000	2200	2200
Treat gas rate, SCF/B	1500	3500	5000
H <sub>2</sub> Purity, vol%	85	85	85
H <sub>2</sub> consumption as 100% H <sub>2</sub> , SCF/B	300	700	1000
SOR Reactor Temperature, °F (°C)			
Inlet	650 (343)	660 (349)	810 (432) WABT
ΔT	40 (23)	70 (39)	0 (0)
Outlet	690 (366)	730 (388)	810 (432) WABT
Sulfur removal, %	88	85	80
Nitrogen removal, %	40	40	35
Cycle life, B/lb	70	104	4

Source: 214A525

The effects of reactor weighted average bed temperature and hydrogen pressure on the composition of a heavy oil feed are shown in Table 5.17 at constant LHSV. The increase in saturates indicates hydrogenation increases as temperature increases and as pressure increases. The polar compounds are almost completely removed by 730°F (388°C). The higher ring aromatics are reduced preferentially as the temperature increased and at higher pressure [214A147].

**Table 6.17**  
**EFFECTS OF HDT WABT TEMPERATURE AND PRESSURE ON PRODUCT**  
**HYDROCARBON TYPE**

	<u>Saturates, wt%</u>	<u>Aromatics, wt%</u>	<u>Polars, wt%</u>
Feedstock	28.3	64.4	7.3
Temperature effect at 2250 psig, 1.2 LHSV:			
700°F (371°C)	52.1	47.0	0.9
730 (388)	68.2	31.8	0
760 (404)	71.6	28.4	0
Pressure effect at 760°F (404°C), 1.2 LHSV			
1710 psig	60.4	39.3	0.3
2250	71.6	28.4	0

Source: 214A147

As the reactor pressure and temperature increase, more aromatics in Athabasca bitumen derived gas oil hydrotreated over a commercial NiMo on alumina catalyst are saturated. At low to moderate pressure (1102 to 1276 psi, 7.6 to 8.8 MPa) product aromatic content decreases sharply but with further increases in pressure, the rate of decrease in aromatic content slows and the aromatic concentration approaches and equilibrium value [214A364].

An exploratory study directly hydrotreated Maya heavy crude oil over an experimental NiMo on alumina-titania catalyst. Operating conditions ranged as follows: 768 to 1422 psi; 716°F to 788°F (380°C to 420°C); 0.5-1.5 h<sup>-1</sup> LHSV; and 5,000-10,000 ft<sup>3</sup>/B H<sub>2</sub>/oil ratio. Results showed in general that the synthetic crude oil product quality improved as the temperature, pressure and hydrogen-to-oil ratio increased. API gravity increased. Sulfur, nitrogen, metals (Ni + V), asphaltenes, Ramsbottom carbon residue decreased [214A267].

### Pressure

High reaction total pressure has a dramatic effect on hydrotreating, increasing both HDS and HDN conversions and decreasing the rate of catalyst deactivation. The maximum reactor pressure is limited not only by capital and operating costs but also physically by saturation that causes the activity to plateau with further increases in pressure. Laboratory data hydrotreating Athabasca gas oil over commercial NiMo on alumina catalyst (Table 6.18) show the effect of pressure. Changes in conversion of sulfur are not as significant as the changes in conversion of nitrogen. The reason may be the prominence of the direct HDS pathway, which is not much effected by pressure, over the prehydrogenation pathway (Section 5). As the pressure is increased, selectivity for HDN increases relative to HDS. The selectivity for basic nitrogen removal generally decreases with increasing pressure, an initial increase seen in the data from 6.5 to 7.6 MPa may be due to competitive adsorption of BN at low temperatures and a sharp

increase in nonbasic nitrogen HDN conversion at high pressures. Conversions of both sulfur and nitrogen compounds approach equilibrium levels at 11 MPa. Table 6.19 shows the light cycle oil increases with an increase in pressure while heavy gas oil remains almost unchanged and vacuum gas oil decreases. In summary, sulfur and basic nitrogen removal can be removed at high selectivity at low pressure while selectivities for total nitrogen and nonbasic nitrogen are highest at high pressure [214A364].

**Table 6.18**  
**EFFECT OF TEMPERATURE AND PRESSURE ON HYDROTREATING OF ATHABASCA**  
**BITUMEN GAS OIL<sup>a</sup>**

Pressure,  <u>Psi (MPa)</u>	<u>Sulfur</u>	<u>Conversion, wt%</u>			<u>Selectivity, wt/wt</u>	
		<u>Total Nitrogen</u>	<u>Basic Nitrogen</u>	<u>Non-basic Nitrogen</u>	<u>S<sub>S/TN</sub></u> <sup>b</sup>	<u>S<sub>BN/NBN</sub></u> <sup>b</sup>
Hydrotreating at 680°F (360°C)						
943 (6.5)	86.2	38.0	46.5	33.4	30.6	76.8
1102 (7.6)	87.7	42.2	54.9	35.1	28.1	86.4
1276 (8.8)	89.6	46.5	63.1	37.3	26.1	93.6
1595 (11.0)	87.7	54.0	65.6	47.5	22.0	76.2
Hydrotreating at 716°F (380°C)						
943 (6.5)	93.7	52.3	71.8	41.6	24.2	95.4
1102 (7.6)	94.8	59.5	78.9	48.7	21.5	89.4
1276 (8.8)	95.7	68.1	85.8	58.4	19.0	81.2
1595 (11.0)	95.2	75.0	87.4	68.2	17.2	70.8
Hydrotreating at 752°F (400°C)						
943 (6.5)	97.5	68.4	89.7	56.6	19.3	87.7
1102 (7.6)	97.8	79.1	93.9	69.4	16.9	74.7
1276 (8.8)	98.4	86.9	96.6	81.5	15.3	65.5
1595 (11.0)	98.6	91.1	97.1	87.8	14.6	61.1

Source: 2114A364

<sup>a</sup> Commercial NiMo/alumina catalyst at 1 h<sup>-1</sup> LHSV, 600 mL/mL H<sub>2</sub>/oil ratio.

<sup>b</sup> S<sub>S/TN</sub> denotes selectivity for removal of sulfur relative to total nitrogen; S<sub>BN/NBN</sub> denotes selectivity for removal of basic nitrogen relative to nonbasic nitrogen where Si/j = wt% of species j removed/wt% of species j removed.



**Table 6.19**  
**EFFECT OF TEMPERATURE AND PRESSURE ON PRODUCTS OF HYDROTREATING OF**  
**ATHABASCA BITUMEN GAS OIL<sup>a</sup>**

Pressure,  <u>Psi (MPa)</u>	Product Content, wt%				
	Gasoline	Kerosene	LCO <sup>b</sup>	HCO <sup>c</sup>	VGO <sup>d</sup>
	IBP-401°F <u>IBP-205°C</u>	401-500°F <u>205-260°C</u>	500-600°F <u>260-315°C</u>	600-797°F <u>315-425°C</u>	797-1112°F <u>425-600°C</u>
Feedstock	0	2	8	45	45
Hydrotreating at 680°F (360°C)					
943 (6.5)	1	6	13	44	36
1102 (7.6)	1	6	13	45	35
1276 (8.8)	1	5	14	44	35
1595 (11.0)	1	6	13	45	35
Hydrotreating at 716°F (380°C)					
943 (6.5)	2	6	15	44	33
1102 (7.6)	2	7	14	44	33
1276 (8.8)	3	6	15	44	32
1595 (11.0)	2	7	15	44	32
Hydrotreating at 752°F (400°C)					
943 (6.5)	4	8	16	44	28
1102 (7.6)	5	8	16	44	27
1276 (8.8)	5	8	17	43	27
1595 (11.0)	5	8	17	43	27

Source: 2114A364

<sup>a</sup> Commercial NiMo/alumina catalyst at 1 h<sup>-1</sup> LHSV, 600 mL/mL H<sub>2</sub>/oil ratio.

<sup>b</sup> LCO

<sup>c</sup> Heavy Gas Oil

<sup>d</sup> Vacuum Gas Oil

The system pressure largely determines the hydrogen partial pressure. With heavy liquid feeds, high reactor pressure favors the dissolution of hydrogen through the liquid film to the catalyst surface. The H<sub>2</sub> partial pressure is a critical process design factor that depends upon the molecular weight of the feed and desired reactions: the heavier the feed, the higher the H<sub>2</sub> partial pressure. The more difficult the reaction (for example, deep hydrogenation > mild hydrogenation > HDS), the higher the H<sub>2</sub> pressure used. As the hydrogen concentration on the surface of the catalyst rises, the rate of reaction accelerates. Once the surface is saturated, further increases in partial pressure have little effect on the reaction rate. H<sub>2</sub> promotes forward reactions and minimizes side reactions such as gas formation and coking. This results in long-lasting, stable operation. The H<sub>2</sub> partial pressure at a total fixed pressure depends also upon the hydrogen recycle rate, the use of recycle hydrogen purification, make-up hydrogen purity and the feed flow rate. The H<sub>2</sub> partial pressure is chosen to increase the activity to minimize the amount of catalyst and reactor size and to minimize thermal cracking and coke formation. In summary, benefits of increased H<sub>2</sub> partial pressure include [214A022, 214A044, 214A045]:

- Longer catalyst life
- Heavier feed processing capability
- Higher throughput capability
- Higher conversion capability
- Better distillate quality
- Possibility of purge H<sub>2</sub> elimination

### Bed Temperature

Hydrotreating units are operated at constant pressure to produce constant product heteroatom content. Temperature is usually the easiest and most cost effective parameter to control the hydrotreater. The guard reactor temperature is hotter than the main reactors to favor HDM reactions. The lower temperature of the main reactors favors the hydrogenolysis and partial hydrogen reactions. Due to the exothermic hydrogenation reactions, fixed bed reactors are adiabatic reactors. Temperature is controlled by injecting quench H<sub>2</sub> streams between the beds. Ebullating bed and slurry reactors operate almost isothermally [214A037, 214A045].

To counteract catalyst deactivation, the reactor temperature is incrementally increased during the catalyst life. Since hydrotreating reactions are exothermic, a rising temperature gradient forms within the catalyst bed. The weight average temperature ( $T_m$ ) is defined as:

$$T_m = (t_1v_1 + t_2v_2 + \dots + t_nv_n)/V$$

where the subscripts designate thermocouple locations and V is the total catalyst volume:

$$V = v_1 + v_2 + \dots + v_n. \text{ (Constant catalyst density is assumed.)}$$

The weight average temperature is approximated by the average of the bed's inlet and outlet temperatures. Increasing temperature usually increases both the rate of reaction and the conversion [214A044, 214A364].

The end-of-run temperature is the maximum temperature the catalyst can tolerate, generally between 752°F and 770°F (400°C and 410°C). At hotter temperatures, thermal cracking and coking become excessive and can not be moderated by raising the H<sub>2</sub> partial pressure. A limited amount of thermal cracking of vacuum residues makes vanadium and nickel accessible to the hydrogenolysis reactions.

The start-of-run temperature depends upon the feedstock properties and is chosen to provide a reasonable reaction rate and the desired run length, generally 1 year for residue feedstocks. The start-of-run temperature rises with the feed molecular weight since heavier fractions contain harder to react sulfur molecules. The start-of-run temperature strongly influences the performance and catalyst life [214A044, 214A045].

Laboratory data hydrotreating Athabasca gas oil over commercial NiMo on alumina catalyst (Table 6.18) show the rate of HDN increases faster than the rate of HDS as the temperature is increased. Conversion of sulfur compounds at all temperatures was higher than the conversion of nitrogen compounds due to the ease of converting nonrefractory sulfur compounds. Selectivity for nonbasic nitrogen removal was higher than that for basic nitrogen removal at all temperatures. Generally the selectivity for basic nitrogen removal relative to nonbasic nitrogen removal decreased at temperature increased. The highest HDS selectivity occurred at the lowest temperature whereas the highest HDN conversion for both total nitrogen and nonbasic nitrogen was the hottest. Additional data at hotter temperatures showed the optimal temperature

recommended was 770°F (410°C). Table 6.19 shows increasing temperature increases the production of light liquid products (gasoline, kerosene and light cycle oil). Heavy gas oil remains almost unchanged with increasing temperature. Vacuum gas oil decreases due to mild hydrocracking with increasing temperature [214A364].

### Liquid Hourly Space Velocity

The liquid hourly space velocity (LHSV), the ratio of the feed volumetric flow rate to the catalyst volume, depends upon the type of feed, catalyst activity and hydrogen partial pressure. There is a tradeoff between LHSV and the temperature raise between the start- and end-of-run [214A044].

Laboratory data hydrotreating Athabasca gas oil over commercial NiMo on alumina catalyst (Table 6.20) show conversion of sulfur is greater than that of nitrogen but conversion of both sulfur and nitrogen compounds increases as the LHSV decreases. The conversion of basic nitrogen compounds is generally much higher than that of nonbasic nitrogen compounds. Changes of LHSV at high temperature did not have much effect on sulfur conversion (<5 wt%). Selectivity for sulfur removal increases as the LHSV increases, which suggests HDS is faster than HDN as expected since HDN is a two step process (hydrogenation and denitrogenation). At low LHSV, nitrogen removal selectivity increases while sulfur removal selectivity decreases. At all three temperatures, basic nitrogen removal shows a maximum (that shifts to higher pressures as the temperature increases according to the authors). In summary, a low LHSV favors maximum HDS and HDN [214A364].

**Table 6.20**  
**EFFECT OF LHSV ON HYDROTREATING OF ATHABASCA BITUMEN GAS OIL <sup>a</sup>**

LHSV, h <sup>-1</sup>	Sulfur	Conversion, wt%			Selectivity, wt/wt	
		Total	Basic	Non-basic	S <sub>S/TN</sub> <sup>b</sup>	S <sub>BN/BN</sub> <sup>b</sup>
		Nitrogen	Nitrogen			
Hydrotreating at 680°F (360°C)						
0.5	92.3	64.7	78.9	56.9	19.3	76.6
1.0	89.6	46.5	63.1	37.2	26.1	93.6
1.5	83.1	35.0	43.6	30.2	32.1	79.8
2.0	77.6	36.0	32.2	38.0	29.2	46.8
Hydrotreating at 716°F (380°C)						
0.5	97.3	83.0	93.9	77.1	15.8	67.3
1.0	95.7	68.1	85.8	58.4	19.0	81.2
1.5	91.9	53.1	69.3	44.1	23.4	86.8
2.0	87.9	48.7	56.5	44.3	24.4	70.4
Hydrotreating at 752°F (400°C)						
0.5	98.6	95.9	98.9	94.2	13.9	58.0
1.0	98.4	86.9	96.6	81.5	15.3	65.5
1.5	96.5	71.1	87.8	61.9	18.4	78.4
2.0	93.4	60.1	78.0	50.2	21.0	85.8

Source: 214A364

<sup>a</sup> Commercial NiMo/alumina catalyst at 1276 psi (8.8 MPa), 600 mL/mL H<sub>2</sub>/oil ratio.

<sup>b</sup> S<sub>S/TN</sub> denotes selectivity for removal of sulfur relative to total nitrogen; S<sub>BN/BN</sub> denotes selectivity for removal of basic nitrogen relative to nonbasic nitrogen where S<sub>i/j</sub> = wt% of species j removed/wt% of species j removed.

## **H<sub>2</sub> Ratio (Recycle Ratio)**

High H<sub>2</sub> partial pressures are maintained by recycling of H<sub>2</sub> above the amount chemically consumed. Recycling H<sub>2</sub> from the separator drum allows the maintenance of high H<sub>2</sub> partial pressure across the reactor(s). The recycle gas also promotes mixing in the reactor and turbulence in the furnace and heat exchangers, which improve the heat transfer and helps minimize coke deposits. The temperature of the reactor beds is controlled by the injection of cold recycle gas between each bed. This quenching allows operation close as possible to isothermal conditions within the bed and minimizes premature catalyst aging by reducing the bed temperature [214A044]. The recycle ratio depends upon the feed, catalyst and hydrogen purity. The benefits of increased H<sub>2</sub>/feed ratio have a maximum beyond which the disadvantages of decreasing catalyst contact time exceed the advantages of a large H<sub>2</sub> excess. The extent of desulfurization and denitrogenation decrease [214A045].

## **H<sub>2</sub>S Concentration**

Hydrogen sulfide in the recycle gas has an inhibiting effect of HDS and hydrogenation reactions. H<sub>2</sub>S can be partially or totally removed by amine scrubbing for deep hydrodesulfurization. Leaving some H<sub>2</sub>S in the recycle gas helps keep the catalyst sulfided [214A044].

## **Optimization of Conditions**

An optimization study of HDM and HDS of one atmospheric residue (12.5 API, 4.45 wt% sulfur, 88 ppm (Ni+V), 2800 ppm nitrogen and 12 wt% Conradson carbon) modeled four industrial reactors in series (guard reactor and first main reactor HDM catalyst, HDS catalyst in the second and third main reactors). The study concluded:

- Decreasing the target degree of desulfurization was always more economical when increasing throughput (LHSV).
- The optimum degree of desulfurization was linearly related to LHSV, which provided additional flexibility in implementing the optimization results.
- The catalyst cost dominated the overall cost at high severity operation; operating cost dominated at low severities.
- Operating at higher throughput and simultaneously producing a lower sulfur product is more economical if catalyst prices drop and/or increased benefits are realized due to deeper desulfurization [214A237].

In hydrotreating of FCC feedstock, for maximum benefit, the operation of the hydrotreater needs to be optimized in conjunction with the operation of the FCCU. Each refinery will have a specific optimization solution depending on relative capacities, supplement feedstocks, hydrogen availability and cost and relative product values. Operation for FCC feedstock hydrotreating may differ from the operation when hydrotreating fuel oil. Before the requirement for very low sulfur gasoline, optimizing the two units largely involved metals removal with benefits reducing nitrogen and carbon residue that could be met at conditions unfavorable to maximum desulfurization. Operating the FCC pretreater at hotter temperature to reduce sulfur to a lower level decreases the saturation of polynuclear aromatics since saturation is limited by equilibrium. Higher polynuclear aromatics in the FCCU decrease the benefits of higher FCCU conversion and increased yields of motor fuels. The Topsoe Aroshift process is technology using a special catalyst that lowers sulfur and polynuclear aromatics to revamp existing FCC pretreaters to reverse the effects of increased severity [214A104]. Sulfur reduction and metals management in both the hydrotreater and RFCCU are discussed in [214A018].

The complexity of combinations of the two units presents the opportunity to improve refinery economics. Results of a pilot plant study involving both processes show both the hydrotreating catalyst system and the operating strategy are critical to producing the highest quality FCC feedstock. In general, NiMo catalysts were found to produce better FCC feed having lower nitrogen and polynuclear aromatics. Operating the hydrotreater to remove nitrogen and polynuclear aromatics needs to be balanced against increased hydrogen consumption and shorter cycle length. Using a sulfur reducing additive in the FCCU can extend the hydrotreater catalyst life when operating in the polynuclear aromatics reduction mode since sulfur removal and polyaromatics removal respond differently to rising hydrotreater temperature as the catalyst ages [214A578].

Optimum hydrotreating of FCC feedstock occurs at about 40% aromatic saturation. About 90% desulfurization is by the hydrotreater; the FCCU removes about an additional 40% of the remaining sulfur. Once the sulfur level constraint for ultra low sulfur gasoline is met, typically the refinery gasoline pool octane level sets the optimal hydrotreating severity. Even at severe hydrotreating conditions, LCO will require further hydrotreating to meet the near zero sulfur diesel fuel specification [214A064].

## DESIGN CONSIDERATIONS

Developments in process design are briefly discussed next, starting with data on hydrogen consumption. Brief discussions of H<sub>2</sub>S removal, reactor internals, experimental reactor control, reactor models, materials of construction and heat integration follow.

### Hydrogen Consumption

Hydrogen consumption during hydrotreating varies with feedstock. Table 6.21 shows the hydrogen consumption for various heavy oil feedstocks. Additional hydrogen consumed by metals is indicated in Table 6.22 and by nitrogen in Table 6.23.

**Table 6.21**  
**HYDROGEN CONSUMPTION DURING HYDROTREATING OF VARIOUS FEEDSTOCKS**

	<b>Gravity, API</b>	<b>Sulfur, wt%</b>	<b>Nitrogen, wt%</b>	<b>Conradson Carbon Residue, wt%</b>	<b>Hydrogen, SCF/B</b>
West Texas, atmospheric	17.7-17.9	2.2-2.5	---	8.4	520-670
Kuwait, atmospheric	15.7-17.2	3.7-4.0	0.20-0.23	8.6-9.5	470-815
Venezuela, atmospheric	15.3-17.2	2.1-2.2	---	9.9-10.4	425-730
Khafji, atmospheric	15.1-15.7	4.0-4.1	---	11.0-12.2	725-800
Boscan (whole crude)	10.4	5.6	0.52	---	1100
West Texas, vacuum	10.0-13.8	2.3-3.2	---	12.2-14.8	675-1200
Arabian Light, vacuum	8.5	3.8	---	---	435-1180
Tia Juana, vacuum	7.8	2.5	0.52	21.4	490-770
Bachaquero, vacuum	5.8	3.7	0.56	23.1	1080-1260
Kuwait, vacuum	5.5-8.0	5.1-5.5	---	16.0	290-1200
Khafji, vacuum	5.0	5.4	---	21.0	1000-1100
Venezuela, vacuum	4.5-7.5	2.9-3.2	---	20.5-21.4	825-950

Source: 214A557

**Table 6.22**  
**ADDITIONAL HYDROGEN CONSUMPTION CAUSED BY METALS DURING**  
**HYDRODESULFURIZATION**

<u>Metals (Ni+V), ppm</u>	<u>Corrections (%) to hydrogen consumption</u>
0-100	-2
200	1
300	2.5
400	4
500	6.5
600	9
700	12
800	16
900	21
1000	28
1100	38
1200	50

Source: 214A557

**Table 6.23**  
**ADDITIONAL HYDROGEN CONSUMPTION CAUSED BY NITROGEN DURING**  
**HYDRODESULFURIZATION**

	<b>Additional hydrogen required</b>	
	<u>Mol H<sub>2</sub>/compound</u>	<u>SCF/B feed</u>
Saturated amines	1	83
Pyrrolidine	2	167
Nitriles, pyrroline, alky cyanides	3	250
Pyrrole, nitroparaffins	4	334
Analine, pyridine	5	417
Indole	7	584

Source: 214A557

## H<sub>2</sub>S Removal

Trickle bed microreactor tests using the same total amount of commercial NiMo/alumina catalyst in both single- and two-stage reactors showed advantages of interstage H<sub>2</sub>S removal with heavy gas oil derived from Athabasca bitumen. H<sub>2</sub>S inhibits both HDS and HDN. Conversion of nonbasic nitrogen increased 12.6 wt% but not much effect on basic nitrogen. The gain in HDS and HDN activities decreased with increasing temperature and pressure. Langmuir-Hinshelwood based kinetic HDS and HDN models developed for the two-stage process adequately predicted the experimental data [214A391].

A two-stage micro trickle bed hydrotreating reactor simulation was developed for Athabasca bitumen-derived heavy gas oil to study the effects of H<sub>2</sub>S on HDS and HDN. The catalyst was a commercial NiMo on alumina diluted with silicon carbide particles to prevent axial dispersion. The simulation contained a one dimensional pseudo-homogeneous mass transfer model, a two

dimensional (axial and radial) heat transfer model and a Langmuir-Hinshelwood based kinetic model. The mass transfer model included the effects of variables including temperature, catalyst loading or liquid hourly space velocity on the trends of H<sub>2</sub>S generation and conversion of sulfur and nitrogen compounds along the catalyst bed. The case with 25% of the catalyst in the first stage reactor and 75% in the second stage reactor using inter-stage H<sub>2</sub>S removal gave the best HDN and HDS activities. In all experimental runs were at was 1.0 h<sup>-1</sup> LHSV, 8.8 MPa pressure and 600 vol/vol H<sub>2</sub>-to-oil ratio. Doubling the catalyst weight (0.5 h<sup>-1</sup> LHSV) and operating at 1207°F (653°C) with inter-stage H<sub>2</sub>S removal gave product oil containing 6 ppm sulfur and 179 ppm nitrogen. Without H<sub>2</sub>S removal, only 49 ppm sulfur and 302 ppm nitrogen product oil could be obtained [214A360].

H<sub>2</sub>S's effect on a commercial VGO reactor's HDS over a NiMo catalyst as a function of H<sub>2</sub>S concentration shows the decrease in removal from 0 to 2 mol% H<sub>2</sub>S is smaller than the linear decrease seen at H<sub>2</sub>S concentrations from 2 to 10 mol%. HDS decreased from over 98% without H<sub>2</sub>S to about 60% at 10 mol% H<sub>2</sub>S [214A489].

### Reactor Internals

If low sulfur specifications are to be met, it is essential that mixed bed reactor internals must uniformly mix the feedstock or effluent from the preceding bed with hydrogen and distribute the mixture evenly across the next bed. General distribution tray design up to the late 1990's is reviewed in [#24505].

The upper bed layer of the first fixed bed reactor traditionally consists of guard material to retain particles in the feed. The particles often are iron but may be salt, coke from furnace tubes, sediments, catalyst fines, solids formed by reaction of additives. Particle diameters range up to over 100 microns. If not retained, the particles would deposit on the outer surface of the catalyst or between catalyst particles and raise the bed pressure drop. The guard material (<5 wt% of the bed) has no or little catalytic activity and macropores of about 100 micron diameter. Capacity for iron is about 20 times that of hydrotreating catalyst [214A037, 214A045].

Major vapor-liquid distributors are either overflow or suction types. Overflow types (examples: long/short pipe, bevel pipe and box type with V notch) separate gas and liquid streams. Liquid exits through an overflow hole while gas creates shear force to disperse the liquid into droplets. Even distribution with good microscopic homogeneity over the area is obtained by a single distributor. However, the distribution performance is very sensitive to levelness of the tray. In suction type distributors (examples: bubble cap, venture type, vapor lift, suction stream breaker, and CZ type distributor), both liquid and gas flow through the same channels. The suction of the gas flow mainly breaks and distributes the liquid. Good distribution with good macroscopic homogeneity is obtained. Since the motive force of the overflow is generated by the gas suction, the performance is less sensitive to the tray levelness than the overflow types. A center liquid stream, accompanied by a small liquid stream spray angle, beneath a single distributor tray is hard to disperse under practical conditions. A novel bubble cap distributor having a swirl flow device with many blades overcomes these disadvantages at the expense of slightly higher pressure drop that is still within the recommended range [214A556].

Principals of development and optimization at IFP of fluid distribution for diesel hydrotreating to near zero sulfur specifications appear applicable to heavier feedstocks [214A506]. UOP has recently introduced the Ultramax reactor internals with a new design to be introduced in 2007 that provides superior liquid distribution and improved performance over a wide range of operating conditions. A case study by Haldor Topsoe of the improvement of distribution in heavy gas oil hydrotreaters discusses how peak temperatures were reduced and radial temperature differences reduced to less than 1.8-3.6°F (1-2°C), allowing the reactor to operate closer to

design temperature limit with a 10% increase in unit capacity [214A012]. Haldor Topsoe also recently commercialized new reactor internals, which, since they are simpler to install, reduce on-site installation time thereby improving hydrotreating unit utilization [214A529].

An estimated 30% of all hydroprocessing units are limited by reactor fouling problems, the single largest common problem. Several approaches are used to minimize fouling. A filter tray from Shell Global Solutions (HD-trays) has demonstrated significant improvement in reactor pressure drop tolerance and unit cycle life when previous attempts failed. Reactor cycle life improvement of 100% is common. In one case, a 30°F (17°C) lower start of run WABT and a 2.5 fold reduction in deactivation rate resulted in a tripling of cycle length. Crystaphase Products Inc. provides reticulated ceramics in a wide range of pore sizes specifically designed to filter particles in a target size from 1 to 2000 microns. This technology creates tortuosity that separates particles by inertia as the fluid is forced to change directions. Particles are captured in the pores of the material, which has 85% internal void volume for high storage capacity before plugging. Large-sized ceramics result in large open channels between porous disks, such that after the internal voids are full, flow is not restricted so pressure drop does not increase [214A529, 214A546].

Understanding the temperature measurement system, their accuracy and responsiveness are important in critically evaluating reactor internals with tight tolerances, catalyst loading results and process optimization and proper response to potentially unsafe conditions. The main types of temperature measurement systems and the parameters affecting their accuracy and their impact on meeting low sulfur fuel requirements are discussed [214A024].

### **Reactor Control (Experimental)**

A constrained model predictive control significantly improved pilot plant control compared with PID-based control scheme. The pilot fixed bed reactor was operated with the same catalyst (a commercial MoNiP/alumina type catalyst) and under the same operating conditions as an actual refinery atmospheric residue hydrotreating process. Conditions depended upon the feedstock properties and the desired product purity. The control objective was to maintain product sulfur content at a desired limit. The CMPC controller optimized the reaction zone temperatures to achieve the sulfur target. The authors considered the pilot plant to be a test for implementing online optimum control and nonlinear control strategies for industrial hydrotreaters [214A412].

### **Reactor Models**

A trickle bed reactor model simulated the behavior of a commercial NiMo catalyst during nonisothermal operation of a commercial reactor. The model included HDS, HDN and hydrodearomatization reactions as a function of temperature. Langmuir-Hinshelwood kinetics described HDS. A consecutive reaction scheme modeled HDN in which nonbasic compounds were hydrogenated first to basic nitrogen compounds that react further to eliminate nitrogen from the molecule. A first order reversible reaction kinetic model represented aromatics hydrogenation. Correlations based on two-film theory determined the mass transfer coefficients. The kinetic parameters were estimated from pilot plant data [214A489].

A lumped dynamic simulation model developed from commercial data from 14 hydrotreaters accurately simulates local disturbances and performs well over the entire run length (start, middle and end of run). The model accounts for intrinsic reaction rate changes from catalyst deactivation, feed properties and operating changes to provide useful information such as required operating temperature, optimal hydrogen partial pressure (function of operating pressure and hydrogen purity) and chemical hydrogen consumption. The model can be used to



demonstrate tangible economic benefits such as increasing hydrogen use to increase run length [214A554].

### **Materials of Construction**

The chemical environment of the reactors and distillation sections contains H<sub>2</sub>, sulfurous hydrocarbons, H<sub>2</sub>S, ammonia and water at elevated pressure and temperature. Above 500°F (260°C) at high hydrogen partial pressure, chromium-molybdenum steels with stainless steel (18Cr-10Ni) cladding are used to avoid decarburization and cracking and to control corrosion by H<sub>2</sub>S. The thickness of the stainless steel cladding is a function of temperature, H<sub>2</sub>S partial pressure and the required equipment lifetime (10-20 years). Below 500°F (260°C), carbon steel or low Cr-Mo steel is used. Code requirements should be followed in the presence of free water and H<sub>2</sub>S [214A044].

One refiner reported their experience with unusual corrosion of reactor effluent air cooler tubes [214A576].

### **Heat Integration**

The process alternatives for heat integration of a two-stage heavy crude hydrotreater unit were studied. Four cases, each a combination of quenching with heat exchangers, were evaluated. One H<sub>2</sub> quench in each of the reactors and three heat exchangers to preheat the feed with the stripper bottoms stream, the desalted crude and the heavy crude fraction was the best case from energetic considerations [214A322].

### **FCC FEED HYDROTREATING**

FCC gasoline is typically the main producer of gasoline in a FCC refinery, typically providing from 30% up to 50% of the gasoline but contributing about 90% of the gasoline pool sulfur [214A103, 214A368]. To meet low environmental emission gasoline and diesel fuel sulfur and aromatic (cetane number) specifications, sulfur can be removed and aromatics reduced either by hydrotreating the FCCU feedstock or individually hydrotreating each FCC product. Although the benefits can vary with feedstock, hydrotreater severity and FCC operation mode, hydrotreating the FCC feed offers FCC yield and operational improvements post hydrotreating can not provide. Gasoline hydrodesulfurization has the disadvantage of reducing the gasoline octane rating.

Hydrotreating of FCC feed is performed mainly to remove sulfur, metals and carbon residue to improve the FCCU performance. Ultra low sulfur gasoline and near zero sulfur diesel fuel requirements have increased the benefits of severe feed hydrotreating. With sufficient hydrotreating, the FCCU remains the primary conversion process capable of producing ultra low sulfur gasoline and LCO that is easier to hydrotreat for blending to make near zero sulfur diesel fuel. As briefly discussed in this Section's subsection on Optimization of Conditions, the degree of removal must be optimized over both the hydrotreater and the FCCU to minimize the total catalyst cost and maximize product yields while meeting the refinery's product specifications.

Hydrotreating FCC feed directly and indirectly benefits the FCCU:

- Removing sulfur and nitrogen from the FCCU feedstock reduces the SO<sub>x</sub> and NO<sub>x</sub> emissions from the FCC regenerator. Pretreating the FCC feed also produces lower emissions than post treating the FCC products [214A072, 214A074].
- Conversion to naphtha and lighter products increases. The poisoning effect of nitrogen on the FCC catalyst is reduced. Activity and selectivity loss due to neutralization of the acid sites is decreased.

- Hydrotreating reduces the number of rings in multi-ring sulfur molecules. Increasing saturation of multi-ring aromatics increases the FCCU's capability to produce less than 15 ppm level sulfur gasoline.
- Yields of LCO, slurry oil and coke are decreased. The HCO yield is also reduced as HCO boiling compounds are cracked to gasoline range compounds
- The sulfur level of diesel (LCO) is reduced from the 800 ppm to the 15 ppm level. The distribution of dibenzothiophenes and other multi-ring compounds in the LCO are dramatically reduced by hydrotreating the FCC feed.
- Reducing the metals decreases undesired dehydrogenation reactions, especially those catalyzed by nickel that reduce the yields of coke and hydrogen. Reduced hydrogen production reduces the load on the process gas compressor, which can allow increased cracking severity or increased throughput.
- Reducing the FCC feedstock metals level decreases FCC catalyst consumption.
- Carbon residue is reduced as polynuclear aromatics are saturated to easily cracked naphthenes. Since polynuclear aromatics are the main coke precursors, FCC coke yield is also reduced. Catalyst activity is maintained at a higher level as coke on the catalyst decreases [214A064, 214A175, 214A368].

To maintain a constant feed rate to the FCC, the feed to the hydrotreater is increased as the catalyst ages. The feed rate is also increased as hydrotreater severity increases, producing more gases. Since conversion in the hydrotreater increases with increasing severity, the yields of gasoline and LCO from the combined hydrotreater and FCC also increase with severity and the yield of fuel oil decreases [214A074].

Feedstock for the FCC hydrotreater is usually a blend of atmospheric gas oil, light vacuum gas oil, heavy vacuum gas oil and heavy coker gas oil. Feedstock for a residue FCC (RFCC) hydrotreater is atmospheric residue and/or vacuum residue. The feed distillation units supplying FCC gas oils must consistently minimize the gas oil carbon residue, metals and asphaltenes to achieve optimum hydrotreater run lengths and FCC feed desulfurization. To produce low sulfur gasoline during periods of hydrotreater upset, the FCC or RFCC main fractionator must be able to undercut the high sulfur gasoline fraction to the LCO. For a full range gasoline (C<sub>5</sub>-430°F, C<sub>5</sub>-221°C), the product gasoline sulfur content increases by about 10 ppm per 100 ppm increase in FCC feed sulfur. Optimization of the atmospheric and vacuum crude towers and the coker and FCC main fractionators is discussed by Barletta and Golden [214A400].

A typical FCC feedstock is a blend of 38 vol% heavy atmospheric gas oil, 18% light vacuum gas oil and 44% heavy vacuum gas oil. When hydrotreated separately in a pilot plant at relatively low pressure of 768 psi under the same conditions, removal of all heteroatoms from these FCC feed gas oil components followed the trend: heavy atmospheric gas oil > light vacuum gas oil > heavy vacuum gas oil. Total aromatic hydrogenation showed reverse order due to the relatively higher content of harder to hydrogenate aromatics in the heavy vacuum gas oil. When the mixture is hydrotreated under the same conditions as each component individually hydrotreated and then the products blended in the same percentages, in general the product quality is slightly poorer. The competition for active sites is less when each gas oil is hydrotreated separately. For the heavy atmospheric gas oil, less complex heteroatoms are present than in the two heavier gas oils. The complex molecules of the heavier gas oils adversely affect the removal of heteroatoms and the hydrogenolysis of polyaromatics when the gas oils are hydrotreated as a mixture. Hydrogenation of polyaromatics is less in the mixture, which produces less mono- and di-aromatics than when individually hydrotreated [214A175].

Hydrotreating of feedstocks derived from Canadian oil sands, including a comparison of hydrotreated feed and product properties, was discussed by Benham and Kuehler with special attention to the interaction of deep FCC feed hydrodesulfurization with the performance of the FCCU [214A021]. Processing of Brazilian heavy residues was evaluated in an economic study combining both vacuum residue hydrotreating and RFCC pilot plants [214A073].

Although the distribution of sulfur in FCC products from severely hydrotreated FCC feedstock is independent of the type of hydrotreater catalyst and depends only on the amount of sulfur in the feed, the type of pretreater catalyst strongly influences the FCC yields [214A102]. The optimum catalyst system for HDS and HDN depends upon the severity of HDT required. At constant coke yield, FCC conversion and the yield of gasoline both increase linearly with decreasing FCC feed nitrogen content. The change of properties upon hydrotreating atmospheric residue and vacuum residue oils and the residual fluid catalytic cracking (RFCC) unit yields are shown in Table 16.24. The RFCC yields are both at 70% conversion [214A017].

**Table 6.24**  
**PROPERTIES OF STRAIGHT RUN AND HYDROTREATED RESIDUES AND RFCC YIELDS**

	Atmospheric Straight Run <u>Resid</u>	Hydrotreated <u>AR</u>	Vacuum Straight Run <u>Residue</u>	Hydrotreated <u>VR</u>
RFCC Feed Characteristics				
Specific gravity, 59°F/39°F (15°C/4°C)	0.962	0.922	1.022	0.963
Viscosity at 212°F (100°C), cSt	33	20	1100	92
Sulfur, wt%	3.34	0.19	4.20	0.40
Nitrogen, ppm	2,070	1,200	3,100	1,950
Hydrogen, wt%	11.2	12.2	10.2	11.9
Nickel, ppm	9	<2	19	<4
Vanadium, ppm	40	<2	101	<4
Conradson carbon residue, wt%	9.5	3.8	22.0	8.0
C <sub>7</sub> asphaltenes, wt%	3.1	0.3	7.0	0.8
Aromatic carbon, %	26	17	31	20
Conversion, %	---	70	---	70
RFCC Yields, wt% of RFCC feed				
Fuel gas	---	2.1	---	3.4
LPG	---	15.3	---	14.4
Gasoline, C <sub>5</sub> -392°F (C <sub>5</sub> -200°C)	---	46.2	---	43.1
LCO, 392-662°F (200-350°C)	---	16.2	---	16.0
Slurry oil, 662°F+ (200°C+)	---	13.7	---	14.0
Coke	---	6.5	---	9.1

Source: 214A017

The total amount of sulfur and the distribution of sulfur compounds in FCC products from severely hydrotreated feedstock are independent of the hydrotreating catalyst system but depend entirely upon the sulfur level of the FCC feed. Remaining sulfur species in the gasoline are mostly benzothiophenes and alkyl thiophenes. Their concentration decreases linearly with

decreasing FCC feed sulfur. In LCO, the main sulfur compounds are alkylbenzothiophenes, methyl dibenzothiophenes and dimethyldibenzothiophenes, which also decrease linearly with decreasing FCC feeds sulfur [214A102].

With coker gas oil feed, the remaining sulfur compounds in the FCCU LCO are easier to hydrotreat than those from untreated coker gas oil. The distribution of dibenzothiophenes and other multi-ring compounds in the LCO are dramatically reduced by hydrotreating the FCC feed. The HCO yield is reduced by 50% when the coker gas oil aromatics are lowered by 70%. Chemical hydrogen consumption required to lower coker gas oil aromatics by 70% is 600 to 750 SCF/B [214A064].

The effect of increasing hydrotreating severity when treating FCC feedstock is shown in Table 6.25. The feed is a blend of 89.1 wt% straight run VGO and 10.9 wt% coker gas oil obtained from sour Middle Eastern crude. The blend distillation curve ranges from an initial boiling point of 664°F (351°C) to a final boiling point of 1050°F (566°C) with 50% and 90% overhead temperatures of 817°F (436°C) and 965°F (518°C) respectively. The increase in API gravity from 20.5 to 26.0 clearly indicates the feed is increasingly being saturated as the sulfur level is reduced from 2.6 to 0.02 wt% (200 ppmw).

**Table 6.25**  
**EFFECT OF HYDROTREATING SEVERITY ON FCC FEED PROPERTIES**

	Feed Desulfurization			
	<u>Untreated</u>	<u>90% HDS</u>	<u>98% HDS</u>	<u>99% HDS</u>
Operating pressure, psig	---	900	1,000	1,000
Feed Properties				
API gravity	20.5	23.5	24.8	26.0
Sulfur, wt%	2.6	0.25	0.06	0.02
Nitrogen, ppmw	880	500	450	400
Carbon residue, wt%	0.4	0.25	0.1	0.1
Metals (Ni+V), ppmw	0.36	<1	<1	<1
Hydrogen addition to feed, wt%	0	0.51	0.74	0.94

Source: 214A074

When severity is increased by raising temperature or lower LHSV, the total sulfur, total nitrogen, basic nitrogen, carbon residue and metals removal increase. Density of the hydrotreated products is reduced due to increased hydrocracking. Saturation of aromatics increases. Di-aromatics and higher ring compounds decrease but mono-aromatics increase. Naphthene and substituted naphthenes are one order of magnitude more reactive than mono-aromatics [214A175].

The trends in FCC yields and product properties with increasing hydrotreating severity are seen in Table 6.26. A major benefit is the reduction in slurry oil and poor quality LCO yields with increasing severity. The very little increase in cetane index indicates the LCO aromatic content is still high. Since the feed is easier to crack, the yield of naphtha increases with increasing severity as heavier components are cracked into the naphtha boiling range.

**Table 6.26**  
**EFFECT OF HYDROTREATING SEVERITY ON FCC UNIT PERFORMANCE**

	<b>Feed Desulfurization</b>			
	<u>Untreated</u>	<u>Untreated</u>	<u>Untreated</u>	<u>Untreated</u>
Conversion, vol%	74.3	77.7	79.1	80.8
Yields, wt%				
H <sub>2</sub> S	1.1	0.1	<0.1	<0.1
C <sub>2</sub> -	3.3	3.5	3.2	2.8
C <sub>3</sub> +C <sub>4</sub>	16.3	17.6	18.7	19.9
Full range naphtha	48.3	51.5	52.5	53.6
LCO	16.7	15.7	15.0	14.0
Slurry oil	9.0	6.6	5.9	5.2
Coke	5.4	5.0	4.7	4.4
Total	100.0	100.0	100.0	100.0
Key Product Properties				
Naphtha RON	93.2	93.0	92.9	92.7
Naphtha MON	80.5	80.8	81.1	81.0
LCO cetane index	25.7	25.7	26.4	26.5
Sulfur, ppmw				
H <sub>2</sub> S	10,066	753	188	94
Naphtha	3,600	225	55	18
LCO	29,700	3,400	900	300
Slurry oil	57,800	11,000	3,000	1,100
Coke	30,300	5,700	1,554	516
Flue gas SO <sub>x</sub> , ppmv	2,030	410	120	42

Source: 214A074

## 7 VGO HYDROTREATING ECONOMICS

In this section, we evaluate the process economics of two generic PEP vacuum gas oil (VGO) hydrotreating units. The first is a conventional unit; the second is based on the features of the IsoTherming™ process. Both are designed to process 30,000 BPSD or 28,500 barrels per calendar day (BPCD) of the same sour vacuum gas oil feedstock. All capacities are calculated using a 0.95 on stream factor. This plant capacity is typical of hydrotreating plants as discussed in Section 4.

### PROCESS DESCRIPTION

In this subsection, we describe a generic PEP hydrotreating unit designed to process 30,000 barrels per stream day (BPSD) of a sour vacuum gas oil blend. Our design has a product capacity of 30,453 B/SD or 1.510 million mt/yr (3,320 million lb/yr) of hydrotreated vacuum gas oil FCC feedstock.

The conventional hydrotreater is a medium pressure (about 1,500 psig), single-stage process having three catalyst beds. Make-up hydrogen is 99.55 vol% pure. Hydrogen is recovered and purified from the purge gas by a membrane separator unit and combined with the make-up hydrogen. This hydrogen is mostly charged to the first reactor. A higher hydrogen partial pressure is provided in the lead catalyst bed than if recycled hydrogen were charged. Hydrogen separated from the second reactor effluent is amine treated to remove H<sub>2</sub>S and mostly charged to quench to the feed to the second and third catalyst beds.

The process design and utility consumption rates used in this report are based on computations, published information, and nonconfidential information from licensors and vendors. The design may or may not be similar to a licensed process or to processes otherwise in use today.

Tables 7.1 and 7.2 lists the design bases and assumptions of the designs for the conventional and Isotherming type processes respectively. Feedstock and liquid product characterizations for both units are the same and are summarized in Table 7.3. Major process stream flows are summarized in Tables 7.4 and 7.5. The process was modeled using Aspen Technology's Aspen™ Plus process simulator, version 11.1-0, built September 20, 2001. The physical properties method was the Redlich-Kwong Soave equation of state method. Major equipment is listed with size and materials of construction in Tables 7.6 and 7.7 respectively. Similarly, utility requirements are summarized in Tables 7.8 and 7.9.

**Table 7.1**  
**DESIGN BASES AND ASSUMPTIONS – CONVENTIONAL HYDROTREATER**

<b>Feedstock</b>	VGO Blend: 65 vol% Heavy Vacuum Gas Oil, 15% Deasphalted Oil, 10% Light Vacuum Oil, 10% Lube Aromatic Extract		
Feedstock characterization	Please See Table 7.3		
Make-up H <sub>2</sub> supply pressure, psig	285		
Make-up H <sub>2</sub> purity, mol%/wt%	99.55/94.22		
Membrane Unit H <sub>2</sub> recycle purity, mol%	95.55		
Chemical H <sub>2</sub> consumption, SCF/B	610		
H <sub>2</sub> reactor losses, wt% FF	0.15		
<b>Reactor</b>	<b><u>R-101</u></b>	<b><u>R-102</u></b>	<b><u>Overall</u></b>
Type	Trickle Bed	Trickle Bed	
Flow	Co-current	Co-current	
Number of reactors (beds/reactor)	1 (2)	1 (1)	
Catalyst type	NiMo/alumina	NiMo/alumina	
Fresh catalyst metals, Ni/Mo wt% as oxide	3.5/12.5	3.5/12.5	
Catalyst bulk density, lb/ft <sup>3</sup>	43.7	43.7	
Reactor fill (bed 1/bed 2), lb	73,500/84,400	114,400	272,200
ft <sup>3</sup>	1,700/1,900	2,600	6,200
Catalyst life, years	2	2	
Reactor conditions (SOR)			
Inlet/outlet pressure, psig	1533/	/1473	
Inlet/outlet temperature, °F (°C)	642 (339)/	666 (352)/	
	685 (363)	682 (361)	
LHSV, H <sup>-1</sup>	5.55/4.84	3.57	1.5
Recycle H <sub>2</sub> /oil ratio			
<b>Reactor Yields, wt% Fresh VGO feed</b>			
H <sub>2</sub> S			2.5085
NH <sub>3</sub>			0.1081
C <sub>1</sub>			0.0427
C <sub>2</sub>			0.1024
C <sub>3</sub>			0.1281
C <sub>4</sub>			0.1024
Naphtha			0.3000
Hydrotreated VGO FCC Feed			<u>96.8000</u>
Total			100.9922
Liquid products characterizations	Please See Table 7.3		
Spent wash water salt content, wt%			4

**Table 7.2**  
**DESIGN BASES AND ASSUMPTIONS – ISOTHERMING™ HYDROTREATER**

<b>Feedstock</b>	VGO Blend: 65 vol% Heavy Vacuum Gas Oil, 15% Deasphalted Oil, 10% Light Vacuum Oil, 10% Lube Aromatic Extract		
Feedstock characterization	Please See Table 7.3		
H <sub>2</sub> supply pressure, psig	285		
H <sub>2</sub> purity, mol%/wt%	99.55/94.22		
Chemical H <sub>2</sub> consumption, SCF/B	610		
H <sub>2</sub> reactor losses, lb/hr			
<b>Reactor</b>	<b><u>R-101</u></b>	<b><u>R-102</u></b>	<b><u>Overall</u></b>
Type	Liquid Fixed Bed	Liquid Fixed Bed	
Flow	Co-current	Co-current	
Number of reactors (beds/reactor)	1 (1)	1 (1)	
Catalyst type	NiMo/alumina	NiMo/alumina	
Fresh catalyst metals, Ni/Mo wt% as oxide	3.5/12.5	3.5/12.5	
Catalyst bulk density, lb/ft <sup>3</sup>	43.7	43.7	
Reactor fill, lb	125,000	125,000	250,000
ft <sup>3</sup>	2,867	2,867	5,734
Catalyst life, years	2	2	
Reactor conditions (SOR)			
Inlet/outlet pressure, psig	1533/	/1473	
Inlet/outlet temperature, °F (°C)	642 (339)/	666 (352)/	
	685 (363)	682 (361)	
Recycle H <sub>2</sub> /oil ratio			None
Recycle Oil, wt% FF			0.5
LHSV, based on FF, H <sup>-1</sup>	3.267	3.267	1.633
LHSV, based on total oil feed, H <sup>-1</sup>	2.46	2.46	4.91
<b>Reactor Yields, wt% Fresh VGO feed</b>			
H <sub>2</sub> S			2.5085
NH <sub>3</sub>			0.1081
C <sub>1</sub>			0.0427
C <sub>2</sub>			0.1024
C <sub>3</sub>			0.1281
C <sub>4</sub>			0.1024
Naphtha			0.3000
Hydrotreated VGO FCC Feed			<u>0.9700</u>
Total			100.9922
Liquid products characterizations	Please See Table 7.3		
Spent wash water salt content, wt%			4



**Table 7.3**  
**FEEDSTOCK AND PRODUCT CHARACTERIZATIONS**

	<b><u>VGO Blend</u></b> <b><u>Fresh Feed</u></b>	<b><u>Hydrotreated</u></b> <b><u>VGO</u></b>	<b><u>Wild_</u></b> <b><u>Naphtha</u></b>
Gravity, API	20	25.9	62.3
Sulfur, wt%	2.43	0.0713	0.0035
Nitrogen, ppmw	1071	247	5
Conradson Carbon Residue, wt%	1.4	---	---
Metals (Ni+V), ppmw	3.3	---	---
Distillation, °F (°C)	D-1160	D-1160	D-86
T <sub>10</sub>	651 (344)	660 (349)	120 (49)
T <sub>30</sub>	759 (404)	741 (394)	171 (77)
T <sub>50</sub>	849 (454)	809 (432)	212 (100)
T <sub>70</sub>	943 (506)	903 (484)	261 (127)
T <sub>90</sub>	1131 (611)	1091 (588)	329 (165)

**Table 7.4**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) VACUUM GAS OIL  
AT 0.95 STREAM FACTOR

Stream Flows, lb/Hr							
	<u>Mol</u> <u>Wt</u>	<u>(1)</u> <u>Fresh</u> <u>Feed</u>	<u>(2)</u> <u>Injection</u> <u>Hydrogen</u>	<u>(3)</u> <u>Reactor</u> <u>Fresh Oil</u>	<u>(4)</u> <u>Hydrogen</u> <u>to R-101</u>	<u>(5)</u> <u>Make-Up</u> <u>Hydrogen</u>	<u>(6)</u> <u>Recycle</u> <u>Hydrogen</u>
Water	18.0	--	--	--	--	--	--
Hydrogen	2.0	--	1,000	1,000	3,052	4,664	22,283
Nitrogen	28.0	--	--	--	--	280	4,319
Ammonia	17.0	--	--	--	--	--	--
Hydrogen sulfide	34.1	--	--	--	--	--	--
Methane	16.0	--	--	--	--	6	5,099
Ethane	30.1	--	--	--	--	--	3,767
Propane	44.1	--	--	--	--	--	2,941
Isobutane	58.1	--	--	--	--	--	339
n-Butane	58.1	--	--	--	--	--	914
Wild Naphtha	103	--	--	--	--	--	656
VGO Product	738	--	--	408,345	--	--	62
VGO Fresh Feed	762	408,345	--	--	--	--	--
<hr/>							
Total, lb/hr		408,345	1,000	409,345	3,052	4,950	40,380
kg/hr		185,222	454	185,676	1,384	2,245	18,316
lb-mole/hr		536	500	1,032	1,526	2,357	11,877

**Table 7.4 (Continued)**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) VACUUM GAS OIL  
AT 0.95 STREAM FACTOR

Stream Flows, lb/Hr							
	(7)	(8)	(9)	(10)	(11)	(12)	
	<u>Mol</u>	<u>Reactor</u>	<u>Hot High</u>	<u>Hot High</u>	<u>Cold High</u>	<u>Cold High</u>	<u>Cold High</u>
	<u>Wt</u>	<u>Effluent</u>	<u>Pressure</u>	<u>Pressure</u>	<u>Pressure</u>	<u>Pressure</u>	<u>Pressure</u>
			<u>Liquid</u>	<u>Vapor</u>	<u>Liquid</u>	<u>Sour water</u>	<u>Separator</u>
							<u>Vapor</u>
Water	18.0	--	--	--	3	32,779	219
Hydrogen	2.0	24,784	178	24,607	11	--	24,596
Nitrogen	28.0	4,809	48	4,761	4	--	4,757
Ammonia	17.0	441	16	425	15	--	410
Hydrogen sulfide	34.1	10,244	344	9,899	216	--	9,684
Methane	16.0	5,730	96	5,634	18	--	5,616
Ethane	30.1	4,345	131	4,214	66	--	4,149
Propane	44.1	3,565	166	3,399	159	--	3,240
Isobutane	58.1	443	28	415	42	--	373
n-Butane	58.1	1,248	89	1,159	152	--	1,007
Wild Naphtha	103	10,387	5,034	5,353	4,631	--	722
VGO Product	528	390,508	381,671	8,838	8,769	--	68
VGO Fresh Feed	762	--	--	--	--	--	--
Total, lb/hr		456,504	387,799	68,704	14,087	32,779	54,839
kg/hr		207,067	175,903	31,164	6,390	14,868	24,875
lb-mole/hr		14,177	799	13,471	107	1,821	13,375

**Table 7.4 (Continued)**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) VACUUM GAS OIL  
AT 0.95 STREAM FACTOR

	<b>Stream Flows, lb/day</b>						
	(13)	(14)	(15)	(16)	(17)	(18)	
	<u>Mol Wt</u>	<u>Acid Gas</u>	<u>Purge Gas</u>	<u>Membrane Hydrogen</u>	<u>Hot Low Pressure Separator Vapor</u>	<u>Cold Low Pressure Separator Off Gas</u>	<u>Cold Low Pressure Separator Liquid</u>
Water	18.0	219	--	--	--	--	3
Hydrogen	2.0	54	368	1,889	140	148	2
Nitrogen	28.0	--	228	210	35	38	1
Ammonia	17.0	410	--	--	7	10	12
Hydrogen sulfide	34.1	9,684	--	--	150	204	161
Methane	16.0	--	67	450	58	69	8
Ethane	30.1	--	222	160	61	80	46
Propane	44.1	--	198	100	59	78	141
Isobutane	58.1	--	34	--	8	10	40
n-Butane	58.1	--	73	20	23	26	149
Wild Naphtha	103	--	66	--	139	20	4,750
VGO Product	528	--	6	--	241	2	9,009
VGO Fresh Feed	762	--	--	--	--	--	--
Total, lb/hr		10,366	1,262	2,829	920	684	14,323
kg/hr		4,702	572	1,283	417	310	6,497
lb-mole/hr		347	210	975	85	91	101

**Table 7.4 (Concluded)**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) VACUUM GAS OIL  
AT 0.95 STREAM FACTOR

Stream Flows, lb/day						
		(19)	(20)	(21)	(22)	(23)
		Hot Low	Stripper	Stripper	Wild	Hydrotreated
		Pressure	Sour	Off Gas	Naphtha	Vacuum
	Mol	Separator	Water			Gas Oil
	Wt	Liquid				
Water	18.0	--	2,963	28	--	11
Hydrogen	2.0	38	--	40	--	--
Nitrogen	28.0	13	--	14	--	--
Ammonia	17.0	10	--	21	1	1
Hydrogen sulfide	34.1	194	--	342	4	10
Methane	16.0	37	--	44	--	1
Ethane	30.1	70	--	112	1	3
Propane	44.1	107	--	233	7	7
Isobutane	58.1	20	--	54	4	2
n-Butane	58.1	66	--	188	20	7
Wild Naphtha	103	4,895	--	334	557	8,754
VGO Product	528	381,429	--	19	263	390,156
VGO Fresh Feed	762	--	--	--	--	--
<hr/>						
Total, lb/hr		386,879	2,963	1,430	856	398,953
kg/hr		175,485	1,344	649	388	180,962
lb-mole/hr		714	165	54	8	755

**Table 7.5**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**

<b>STREAM FLOWS</b>							
CAPACITY: 30,000 BPSD (6,360 M <sup>3</sup> /SD)							
650°F+ (343°C+) VACUUM GAS OIL							
AT 0.95 STREAM FACTOR							
<b>Stream Flows, lb/Hr</b>							
	<b>(1)</b>	<b>(2)</b>	<b>(3)</b>	<b>(4)</b>	<b>(5)</b>	<b>(6)</b>	
	<b>Fresh Feed</b>	<b>H<sub>2</sub> Injection</b>	<b>Reactor Fresh Oil Feed</b>	<b>Oil Recycle</b>	<b>Hydrogen</b>	<b>Reactor Effluent</b>	
Water	18.0	--	--	--	--	--	--
Hydrogen	2.0	--	942	942	73	4,254	146
Nitrogen	28.0	--	57	57	97	255	194
Ammonia	17.0	--	--	--	193	--	387
Hydrogen sulfide	34.1	--	--	--	4,456	--	8,944
Methane	16.0	--	1	1	73	5	147
Ethane	30.1	--	--	--	180	--	361
Propane	44.1	--	--	--	232	--	467
Isobutane	58.1	--	--	--	47	--	95
n-Butane	58.1	--	--	--	143	--	287
Wild Naphtha	109	--	--	--	4,741	--	9,517
VGO Product	528	--	--	408,345	194,288	--	389,999
VGO Fresh Feed	762	408,345	--	--	--	--	--
<hr/>							
Total, lb/hr	408,345	1,000	409,345	204,523	4,515	410,545	
kg/hr	185,222	454	185,676	92,770	2,048	186,220	
lb-mole/hr	536	469	1,005	581	2,120	1,166	

**Table 7.5 (Continued)**  
**VACUUM GAS OIL ISOTHERMING TYPE HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) VACUUM GAS OIL  
AT 0.95 STREAM FACTOR

Stream Flows, lb/Hr						
	<b>Mol Wt</b>	<b>(7) Hot Separator Liquid</b>	<b>(8) Hot Separator Vapor</b>	<b>(9) Cold Separator Liquid</b>	<b>(10) Separator Column Bottom</b>	<b>(11) Separator Column Overhead</b>
Water	18.0	--	--	4	--	4
Hydrogen	2.0	3	143	--	--	143
Nitrogen	28.0	6	189	1	1	189
Ammonia	17.0	31	356	73	8	421
Hydrogen sulfide	34.1	681	8,263	998	158	9,103
Methane	16.0	6	140	2	1	142
Ethane	30.1	25	336	29	6	359
Propane	44.1	45	421	116	12	525
Isobutane	58.1	12	83	53	3	133
n-Butane	58.1	39	248	228	12	465
Wild Naphtha	109	5,437	4,081	9,432	7,786	5,727
VGOI Product	528	381,607	8,392	8,626	15,348	1,669
VGO Fresh Feed	762	--	--	--	--	--
Total, lb/hr		387,892	22,653	19,562	23,335	18,880
kg/hr		175,945	10,275	8,873	10,585	8,564
lb-mole/hr		713	453	179	148	484

**Table 7.5 (Continued)**  
**VACUUM GAS OIL ISOTHERMING TYPE HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) VACUUM GAS OIL  
AT 0.95 STREAM FACTOR

Stream Flows, lb/day						
		(12)	(13)	(14)	(15)	(16)
	<b>Mol</b>	<b>Reactor</b>	<b>Stripper</b>	<b>Dry</b>	<b>V-202</b>	
	<b>Wt</b>	<b>Vent Gas</b>	<b>Overhead</b>	<b>V-202</b>	<b>Sour</b>	<b>V-202</b>
				<b>Feed</b>	<b>Water</b>	<b>Vapor</b>
Water	18.0	--	2,284	2,288	35,201	83
Hydrogen	2.0	56	4	203	--	203
Nitrogen	28.0	61	6	256	--	255
Ammonia	17.0	54	39	514	--	439
Hydrogen sulfide	34.1	1,299	839	11,241	--	10,210
Methane	16.0	33	8	182	--	180
Ethane	30.1	57	31	447	--	417
Propane	44.1	57	57	639	--	519
Isobutane	58.1	10	15	158	--	103
n-Butane	58.1	27	50	542	--	306
Wild Naphtha	109	214	4,388	10,329	--	577
VGO Product	528	447	6,832	8,949	--	31
VGO Fresh Feed	762	--	--	--	--	--
<hr/>						
Total, lb/hr		2,315	14,552	35,747	35,201	13,322
kg/hr		1,050	6,600	16,215	15,967	6,043
lb-mole/hr		82	232	798	1,956	492



**Table 7.5 (Concluded)**  
**VACUUM GAS OIL ISOTHERMING TYPE HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) VACUUM GAS OIL  
AT 0.95 STREAM FACTOR

Stream Flows, lb/day						
	(17)	(18)	(19)	(20)	(21)	
	<u>Mol</u> <u>Wt</u>	<u>Acid</u> <u>Gas</u>	<u>Off Gas</u> <u>Product</u>	<u>Wild</u> <u>Naphtha</u>	<u>Stripper</u> <u>Feed</u>	<u>Hydrotreated</u> <u>Vacuum</u> <u>Gas Oil</u>
Water	18.0	83	--	--	--	16
Hydrogen	2.0	54	149	--	4	--
Nitrogen	28.0	--	255	--	6	--
Ammonia	17.0	439	--	3	39	--
Hydrogen sulfide	34.1	10,210	--	34	839	--
Methane	16.0	--	180	0	8	--
Ethane	30.1	--	417	1	31	--
Propane	44.1	--	519	4	57	--
Isobutane	58.1	--	103	2	15	--
n-Butane	58.1	--	306	8	50	--
Wild Naphtha	109	--	577	319	13,223	8,835
VGO Product	528	--	31	292	396,956	390,124
VGO Fresh Feed	762	--	--	--	--	--
<hr/>						
Total, lb/hr		10,785	2,537	662	411,227	398,976
kg/hr		4,892	1,151	300	186,529	180,972
lb-mole/hr		357	134	6	860	755

**Table 7.6**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**MAJOR EQUIPMENT**

CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)  
HDT VGO FCC FEED  
AT 0.95 STREAM FACTOR

EQUIPMENT NUMBER	NAME	SIZE	MATERIAL OF CONSTRUCTION	REMARKS
REACTORS				
R-101	FIXED BED REACTOR	44,000 GAL	SHELL: 1.25 CR-0.5 MO	12 FT ID X 52 FT T-T 73,500 + 84,400 LB CATALYST
R-102	FIXED BED REACTOR	28,000 GAL	SHELL: 1.25 CR-0.5 MO	12 FT DIA. X 33 FT T-T 114,400 LB CATALYST
COLUMNS				
C-301	STRIPPER	5 FT DIA 48 FT	SHELL: C.S. TRAYS: C.S.	24 VALVE TRAYS, 24 INCH SPACING
COMPRESSORS				
K-101A, B	H2 MAKE-UP COMPRESSOR	2,047 BHP	C.S.	
K-102A, B	H2 MAKE-UP COMPRESSOR	2,196 BHP	C.S.	
K-201A, B	H2 RECYCLE COMPRESSOR	700 BHP	C.S.	
K-301	OFF GAS COMPRESSOR	27.4 BHP	C.S.	
HEAT EXCHANGERS				
E-101	FEED-STRIPPER BTMS EX	8,500 SQ FT 55.34 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-102	REACTOR FEED-EFFLUENT	5,500 SQ FT 32.21 MMBTU/HR	SHELL: 1.25 CR- 0.5 MO TUBES: C.S.	
E-103	REACTOR FEED-EFFLUENT	2,550 SQ FT 33.37 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-104	MAKE-UP H2 COOLER	900 SQ FT 4.665 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-201	V-201 VAPOR-MAKE-UP EXCHANGER	375 SQ FT 1.42 MMBTU/HR	SHELL: 1.25 CR- 0.5 MO TUBES: 316 SS	
E-202	V-201 VAPOR STEAM BOILER	2,400 SQ FT 29.66 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-203	V-201 VAPOR AIR CONDENSER	3,050 SQ FT 9.84 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-204	V-201 VAPOR TRIM CONDENSER	2,300 SQ FT 5.21 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-205	V-202 VAPOR-V-203 LIQUID	100 SQ FT 0.4 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-301	STRIPPER OVERHEAD CONDENSER	1,350 SQ FT 4.9 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-302	STRIPPER OVERHEAD TRIM COOLER	300 SQ FT 0.513 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
PROCESS FURNACES				
F-101	FEED HEATER	14.6 MMBTU/HR	316 SS	

**Table 7.6 (Concluded)**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**MAJOR EQUIPMENT**

CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)  
HDT VGO FCC FEED  
AT 0.95 STREAM FACTOR

EQUIPMENT NUMBER	NAME	SIZE	MATERIAL OF CONSTRUCTION	REMARKS
TANKS				
T-101A, B	VACUUM GAS OIL FEED TANK	1,890,000 GAL	C.S.	
T-301	WILD NAPHTHA TANK	15,000 GAL	C.S.	
T-302A, B	HYDROTREATED VGO FCC TANK	2,001,000 GAL	C.S.	
PRESSURE VESSELS				
V-101	FEED SURGE DRUM	9,250 GAL	C.S.	
V-102	MAKE-UP H2 KNOCK OUT DRUM	400 GAL	C.S.	
V-103	MAKE-UP H2 KNOCK OUT DRUM	400 GAL	C.S.	
V-201	HOT HIGH PRESSURE SEPERATOR	15,500 GAL	1.25 CR-0.5 MO	
V-202	COLD HIGH PRESSURE SEPERATOR	18,250 GAL	C.S.	
V-203	COLD LOW PRESSURE SEPERATOR	1,000 GAL	C.S.	
V-204	HOT LOW PRESSURE SEPERATOR	750 GAL	C.S.	
V-301	STRIPPER REFLUX DRUM	300 GAL	C.S.	
SPECIAL EQUIPMENT				
S-101A, B	FEED FILTERS		CARBON STEEL	
S-201	EXPANDER	388 KW	2.25 CR-1 MO	
PACKAGE UNITS				
G-103	INITIAL CATALYST FILL	272230 LB	HDS CATALYST	
G-201	AMINE UNIT		CARBON STEEL	MDEA ABSORPTION
G-202	MEMBRANE H2 SEPARATOR		CARBON STEEL	
PUMPS				
	SECTION	OPERATING	SPARES	OPERATING BHP
	100	6	2	3,882
	200	2	1	112
	300	6	3	85

**Table 7.7**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**  
**30,000 BPSD**

**MAJOR EQUIPMENT**

CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)  
HDT VGO FCC FEED  
AT 0.95 STREAM FACTOR

EQUIPMENT NUMBER	NAME	SIZE	MATERIAL OF CONSTRUCTION	REMARKS
REACTORS				
R-101	FIXED BED REACTOR	24,500 GAL	SHELL: 1.25 CR-0.5 MO	10 FT DIA. X 41.5 FT T-T
R-102	FIXED BED REACTOR	24,500 GAL	SHELL: 1.25 CR-0.5 MO	10 FT DIA. X 41.5 FT T-T
COLUMNS				
C-201	SEPARATOR COLUMN	3 FT DIA 16 FT	SHELL: C.S. TRAYS: C.S.	8 SIEVE TRAYS, 24 INCH SPACING
C-301	STRIPPER	5 FT DIA 48 FT	SHELL: C.S. TRAYS: C.S.	24 VALVE TRAYS, 24 INCH SPACING
COMPRESSORS				
K-101A, B	H2 MAKE-UP COMPRESSOR	1,337 BHP	C.S.	
K-102A, B	H2 MAKE-UP COMPRESSOR	1,397 BHP	C.S.	
HEAT EXCHANGERS				
E-101A-C	FEED-STRIPPER BTMS EXCHANGER	10,000 SQ FT 32.34 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-102	REACTOR FEED-EFFLUENT EXCHANGE	6,500 SQ FT 23.3 MMBTU/HR	SHELL: 1.25 CR- 0.5 MO TUBES: C.S.	
E-103	H2 COMPRESSOR COOLER	600 SQ FT 3.11 MMBTU/HR	SHELL: C.S. TUBES: C.S.	AIR COOLER
E-201	V-201 VAPOR-H2 EXCHANGER	1,250 SQ FT 0.933 MMBTU/HR	SHELL: 1.25 CR- 0.5 MO TUBES: 316 SS	
E-202	V-201 VAPOR CONDENSER	2,000 SQ FT 7.72 MMBTU/HR	SHELL: C.S. TUBES: C.S.	AIR COOLER
E-203	V-201 VAPOR TRIM CONDENSER	1,200 SQ FT 2.35 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
PROCESS FURNACES				
F-101	FEED HEATER	15.33 MMBTU/HR	316 SS	
TANKS				
T-101A, B	VACUUM GAS OIL FEED TANK	1,890,000 GAL	C.S.	3 DAYS SUPPLY
T-301	WILD NAPHTHA TANK	15,000 GAL	C.S.	3 DAYS PRODUCTION
T-302A, B	HYDROTREATED VGO FCC TANK	2,001,000 GAL	C.S.	
PRESSURE VESSELS				
V-101	FEED SURGE DRUM	9,250 GAL	C.S.	
V-102	H2 KNOCK OUT DRUM	200 GAL	C.S.	
V-103	MAKE-UP H2 KNOCK OUT DRUM	200 GAL	C.S.	
V-201	HOT LOW PRESSURE SEPARATOR	16,131 GAL	1.25 CR-0.5 MO	
V-202	COLD LOW PRESSURE SEPARATOR	18,250 GAL	C.S.	

**Table 7.7 (Concluded)**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**  
**30,000 BPSD**

**MAJOR EQUIPMENT**

CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)  
HDT VGO FCC FEED  
AT 0.95 STREAM FACTOR

EQUIPMENT NUMBER	NAME	SIZE	MATERIAL OF CONSTRUCTION	REMARKS
MISCELLANEOUS EQUIPMENT				
M-101	FEED MIXER		2.25 CR-1 M0	STATIC MIXER
M-102	FEED MIXER		2.25 CR-1 M0	STATIC MIXER
SPECIAL EQUIPMENT				
S-101A, B	FEED FILTERS		CARBON STEEL	
S-201	EXPANDER	556 KW	2.25 CR-1 M0	
PACKAGE UNITS				
G-101	INITIAL CATALYST FILL	340,300 LB	HDS CATALYST	
G-201	AMINE UNIT		CARBON STEEL	MDEA ABSORPTION
PUMPS				
SECTION	OPERATING	SPARES	OPERATING BHP	
100	8	3	1,231	
200	4	2	4	
300	2	1	51	

**Table 7.8**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**UTILITIES SUMMARY**

CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)  
HDT VGO FCC FEED  
AT 0.95 STREAM FACTOR

	<b>UNITS</b>	<b>BATTERY LIMITS TOTAL</b>	<b>SECTION 100</b>	<b>SECTION 200</b>	<b>SECTION 300</b>
<b>AVERAGE CONSUMPTIONS</b>					
COOLING WATER	GPM	3,402	--	3,334	68
PROCESS WATER	GPM	66	--	66	--
ELECTRICITY	KW	9,088	7,369	1,616	104
NATURAL GAS	MM BTU/HR	19	19	--	--
STEAM, 50 PSIG	M LB/HR	28	--	28	--
STEAM, 150 PSIG	M LB/HR	3	--	--	3
STEAM, 150 PSIG	M LB/HR	-27	--	-27	--
<b>PEAK DEMANDS</b>					
COOLING WATER	GPM	4,082	--	4,001	82
PROCESS WATER	GPM	79	--	79	--
STEAM, 50 PSIG	M LB/HR	33	--	33	--
STEAM, 150 PSIG	M LB/HR	4	--	--	4

**Table 7.9**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**  
**30,000 BPSD**

<b>UTILITIES SUMMARY</b>					
CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)					
HDT VGO FCC FEED					
AT 0.95 STREAM FACTOR					
	<b>UNITS</b>	<b>BATTERY LIMITS TOTAL</b>	<b>SECTION 100</b>	<b>SECTION 200</b>	<b>SECTION 300</b>
<b>AVERAGE CONSUMPTIONS</b>					
COOLING WATER	GPM	3,097	--	3,097	--
ELECTRICITY	KW	3,632	4,076	-499	55
NATURAL GAS	MM BTU/HR	36	36	--	--
STEAM, 50 PSIG	M LB/HR	29	--	29	--
STEAM, 150 PSIG	M LB/HR	2	--	2	--
<b>PEAK DEMANDS</b>					
COOLING WATER	GPM	3,716	--	3,716	--
ELECTRICITY	KW	5,910	6,354	-499	55
STEAM, 50 PSIG	M LB/HR	35	--	35	--
STEAM, 150 PSIG	M LB/HR	3	--	3	--

## **Conventional Hydrotreater**

The process flow diagram for the conventional hydrotreater, Figure 7.1 (in Appendix E) is divided into three sections:

- Section 100—Reaction
- Section 200—Gas Recovery
- Section 300—Product Recovery

### **Section 100 - Reaction**

Fresh feedstock is pumped from surge drum V-101 and heated to the reactor inlet temperature by a series of heat exchangers and a furnace. A stream of make-up hydrogen is injected to minimize exchanger and furnace tube fouling. The feed is first heat exchanged (E-101) with the hydrotreated gas oil product from the stripper, C-301. The feed is then heat exchanged with the second reactor's effluent (E-102 and E-103). Furnace F-101 heats the feed to the reactor inlet temperature. During startup, VGO feed is heated in this furnace and circulated until sufficient heat is available at E-101 for feed preheating.

Make-up hydrogen is combined with purified recycle hydrogen and compressed to reactor pressure by two-stage reciprocating compressors (K-101A, B and K-102A, B) with inter-stage cooling (E-104). The high purity hydrogen is heated by heat exchange with reactor vapor effluent in E-201. A portion of the hydrogen is charged to the fresh feed line before E-101, the balance is charged before the first reactor R-101. Cool recycle hydrogen quenches the effluent of the first catalyst bed of R-101. Reactor effluent is quenched before entering the second reactor (R-102). Effluent from R-102 is cooled by exchange (E-103 and E-102) before flowing to the Gas Recovery Section.

### **Section 200 - Gas Recovery**

Cooled reactor effluent flows to the hot, high pressure separator V-201. The liquid from the separator flows through expander S-201 on the way to the hot low pressure separator (V-204). Vapor from V-201 is cooled in exchanger E-201, heating the make-up hydrogen. The temperature is further reduced by steam boiler E-202 and by the addition of wash water. Wash water is added to control the buildup of  $\text{NH}_4\text{SH}$  salt in air cooled condenser E-203 and trim condenser E-204.

Hydrogen rich gas from the cold, high pressure separator V-202 flows to the amine treater (G-201) where acid gas is removed. A portion of the sweet gas from G-201 is purged through membrane separator G-202. The purified hydrogen is combined with the make-up hydrogen and compressed in the make-up hydrogen compressors (K-101A, B and K-102A, B). The tail gas from the membrane separator is purged to the refinery fuel gas system.

Liquid from V-202 is reduced in pressure and combined with vapor from E-205 as the liquid flows to the cold, low pressure separator V-203. Offgas from V-203 flows offsite to the refinery's sour gas scrubber. Liquid from V-203 is heated by exchange with vapor from the hot, low pressure separator (V-204). Liquids from V-203 and V-204 flow separately to the Product Recovery Section.



## **Section 300 - Product Recovery**

Liquids from separators V-203 and V-204 are charged to the stripper column (C-301) for the removal of light oils and vapors. Overhead from the stripper is partially condensed in air cooled heat exchanger E-301 and then in trim condenser E-302. Offgas from the stripper receiver V-301 is compressed in K-301 and flows offsite to the refinery sour gas scrubber. Sour water from V-301 flows offsite to the refinery's sour water system. A portion of the naphtha from V-301 is returned to C-301 as reflux. The balance is produced as wild naphtha product. The hydrotreated VGO FCC Feedstock flows from the stripper bottom and is cooled by heat exchange with the fresh feedstock. Optionally the VGO product is cooled (E-303) for storage instead of flowing directly to the FCCU.

## **IsoTherming™ Type Hydrotreater**

The process flow diagram for the IsoTherming type hydrotreater, Figure 7.2 (in Appendix E) is divided into three sections:

- Section 100—Reaction
- Section 200—Gas Recovery
- Section 300—Product Recovery

### **Section 100 - Reaction**

VGO fresh feed is pumped from surge drum V-101, hydrogen is injected to prevent fouling of downstream heat exchanger tube. The stream is heated, first by the feed-product exchanger (E-101) and then by the feed-reactor effluent exchanger (E-102). Feed furnace F-101 heats the fresh feed before the feed is combined with hot recycle oil and cooler hydrogen. The furnace heats the fresh feed hot enough to raise the combined reactor feed to the desired reactor inlet temperature. Static mixer M-101 ensures a uniform mixture in composition and temperature enters the first R-101 of two reactors in series. Both reactors R-101 and R-102 are liquid full, fixed bed reactors containing a single bed of HDS catalyst. A small amount of vapor from each reactor is vented and recovered downstream. Additional cool hydrogen is mixed with effluent from R-101 in static mixer M-102 before entering the second reactor (R-102).

A portion of the effluent oil from the second reactor (R-102) is recycled to mixer M-101. The remaining effluent is reduced in pressure by expander S-102. The effluent is then cooled by heat exchange (E-102) with the fresh feed before flowing to the Gas Recovery Section.

### **Section 200 - Gas Recovery**

Vapor in the cooled reactor effluent from E-102 is separated from the liquid in the hot separator (V-201). Heavy hydrocarbons carried over in the vapor are recovered by separator column C-201 and combined with the liquid from V-201. Vapor from V-201 is combined with vented vapor from the reactors (R-101 and R-102) and from the stripper (C-301). The combined vapor is cooled by heat exchange with the feed hydrogen (E-201). Wash water is charged to prevent  $\text{NH}_4\text{SH}$  buildup in downstream heat exchangers. Air cooled condenser E-202 and trim condenser E-203 partially condense the stream. The water, oil and vapor are separated in the cold separator V-203. Sour water flows offsite to the refinery's sour water scrubber. A portion of the naphtha is reflux for the separator column (C-201); the remainder is wild naphtha product.

Oil from separator V-201 and from the separator column (C-201) and the vapor from the cold separator V-202 flows to the Product Recovery Section.

## Section 300 - Product Recovery

The vapor from the cold separator V-202 is amine treated (G-301) to remove H<sub>2</sub>S. The treated offgas from the amine treater flows to the refinery fuel gas system.

Liquids from separator V-201 and column C-201 are combined and steam stripped (C-301) to remove light hydrocarbons and gases. The stripper overhead flows to the Gas Recovery Section. Hydrotreated VGO FCC feedstock from the stripper bottom is cooled in the Reactor Section in the feed-product exchanger E-101 before flowing either to storage or directly to the FCCU.

## PROCESS DISCUSSION

The on stream factor of 0.95 is conservative since usual experience is higher. The conditions given are generally for the start-of-run. At end-of-run conditions, the reactor inlet temperatures will have been raised to the maximum. The reactor pressure drops are often larger than at the start of run.

The designs are not fully optimized, especially for energy utilization. Our goal is to derive a reasonable process for cost estimating within our  $\pm 25\%$  accuracy. The model should be considered as a preliminary design that should serve as a good starting point for performing more detailed process design. Hydrotreater units are customized to meet feedstock flexibility, catalyst conditions and owner preferences. Process licensors and contractors have decades of experience to draw upon in designing specific plants.

The basic design of the conventional hydrotreater is generally based on information reported for a revamped unit [214A019] with additional information from our literature review in Sections 5 and 6. The design of the IsoTherming type unit is generally based on published information [214A029, 214A587] and patents [US 2005 0082202, US 6123835, US 6428686, US 6881326].

## Feedstock

The feedstock is a VGO blend: 65 vol% heavy vacuum gas oil, 15% deasphalted oil, 10% light vacuum oil, 10% lube aromatic extract. The assumed feedstock is characterized in Table 7.3.

## Section 100 - Reaction

The reactors of the conventional hydrotreater are trickle-bed reactors; the first contains two catalyst beds of 15 and 17 ft in height. The vessel is 12 ft. diameter by 52 ft tall tangent-to-tangent (T-T) including 10 ft. for internals. The size is based upon the LHSV for determining the total catalyst volume, and then the length-to-diameter ratio of the bed. Similarly, the second reactor contains a single bed of 23 ft depth and is 12 ft. diameter by 33 ft tall tangent-to-tangent.

The reactors of the IsoThermal type hydrotreater are liquid full fixed bed reactors and are smaller due to the absence of the gas phase and operation at higher LHSV than the conventional reactors. Both reactors are 10 ft. diameter by 41.5 ft tall tangent-to-tangent (T-T). Each reactor contains a single bed of catalyst of 36.5 ft deep. Both reactors contain catalyst supports as well as advanced internals for distributing the liquid feed. Since inert packing at the top and bottom of a bed was assumed to be minimal, an allowance of 5 ft of height was used.

The HDS catalyst system is assumed to use a NiMo on alumina catalyst of bulk density of 43.7 lb/ft<sup>3</sup>.

Since the design conditions were based on information from a revamped unit, the reactor temperatures are probably lower than usual.

### **Section 200 - Gas Recovery**

Major differences in the flowsheets of the two processes are most apparent in the gas recovery schemes. The conventional unit increases the reactor hydrogen partial pressure by recovering hydrogen by membrane separation from the purge gas. In the simulation, it was not possible within practical conditions to obtain a hydrogen concentration in the 80 vol% range, hence what appears to be a purer than expected feed to the membrane separator.

That the IsoTherming type process does not recycle hydrogen is reflected in the separation scheme. A separator column was added to reduce the amount of desired VGO boiling range product leaving as vapor with the naphtha and lighter products. The temperature of the hot separator was kept as hot as possible for the benefit of the stripper operation.

### **Section 300 - Product Recovery**

The stripper operation is aided by the naphtha contained in the feed stream, thus potentially reducing the amount of stripping steam. The bottom temperature of the stripper is a function of the feed temperature, the hotter the better to keep water out of the bottoms product. Although the FCCU can tolerate some water in the feed, the drier the feed the less potential for flow problems.

### **Hydrogen System**

Makeup hydrogen supplied is assumed to be vendor provided 99.55 mol% pure hydrogen. The hydrogen is assumed to be made by steam methane reforming with pressure swing adsorption purification. Makeup hydrogen replaces hydrogen consumed by reaction to form  $\text{H}_2\text{S}$  and ammonia and to saturate aromatics and olefins as well as losses through venting to the fuel gas system and small leaks.

Each hydrogen compressor load is split between two compressors in parallel to increase reliability and safety at the cost of a slightly lower efficiency and slightly higher capital cost than a single compressor. It is assumed package reciprocating compressor units are used that include lubricating systems and controls.

The compressors are generally sized for start-of-run (SOR) conditions. At the end-of-run (EOR), the pressure drop across the first reactor could well be higher, resulting in lower pressure in the stripper column and the gas recovery train to the amine unit.

### **Materials of Construction**

The presence of  $\text{H}_2\text{S}$  and  $\text{H}_2$  requires chrome-molybdenum or stainless steel clad vessels and exchanger shells and stainless steel exchanger tubes. The reactors and down stream vessels and exchanger shells that operate above 500°F (260°C) are either 2¼ Cr 1 Mo or 1¼ Cr ½ Mo. Stainless steel is used for the furnace tubes. The piping around the reactors is also Cr-Mo steel. Unless noted in the equipment list (Table 7.6 and 7.7), all other equipment is carbon steel.

### **Waste Treatment and Disposal**

Wastes from the hydrotreater include sour water, sour gas and spent catalysts.  $\text{H}_2\text{S}$  is recovered by amine scrubbing. The  $\text{H}_2\text{S}$  rich stream from the amine unit is sent to the refinery's sulfur recovery unit, typically a Claus-type process with tail gas treater, for recovery as elemental

sulfur. Sulfur recovery is reviewed in PEP Report 216 “Acid Gas Treatment and Sulfur Recovery” (1997). The sour water is treated and the ammonia recovered. Oily condensate is sent to the refinery’s gravity settler (API settler). Oil is recovered and the water is further purified in the refinery’s wastewater treatment system.

The U.S. Environmental Protection Agency now lists hydrotreating catalysts as Hazardous Wastes (K171 and K172). Some European agencies are reviewing the disposal of spent hydrotreating catalyst [214A588]. Landfilling is increasingly becoming unattractive. Spent HDS catalyst is usually sent to a metals reclaimer for processing to recover the valuable metals, as discussed in Section 5, which is the option we assume.

## **COST ESTIMATES**

We present here the capital investment and production cost estimates for hydrotreating vacuum gas oil to produce FCC feedstock. Allowance for interest on funds spent during construction is not included (i.e. overnight construction). The location is the U.S. Gulf Coast. Construction begins in the second quarter of 2006.

Equipment costs and production costs are estimated primarily using the PEP COST database, version 3.1.5, developed by PEP [PEP Report 162].

### **Capital Costs**

Capital costs at a PEP Cost Index of 718 (mid 2006) are developed for hydrotreating 30,000 BPSD of a vacuum gas oil feedstock for each process. We present the capital costs for each hydrotreater individually.

For the conventional hydrotreater, Table 7.10 shows the Total Fixed Capital (TFC) investment is \$88.0 million. The Battery Limits Investment (BLI), which includes PEP’s contingency of 15%, is \$57.7 million. The Battery Limits Installed cost is \$50.4 million. This installed cost includes \$1.6 million for the initial reactor fill of the catalysts (added to the capital costs calculated without the catalyst). The investment cost of the amine unit only includes the absorption and amine regeneration section [PEP Report 216]. The sulfur recovery sections are excluded since the refinery’s existing Claus unit is assumed to be used. The Battery Limits Investment of \$57.7 million compares favorably with a published estimate of \$55 million estimate for a hydrotreater of the same size adjusted to 2006 using the PEP COST Indices [214A574]. The off-sites utility and tankage investment is \$9.9 million. Allotments for general services and waste treatment bring the total offsites investment to \$30.3 million including a 15% contingency. The costs of each section are shown in Table 7.11.

**Table 7.10**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

<b>TOTAL CAPITAL INVESTMENT</b>			
CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)			
HDT VGO FCC FEED			
AT 0.95 STREAM FACTOR			
PEP COST INDEX: 718			
	<b>COST (\$1,000)</b>	<b>CAPACITY EXPONENT</b>	
		<b>UP</b>	<b>DOWN</b>
BATTERY LIMITS EQUIPMENT, F.O.B.			
REACTORS	4,364	0.97	0.88
COLUMNS	68	0.42	0.33
VESSELS & TANKS	1,367	0.86	0.76
HEAT EXCHANGERS	744	0.82	0.64
FURNACES	650	0.82	0.82
COMPRESSORS	4,811	0.76	0.76
SPECIAL EQUIPMENT	235	0.95	0.95
PUMPS	817	0.76	0.73
TOTAL	13,056	0.85	0.79
DIRECT INSTALLATION COSTS	12,072	0.79	0.60
PACKAGE UNIT	9,387	0.76	0.66
INDIRECT COSTS	11,436	0.70	0.59
UNSCHEDULED EQUIPMENT, 10%	4,436	0.78	0.66
BATTERY LIMITS, INSTALLED	50,387	0.78	0.66
CONTINGENCY, 15%	7,320	0.78	0.66
BATTERY LIMITS INVESTMENT	57,707	0.78	0.66
OFF-SITES, INSTALLED			
CLARIFIED WATER	426	0.29	0.00
COOLING WATER	794	0.92	0.92
PROCESS WATER	248	0.62	0.17
BOILER FEED WATER	757	0.00	0.00
STEAM	1,734	0.00	0.00
TANKAGE	5,971	0.65	0.64
UTILITIES & STORAGE	9,930	0.52	0.43
GENERAL SERVICE FACILITIES	13,527	0.74	0.63
WASTE TREATMENT	2,885	0.78	0.66
TOTAL	26,342	0.67	0.55
CONTINGENCY, 15%	3,951	0.67	0.55
OFF-SITES INVESTMENT	30,294	0.67	0.55
TOTAL FIXED CAPITAL	88,001	0.74	0.62

**Table 7.11**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**CAPITAL INVESTMENT BY SECTION**

CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)  
HDT VGO FCC FEED  
AT 0.95 STREAM FACTOR

PEP COST INDEX: 718

	REACTION SECTION			GAS RECOVERY SECTION			PRODUCT RECOVERY SECTION		
	COST (\$1,000)	CAPACITY EXPONENT		COST (\$1,000)	CAPACITY EXPONENT		COST (\$1,000)	CAPACITY EXPONENT	
		UP	DOWN		UP	DOWN		UP	DOWN
BATTERY LIMITS EQUIPMENT, F.O.B.									
REACTORS	4,364	0.97	0.88	--	--	--	--	--	--
COLUMNS	--	--	--	--	--	--	68	0.42	0.33
VESSELS & TANKS	82	0.46	0.41	1,270	0.89	0.80	15	0.27	0.25
HEAT EXCHANGERS	480	0.89	0.63	241	0.69	0.66	22	0.61	0.61
FURNACES	650	0.82	0.82	--	--	--	--	--	--
COMPRESSORS	4,073	0.76	0.76	680	0.76	0.76	58	0.76	0.76
SPECIAL EQUIPMENT	--	--	--	235	0.95	0.95	--	--	--
PUMPS	642	0.80	0.80	58	0.65	0.55	117	0.58	0.47
TOTAL	10,291	0.86	0.80	2,484	0.84	0.78	280	0.57	0.48
DIRECT INSTALLATION COSTS	8,220	0.83	0.59	2,985	0.76	0.69	868	0.46	0.34
PACKAGE UNIT	157	1.00	1.00	7,800	0.72	0.63	--	--	--
INDIRECT COSTS	6,429	0.75	0.62	4,595	0.65	0.57	398	0.38	0.28
UNSCHEDULED EQUIPMENT, 10%	2,494	0.83	0.69	1,786	0.73	0.64	155	0.46	0.35
BATTERY LIMITS INSTALLED	29,021	0.83	0.69	19,650	0.73	0.64	1,700	0.46	0.35
CONTINGENCY, 15%	4,115	0.83	0.69	2,948	0.73	0.64	255	0.46	0.35
BATTERY LIMITS INVESTMENT	33,137	0.83	0.69	22,598	0.73	0.64	1,955	0.46	0.35
OFFSITES, INSTALLED									
CLARIFIED WATER	--	--	--	418	0.29	0.00	8	0.29	0.00
COOLING WATER	--	--	--	778	0.92	0.92	16	0.92	0.92
PROCESS WATER	--	--	--	164	0.62	0.17	3	0.62	0.17
BOILER FEED WATER	--	--	--	683	0.00	0.00	74	0.00	0.00
STEAM--	--	--	1,734	0.00	0.00	--	--	--	--
TANKAGE	2,886	0.65	0.65	--	--	--	3,085	0.64	0.64
UTILITIES & STORAGE	2,886	0.65	0.65	3,777	0.30	0.16	3,186	0.63	0.62

For the IsoTherming type hydrotreater, Table 7.12 shows the Total Fixed Capital (TFC) investment is \$70.7 million. The total battery limits investment (BLI), which includes PEP's contingency of 15% is \$44.4 million. The total Battery Limits Installed cost is \$38.8 million. This installed cost includes \$1.5 million for the initial reactor fill of the catalysts (added to the capital costs calculated without the catalyst). The investment cost of the amine unit only includes the absorption and amine regeneration section [PEP Report 216]. The sulfur recovery sections are excluded since the refinery's existing Claus unit is assumed to be used. The Battery Limits Investment of \$44.4 million is less than the \$57.7 million BLI of the conventional hydrotreater mainly due to no recycle compressor and considerably smaller amine unit, smaller reactors and only two separators. The costs of each section are shown in Table 7.13. The off-sites utility and tankage investment is \$9.8 million. Allotments for general service facilities and waste treatment bring the total offsite investment to \$26.3 million. The costs of each section are shown in Table 7.13.

**Table 7.12**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**  
**30,000 BPSD**

<b>TOTAL CAPITAL INVESTMENT</b>			
CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)			
HDT VGO FCC FEED			
AT 0.95 STREAM FACTOR			
PEP COST INDEX: 718			
	<b>COST</b>	<b>CAPACITY</b>	
	<b>(\$1,000)</b>	<b>EXPONENT</b>	
		<b>UP</b>	<b>DOWN</b>
BATTERY LIMITS EQUIPMENT, F.O.B.			
REACTORS	2,538	0.97	0.93
COLUMNS	97	0.37	0.31
VESSELS & TANKS	496	0.71	0.68
HEAT EXCHANGERS	948	0.92	0.66
FURNACES	676	0.82	0.82
COMPRESSORS	2,917	0.76	0.76
SPECIAL EQUIPMENT	330	0.95	0.95
MISCELLANEOUS EQUIPMENT	50	0.71	0.71
PUMPS	723	0.76	0.72
TOTAL	8,775	0.85	0.79
DIRECT INSTALLATION COSTS	13,556	0.78	0.53
PACKAGE UNIT	4,385	0.57	0.48
INDIRECT COSTS	8,666	0.68	0.52
UNSCHEDULED EQUIPMENT, 10%	3,392	0.75	0.58
BATTERY LIMITS, INSTALLED	38,774	0.75	0.58
CONTINGENCY, 15%	5,597	0.75	0.58
BATTERY LIMITS INVESTMENT	44,371	0.75	0.58
OFF-SITES, INSTALLED			
CLARIFIED WATER	426	0.00	0.00
COOLING WATER	728	0.92	0.92
PROCESS WATER	220	0.36	0.00
BOILER FEED WATER	757	0.00	0.00
STEAM	1,734	0.45	0.00
TANKAGE	5,971	0.65	0.64
UTILITIES & STORAGE	9,835	0.57	0.42
GENERAL SERVICE FACILITIES	10,841	0.72	0.55
WASTE TREATMENT	2,219	0.75	0.58
TOTAL	22,895	0.66	0.50
CONTINGENCY, 15%	3,434	0.66	0.50
OFF-SITES INVESTMENT	26,330	0.66	0.50
TOTAL FIXED CAPITAL	70,700	0.72	0.55



**Table 7.13**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**  
**30,000 BPSD**

**CAPITAL INVESTMENT BY SECTION**

CAPACITY: 3,320 MILLION LB/YR (1,510,000 T/YR)  
HDT VGO FCC FEED  
AT 0.95 STREAM FACTOR

PEP COST INDEX: 718

	REACTION SECTION			GAS RECOVERY SECTION			PRODUCT RECOVERY SECTION		
	COST (\$1,000)	CAPACITY EXPONENT		COST (\$1,000)	CAPACITY EXPONENT		COST (\$1,000)	CAPACITY EXPONENT	
		UP	DOWN		UP	DOWN		UP	DOWN
BATTERY LIMITS EQUIPMENT, F.O.B.									
REACTORS	2,538	0.97	0.93	--	--	--	--	--	--
COLUMNS	--	--	--	28	0.22	0.26	68	0.42	0.33
VESSELS & TANKS	300	0.74	0.75	196	0.65	0.59	--	--	--
HEAT EXCHANGERS	762	0.95	0.63	186	0.78	0.79	--	--	--
FURNACES	676	0.82	0.82	--	--	--	--	--	--
COMPRESSORS	2,917	0.76	0.76	--	--	--	--	--	--
SPECIAL EQUIPMENT	--	--	--	330	0.95	0.95	--	--	--
MISCELLANEOUS EQUIPMENT	50	0.71	0.71	--	--	--	--	--	--
PUMPS	0.79	0.77	25	0.19	0.14	29	0.46	0.39	--
TOTAL	7,912	0.86	0.80	766	0.79	0.75	97	0.43	0.34
DIRECT INSTALLATION COSTS	10,356	0.77	0.47	2,814	0.85	0.78	387	0.31	0.28
PACKAGE UNIT	1,458	0.57	0.48	2,927	0.57	0.48	--	--	--
INDIRECT COSTS	6,268	0.71	0.52	2,224	0.63	0.55	165	0.25	0.21
UNSCHEDULED EQUIPMENT, 10%	2,454	0.78	0.58	873	0.70	0.61	65	0.32	0.27
BATTERY LIMITS INSTALLED	28,447	0.78	0.58	9,604	0.70	0.61	714	0.32	0.27
CONTINGENCY, 15%	4,048	0.78	0.58	1,441	0.70	0.61	107	0.32	0.27
BATTERY LIMITS INVESTMENT	32,495	0.78	0.58	11,044	0.70	0.61	821	0.32	0.27
OFFSITES, INSTALLED									
CLARIFIED WATER	--	--	--	426	0.00	0.00	--	--	--
COOLING WATER	--	--	--	728	0.92	0.92	--	--	--
PROCESS WATER	--	--	--	220	0.36	0.00	--	--	--
BOILER FEED WATER	--	--	--	757	0.00	0.00	--	--	--
STEAM--	--	--	1,734	0.45	0.00	--	--	--	--
TANKAGE	2,886	0.65	0.65	--	--	--	3,085	0.64	0.64
UTILITIES & STORAGE	2,886	0.65	0.65	3,864	0.43	0.13	3,085	0.64	0.64

As discussed in Section 4, the price of catalysts can vary widely with the cost of the metals. The cost of the second batch of catalyst is included as an operating materials expense. For our estimate, the HDS treatment catalyst is priced at 5.83 \$/lb determined from the cost of metals (3.5% NiO/12.5% MoO<sub>3</sub> was assumed) plus a base charge of \$4.00/lb.

The BLI costs in Tables 7.10 and 7.12 include factors for indirect costs and unscheduled equipment. Indirect costs include such items as equipment rental (scaffolding and lifting for example), testing, freight, and sales taxes and insurance. The indirect cost also includes labor overhead expenses, engineering and contractor's profit. Indirect costs are discussed in Appendix B. We apply the unscheduled equipment allowance factor of 10% to the sum of equipment cost, direct installation costs, package unit costs and indirect costs. Licensing or royalty fees are regarded as proprietary and are not included in these costs.

Off-site utilities and tankage installed investments totaled about \$9.9 million for the each process. Of this total, tankage for three days feedstock and three hours production cost \$6.0 million in each case. Some tankage is required for handling upsets and for good product quality control.

Allowances of \$13.5 and \$10.8 million are made for investment in general services facilities, which includes items such as roads, parking, fences, administrative offices, craft shops, fire and safety equipment, plant communications and warehouses. \$2.8 million and \$2.3 million allowances are made respectively for investments expanding or providing waste treatment facilities. The off-sites investment totals \$30.2 million for the conventional unit and \$26.3 million for the IsoTherming type unit with the inclusion of the general services facilities, waste treatment investments and 15% contingency.

The BLI in Tables 7.10 and 7.12 includes PEP's contingency of 15% for established refinery processes. All the major licensors and engineering contractors have experience building hydrotreaters for treating all types of feedstocks. With a 25% contingency, the BLI of the conventional unit becomes \$60.1 million and the TFC rises to \$91.8 million with an off-sites investment of \$31.6 million. Similarly for the IsoTherming type case, the TFC rises to \$73.7 million, the BLI becomes \$46.2 million and the off-sites total \$27.4 million.

## **Production Costs**

Table 7.14 shows our production cost estimate for a 30,000 BPSD conventional hydrotreating unit along with estimates for 15,000 BPSD and 60,000 BPSD units. The feedstock, product and utility values are the same for each process. The values are based on mid-year 2006 prices for the U.S. Gulf Coast. The VGO feedstock value was determined to be 15.14 ¢/lb (1.117 \$/gal or 49.47 \$/B). The FCC feedstock was valued as low sulfur fuel oil at 18.84 ¢/lb (1.41 \$/gal or 59.22 \$/B). In the table, all variable costs are expressed as ¢/lb of the FCC feedstock product. Gross raw materials cost 21.10 ¢/lb. By-products and utilities (steam) generated is shown as credits (negative). The by-product credit is 0.18 ¢/lb due to the purge gas and off gas. No value was given to the H<sub>2</sub>S stream. Net total utilities cost 0.18 ¢/lb. The costs of a replacement batch of each catalyst is included assuming a two year catalyst life in each case. This may be conservative as some units have run longer with clean feedstock. Variable costs total 16.53 ¢/lb.

Labor costs are based upon 4 operators per shift (one control room, three outside) at the total compensation rate, including benefits, of \$41.50/H each. Maintenance labor is estimated as 3%/yr of battery limits investment. Since many of the analyses are derived from the online control instrumentation, control laboratory labor is estimated at 20% of direct operating labor costs. Labor costs total 0.10 ¢/lb.

**Table 7.14**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**PRODUCTION COSTS**

PEP COST INDEX: 718

**VARIABLE COSTS**

	UNIT COST	CONSUMPTION PER LB	¢/LB
	-----	-----	-----
RAW MATERIALS			
HYDROGEN	81.04 ¢/LB	0.012407 LB	1.01
VACUUM GAS OIL FEED	15.14 ¢/LB	1.02354 LB	15.50
HDS CATALYST	583 ¢/LB	0.000028 LB	0.02
DEA	84.4 ¢/LB	0.00002 LB	NEGL
SPENT CATALYST FEE	39 ¢/LB	0.000028 LB	NEGL
			-----
GROSS RAW MATERIALS			16.53
BY-PRODUCTS			
PURGE GAS	18.82 ¢/LB	-0.00316 LB	-0.06
OFF GAS (SEPARATOR)	14.55 ¢/LB	-0.001714 LB	-0.02
WILD NAPHTHA	27.31 ¢/LB	-0.002146 LB	-0.06
OFF GAS (STRIPPER)	10.71 ¢/LB	-0.003584 LB	-0.04
			-----
TOTAL BY-PRODUCTS			-0.18

	UNIT COST	CONSUMPTION PER LB	CONSUMPTION PER KG	
	-----	-----	-----	
UTILITIES				
COOLING WATER	10.66 ¢/MGAL	0.512 GAL	4.27 LITERS	0.01
PROCESS WATER	1.13 \$/MGAL	0.00993 GAL	0.0828 LITERS	NEGL
STEAM, 150 PSIG	8.4 \$/MLB	0.0102 LB	0.0102 KG	0.01
ELECTRICITY	5.76 ¢/KWH	0.0228 KWH	0.0502 KWH	0.13
NATURAL GAS	6.74 \$/MMBTU	48.8 BTU	27.1 KCAL	0.03
				-----
TOTAL UTILITIES				0.18

**Table 7.14 (Concluded)**  
**VACUUM GAS OIL CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**PRODUCTION COSTS**

PEP COST INDEX: 718

<b>CAPACITY (MILLION LB/YR)*</b>	<b>1,660</b>	<b>3,320<sup>#</sup></b>	<b>6,640</b>
INVESTMENT (\$ MILLIONS)			
BATTERY LIMITS (BLI)	36.5	57.7	99.0
OFFSITES	20.7	30.3	48.1
TOTAL FIXED CAPITAL (TFC)	57.1	88.0	147.1
SCALING EXPONENTS	0.62	0.74	
PRODUCTION COSTS (¢/LB)			
RAW MATERIALS	16.53	16.53	16.53
BY-PRODUCTS	-0.18	-0.18	-0.18
UTILITIES	0.18	0.18	0.18
VARIABLE COSTS	16.53	16.53	16.53
OPERATING LABOR, 4/SHIFT, \$41.5/HR	0.09	0.04	0.02
MAINTENANCE LABOR, 3%/YR OF BLI	0.07	0.05	0.04
CONTROL LAB LABOR, 20% OF OPER LABOR	0.02	0.01	NEGL
LABOR COSTS	0.18	0.10	0.06
MAINTENANCE MATERIALS, 3%/YR OF BLI	0.07	0.05	0.04
OPERATING SUPPLIES, 10% OF OPER LABOR	0.01	NEGL	NEGL
TOTAL DIRECT COSTS	16.79	16.68	16.63
PLANT OVERHEAD, 80% OF LABOR COSTS	0.14	0.08	0.05
TAXES AND INSURANCE, 2%/YR OF TFC	0.07	0.05	0.04
PLANT CASH COSTS	17.00	16.81	16.72
DEPRECIATION, 10%/YR OF TFC	0.34	0.27	0.22
PLANT GATE COSTS	17.34	17.08	16.94
G&A, SALES, RESEARCH	0.10	0.09	0.09
NET PRODUCTION COST	17.44	17.17	17.03
ROI BEFORE TAXES, 63%/YR OF TFC	2.17	1.67	1.40
PRODUCT VALUE	19.61	18.84	18.43

\* OF HDT VGO FCC FEED

# BASE CASE

Maintenance materials are estimated at 3%/yr of the battery limits investment; operating supplies at 10% of operating labor costs. Adding maintenance materials and supplies to the variable materials and labor costs produces a total direct operating cost of 16.68 ¢/lb or 52.44 \$/B of hydrotreated FCC feedstock.

Our production cost estimates includes charges for plant overhead (80% of labor costs), property taxes and insurance (2%/yr of total fixed cost) and depreciation (10%/yr, straight line). Adding the overhead and taxes and insurance costs to the total direct operating cost gives a plant cash cost of 16.81 ¢/lb. Depreciation further adds 0.27 ¢/lb to bring the plant gate cost to 17.08 ¢/lb or 53.70 \$/B.

General and administrative expenses (G&A), sales, and research and development (R&D) expenses add 0.09 ¢/lb since the product is usually used within the refinery. With G&S, sales and R&S expenses, the net production cost is 17.17 ¢/lb or 53.98 \$/B.

With a before tax return on investment (ROI) of 63%, total product value of the hydrotreated FCC feedstock is 18.84 ¢/lb or 59.23 \$/B, the market price. With a before tax return on investment (ROI) of 25%, a frequently used project screening value, the total product value of the hydrotreated FCC feedstock is 17.83 ¢/lb or 56.06 \$/B.

Table 7.15 shows the production cost for the IsoTherming type process. The raw material costs are less since less hydrogen is consumed. The by-product credit is less since the simulation resulted in less wild naphtha being lost to the off gas. Labor costs, maintenance materials and supplies, plant overhead, and taxes and insurance are all slightly lower since these are determined indirectly by factors of the capital costs. Depreciation, of course, is lower since the TFC is lower than the conventional unit's TFC. Net production cost is 17.03 ¢/lb or 53.54 \$/B.

With a before tax return on investment (ROI) of 85%, total product value of the hydrotreated FCC feedstock of the Isotherming type unit is 18.84 ¢/lb or 59.23 \$/B, the market price. With a before tax return on investment (ROI) of 25%, a frequently used project screening value, the total product value of the hydrotreated FCC feedstock is 17.56 ¢/lb or 55.21 \$/B.

Economy of scale benefits the product value as illustrated for both plants in cases of units of one-half and double the capacity of the base case unit.

### **Profitability**

The value of hydrotreated VGO FCC feedstock was 18.84 ¢/lb or 59.23 \$/B. With this product value, the before tax return on investment (ROI) is 63% for the base capacity conventional hydrotreater, considerably greater than the 25% frequently used to screen projects. Similarly the IsoTherming type unit's ROI is 85%, significantly greater than the return on the conventional unit.

**Table 7.15**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**  
**30,000 BPSD**

<b>PRODUCTION COSTS</b>				
PEP COST INDEX: 718				
<b>VARIABLE COSTS</b>				
	<b>UNIT COST</b>	<b>CONSUMPTION PER LB</b>		<b>¢/LB</b>
	-----	-----		-----
RAW MATERIALS				
HYDROGEN	81.04 ¢/LB	0.011316 LB		0.92
VACUUM GAS OIL FEED	15.14 ¢/LB	1.02348 LB		15.50
HDS CATALYST	583 ¢/LB	0.000037 LB		0.02
DEA	84.4 ¢/LB	0.00002 LB		NEGL
SPENT CATALYST FEE	39 ¢/LB	0.000028 LB		NEGL
				-----
GROSS RAW MATERIALS				16.44
BY-PRODUCTS				
OFF GAS	13.87 ¢/LB	-0.006359 LB		-0.09
WILD NAPHTHA	26.66 ¢/LB	-0.001659 LB		-0.04
				-----
TOTAL BY-PRODUCTS				-0.13
	<b>UNIT COST</b>	<b>CONSUMPTION PER LB</b>	<b>CONSUMPTION PER KG</b>	
	-----	-----	-----	
UTILITIES				
COOLING WATER	10.66 ¢/MGAL	0.466 GAL	3.89 LITERS	NEGL
STEAM, 150 PSIG	8.4 \$/MLB	0.0792 LB	0.0792 KG	0.07
ELECTRICITY	5.76 ¢/KWH	0.0091 KWH	0.0201 KWH	0.05
NATURAL GAS	6.74 \$/MMBTU	89.7 BTU	49.8 KCAL	0.06
				-----
TOTAL UTILITIES				0.18

**Table 7.15 (Concluded)**  
**VACUUM GAS OIL ISOTHERMING™ TYPE HYDROTREATING**  
**30,000 BPSD**

**PRODUCTION COSTS**

PEP COST INDEX: 718

<b>CAPACITY (MILLION LB/YR)*</b>	<b>1,660</b>	<b>3,320<sup>#</sup></b>	<b>6,640</b>
INVESTMENT (\$ MILLIONS)			
BATTERY LIMITS (BLI)	29.7	44.4	74.6
OFFSITES	18.7	26.3	41.5
TOTAL FIXED CAPITAL (TFC)	48.3	70.7	116.1
SCALING EXPONENTS	0.55	0.72	
PRODUCTION COSTS (¢/LB)			
RAW MATERIALS	16.44	16.44	16.44
BY-PRODUCTS	-0.13	-0.13	-0.13
UTILITIES	0.18	0.18	0.18
VARIABLE COSTS	16.49	16.49	16.49
OPERATING LABOR, 4/SHIFT, \$41.5/HR	0.09	0.04	0.02
MAINTENANCE LABOR, 3%/YR OF BLI	0.05	0.04	0.03
CONTROL LAB LABOR, 20% OF OPER LABOR	0.02	0.01	NEGL
LABOR COSTS	0.16	0.09	0.05
MAINTENANCE MATERIALS, 3%/YR OF BLI	0.05	0.04	0.03
OPERATING SUPPLIES, 10% OF OPER LABOR	0.01	NEGL	NEGL
TOTAL DIRECT COSTS	16.71	16.62	16.57
PLANT OVERHEAD, 80% OF LABOR COSTS	0.13	0.07	0.04
TAXES AND INSURANCE, 2%/YR OF TFC	0.06	0.04	0.03
PLANT CASH COSTS	16.90	16.73	16.64
DEPRECIATION, 10%/YR OF TFC	0.29	0.21	0.17
PLANT GATE COSTS	17.19	16.94	16.81
G&A, SALES, RESEARCH	0.10	0.09	0.09
NET PRODUCTION COST	17.29	17.03	16.90
ROI BEFORE TAXES, 85%/YR OF TFC	2.47	1.81	1.49
PRODUCT VALUE	19.76	18.84	18.39

\* OF HDT VGO FCC FEED

# BASE CASE

## 8 ATMOSPHERIC RESIDUE HYDROTREATING ECONOMICS

In this section, we evaluate the process economics of a generic PEP atmospheric residue hydrotreating unit. The unit is designed to process 30,000 BPSD or 28,500 barrels per calendar day (BPCD) of atmospheric residue oil feedstock. Capacities are calculated using a 0.95 on stream factor. This plant capacity is typical of hydrotreating plants as discussed in Section 4.

### PROCESS DESCRIPTION

In this subsection, we describe a generic PEP hydrotreating unit designed to process 30,000 barrels per stream day (BPSD) of Heavy Arabian atmospheric residue (AR). Our design has a product capacity of 30,109 B/SD or 1.553 million mt/yr (3,424 million lb/yr) of hydrotreated atmospheric resid FCC feedstock.

This conventional hydrotreater is a high pressure (about 2,200 psig), single-stage process having three reactors each with a single catalyst bed. Make-up hydrogen is 99.55 vol% pure. Make-up hydrogen is mostly charged to the first reactor. A higher hydrogen partial pressure is provided in the lead catalyst bed than if recycled hydrogen were charged. Hydrogen separated from the third reactor effluent is amine treated to remove H<sub>2</sub>S and mostly charged to quench to the feed to the second and third reactors.

The process design and utility consumption rates used in this report are based on computations, published information, and nonconfidential information from licensors and vendors. The design may or may not be similar to a licensed process or to processes otherwise in use today.

Table 8.1 lists the design bases and assumptions of the design. Feedstock and liquid product characterizations are summarized in Table 8.2. Major process stream flows are summarized in Table 8.3. The process was modeled using Aspen Technology's Aspen™ Plus process simulator, version 11.1-0, built September 20, 2001. The physical properties method was the Redlich-Kwong Soave equation of state method. Major equipment is listed with size and materials of construction in Table 8.4. Process utility requirements are summarized in Table 8.5.



**Table 8.1**  
**DESIGN BASES AND ASSUMPTIONS – ATMOSPHERIC RESIDUE HYDROTREATER**

**Feedstock**

Feedstock characterization	Please See Table 8.2
Make-up H <sub>2</sub> supply pressure, psig	285
Make-up H <sub>2</sub> purity, mol%/wt%	99.55/94.22

Chemical H <sub>2</sub> consumption, SCF/B	930
H <sub>2</sub> reactor losses, wt% FF	0.15

<b>Reactor</b>	<b><u>R-101</u></b>	<b><u>R-102</u></b>	<b><u>R-130</u></b>	<b><u>Overall</u></b>
Type	Moving Bed	Trickle Bed	Trickle Bed	
Flow	Co-current	Co-current	Co-current	
Number of reactors (beds/reactor)	1 (1)	1 (1)	1 (1)	
Catalyst type	HDM NiMo/alumina	HDS NiMo/alumina	HDS NiMo/alumina	
Fresh catalyst metals, Ni/Mo wt% as oxide	2.5/12	3.5/12.5	3.5/12.5	
Catalyst bulk density, lb/ft <sup>3</sup>	31.8	43.7	44.4	
Reactor fill, lb	190,000	320,000	354,000	864,000
ft <sup>3</sup>	6,000	7,300	8,000	21,300
Catalyst life, years	--	2	2	
Fresh catalyst make-up rate	24,150 lb/week	160,000 lb/y	177,000 lb/y	
Reactor conditions (SOR)				
Inlet/outlet pressure, psig	2,200/		/2,132	
Inlet/outlet temperature, °F (°C)	660 (349)/		/730 (388)	
LHSV, H <sup>-1</sup>	2.272	1.349	1.220	0.500
Recycle H <sub>2</sub> /oil ratio				
<b>Reactor Yields, wt% AR Fresh feed</b>				
H <sub>2</sub> S				4.2882
NH <sub>3</sub>				0.2213
C <sub>1</sub>				0.0326
C <sub>2</sub>				0.0784
C <sub>3</sub>				0.0597
C <sub>4</sub>				0.0595
Naphtha				1.3798
Hydrotreated AR FCC Feed				<u>95.3114</u>
Total				101.4308
Liquid products characterizations	Please See Table 8.2			
Spent wash water salt content, wt%				4

**Table 8.2**  
**FEEDSTOCK AND PRODUCT CHARACTERIZATIONS**

	<b>AR</b> <b><u>Fresh Feed</u></b>	<b>Hydrotreated <u>AR</u></b>	<b>Wild</b> <b><u>Naphtha</u></b>
Gravity, API	11.8	25.9	62.3
Sulfur, wt%	4.37	0.35	0.004
Nitrogen, ppmw	3,000	1,400	5
Conradson Carbon Residue, wt%	13.6	5.5	---
Metals, Ni/V, ppmw	34/97	5/5	---
Distillation, °F (°C)	D-1160	D-1160	D-86
T <sub>5</sub>	725 (385)	724 (384)	T <sub>10</sub> 105 (41)
T <sub>10</sub>	770 (410)	779 (415)	T <sub>30</sub> 121 (49)
T <sub>20</sub>	833 (445)	816 (435)	T <sub>50</sub> 141 (61)
T <sub>30</sub>	896 (480)	878 (479)	T <sub>70</sub> 183 (84)
T <sub>40</sub>	959 (515)	928 (498)	T <sub>90</sub> 224 (107)
T <sub>50</sub>	1040 (560)	1000(538)	
T <sub>53</sub>	1067 (575)	1027(553)	

**Table 8.3**  
**ATMOSPHERIC RESIDUE OIL HYDROTREATING**

<b>STREAM FLOWS</b>							
CAPACITY: 30,000 BPSD (6,360 M <sup>3</sup> /SD)							
650°F+ (343°C+) ATMOSPHERIC RESIDUE							
AT 0.95 STREAM FACTOR							
<b>Stream Flows, lb/Hr</b>							
	<b>Mol Wt</b>	<b>(1) Fresh Feed</b>	<b>(2) Injection Hydrogen</b>	<b>(3) Reactor Fresh Oil</b>	<b>(4) Make-Up Hydrogen</b>	<b>(5) Recycle Hydrogen</b>	<b>(6) Reactor Effluent</b>
Water	18.0	--	--	--	--	--	--
Hydrogen	2.0	--	1,000	1,000	11,231	33,427	38,481
Nitrogen	28.0	--	--	--	674	4,449	5,123
Ammonia	17.0	--	--	--	--	--	956
Hydrogen sulfide	34.1	--	--	--	--	--	18,513
Methane	16.0	--	--	--	14	942	1,097
Ethane	30.1	--	--	--	--	1,546	1,884
Propane	44.1	--	--	--	--	728	985
Isobutane	58.1	--	--	--	--	105	170
n-Butane	58.1	--	--	--	--	254	446
Wild Naphtha	80	--	--	--	--	1,808	9,212
AR Product	907	--	--	431,708	--	89	410,109
AR Fresh Feed	926	431,708	--	--	--	--	--
<hr/>							
Total, lb/hr		431,708	1,000	432,708	11,919	43,348	486,975
kg/hr		195,819	454	196,273	5,407	19,662	220,888
lb-mole/hr		466	500	962	5,676	16,672	20,811

**Table 8.3 (Continued)**  
**ATMOSPHERIC RESIDUE OIL HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) ATMOSPHERIC RESIDUE  
AT 0.95 STREAM FACTOR

Stream Flows, lb/Hr						
		(7)	(8)	(9)	(10)	(11)
	Mol	Hot High Pressure Separator		Cold High Pressure Separator		
	<u>Wt</u>	<u>Liquid</u>	<u>Vapor</u>	<u>Liquid</u>	<u>Sour water</u>	<u>Vapor</u>
Water	18.0	--	--	9	71,495	196
Hydrogen	2.0	232	38,249	49	--	38,200
Nitrogen	28.0	40	5,083	13	--	5,070
Ammonia	17.0	19	936	106	--	831
Hydrogen sulfide	34.1	365	18,148	1,274	--	16,873
Methane	16.0	13	1,085	11	--	1,074
Ethane	30.1	34	1,850	89	--	1,761
Propane	44.1	24	961	132	--	829
Isobutane	58.1	5	164	45	--	120
n-Butane	58.1	15	431	142	--	289
Wild Naphtha	80	664	8,548	6,488	--	2,061
AR Product	907	374,065	36,044	35,942	--	102
AR Fresh Feed	926	--	--	--	--	--
Total, lb/hr		375,476	111,499	44,298	71,495	67,406
kg/hr		170,313	50,575	20,093	32,430	30,575
lb-mole/hr		621	20,272	366	3,972	19,825

**Table 8.3 (Continued)**  
**ATMOSPHERIC RESIDUE OIL HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) ATMOSPHERIC RESIDUE  
AT 0.95 STREAM FACTOR

Stream Flows, lb/day							
	(12)	(13)	(14)	(15)	(16)	(17)	
	<u>Mol</u>	<u>Acid</u>	<u>Purge</u>	<u>Hot Low</u>	<u>Cold Low</u>	<u>Cold Low</u>	<u>Hot Low</u>
	<u>Wt</u>	<u>Gas</u>	<u>Gas</u>	<u>Pressure</u>	<u>Pressure</u>	<u>Pressure</u>	<u>Pressure</u>
				<u>Separator</u>	<u>Separator</u>	<u>Separator</u>	<u>Separator</u>
				<u>Vapor</u>	<u>Off Gas</u>	<u>Liquid</u>	<u>Liquid</u>
Water	18.0	196	--	--	--	8	--
Hydrogen	2.0	105	4,666	204	246	7	28
Nitrogen	28.0	--	621	33	44	3	6
Ammonia	17.0	831	--	11	31	85	8
Hydrogen sulfide	34.1	16,873	--	217	561	930	148
Methane	16.0	--	132	10	17	4	3
Ethane	30.1	--	216	21	51	59	13
Propane	44.1	--	102	13	31	113	12
Isobutane	58.1	--	15	2	5	42	3
n-Butane	58.1	--	35	6	12	137	9
Wild Naphtha	80	--	252	122	93	6,517	542
AR Product	907	--	12	326	4	36,263	373,739
AR Fresh Feed	926	--	--	--	--	--	--
Total, lb/hr		18,005	6,051	964	1,096	44,167	374,511
kg/hr		8,167	2,745	437	497	20,034	169,875
lb-mole/hr		606	2,359	115	146	334	506

**Table 8.3 (Concluded)**  
**ATMOSPHERIC RESIDUE OIL HYDROTREATING**

**STREAM FLOWS**

CAPACITY: 30,000 BPSD (6,360 M<sup>3</sup>/SD)  
650°F+ (343°C+) ATMOSPHERIC RESIDUE  
AT 0.95 STREAM FACTOR

Stream Flows, lb/day					
	<b>Mol Wt</b>	<b>(18) Stripper Sour Water</b>	<b>(19) Stripper Off Gas</b>	<b>(20) Wild Naphtha</b>	<b>(21) Hydrotreated Atmospheric Residue</b>
Water	18.0	2,848	44	1	13
Hydrogen	2.0	--	35	--	--
Nitrogen	28.0	--	9	--	--
Ammonia	17.0	66	86	8	--
Hydrogen sulfide	34.1	3	1,021	51	6
Methane	16.0	--	7	--	--
Ethane	30.1	--	68	2	--
Propane	44.1	--	111	13	1
Isobutane	58.1	--	35	10	--
n-Butane	58.1	--	103	41	2
Wild Naphtha	80	--	1,474	3,575	2,009
AR Product	907	--	10	558	409,434
AR Fresh Feed	926	--	--	--	--
<hr/>					
Total, lb/hr		2,917	3,002	4,259	411,465
kg/hr		1,323	1,361	1,932	186,637
lb-mole/hr		162	83	50	709

**Table 8.4**  
**ATMOSPHERIC RESIDUE CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**MAJOR EQUIPMENT**

CAPACITY: 3,424 MILLION LB/YR (1,549,1000 T/YR)  
HDT ATMOSPHERIC RESIDUE  
AT 0.95 STREAM FACTOR

EQUIPMENT NUMBER	NAME	SIZE	MATERIAL OF CONSTRUCTION	REMARKS
REACTORS				
R-101	MOVING BED REACTOR	55,000 GAL	SHELL: 2.25 CR-1 MO	12 FT DIA. X 65 FT T-T 190,000 LB CATALYST
R-102	FIXED BED REACTOR	67,522 GAL	SHELL: 2.25 CR-1 MO	13 FT DIA. X 68 FT T-T 320,000 LB CATALYST
R-103	FIXED BED REACTOR	73,480 GAL	SHELL: 2.25 CR-1 MO	13 FT DIA. X 74 FT T-T 354,000 LB CATALYST
COLUMNS				
C-301	STRIPPER	5 FT DIA 48 FT	SHELL: C.S. TRAYS: C.S.	24 VALVE TRAYS, 24 INCH SPACING
COMPRESSORS				
K-101A, B	H2 MAKE-UP COMPRESSOR	2,851 BHP	C.S.	
K-102A, B	H2 MAKE-UP COMPRESSOR	2,964 BHP	C.S.	
K-103A, B	H2 MAKE-UP COMPRESSOR	2,778 BHP	C.S.	
K-201A, B	H2 RECYCLE COMPRESSOR	215 BHP	C.S.	
K-301	OFF GAS COMPRESSOR	44 BHP	C.S.	
HEAT EXCHANGERS				
E-101	FEED-STRIPPER PRODUCT EXCHANGER	7,500 SQ FT 34 MMBTU/HR	SHELL: C.S. TUBES: 2.25 CR- 1 MO	
E-102	FEED-V-201 VAPOR EXCHANGER	3,600 SQ FT 32 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-103A, B	FEED-V-201 LIQUID EXCHANGER	7,700 SQ FT 24.2 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-104	FEED-EFFLUENT EXCHANGER	1,850 SQ FT 16.45 MMBTU/HR	SHELL: 2.25 CR- 1 MO TUBES: 316 SS	
E-105	MAKE-UP H2 COOLER	1,400 SQ FT 6.5 MMBTU/HR	SHELL: C.S. TUBES: C.S.	AIR COOLER
E-106	MAKE-UP H2 COOLER	1,500 SQ FT 7.42 MMBTU/HR	SHELL: C.S. TUBES: C.S.	AIR COOLER
E-201	V-201 VAPOR-MAKE-UP EXCHANGER	150 SQ FT 2.1 MMBTU/HR	SHELL: 2.25 CR- 1 MO TUBES: 316 SS	
E-202	V-201 VAPOR STEAM BOILER	6,500 SQ FT 50 MMBTU/HR	SHELL: C.S. TUBES: 316 SS	
E-203	V-201 VAPOR AIR CONDENSER	4,200 SQ FT 13.05 MMBTU/HR	SHELL: C.S. TUBES: C.S.	AIR COOLER
E-204	V-201 VAPOR TRIM CONDENSER	5,050 SQ FT 10.04 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-205	V-202 VAPOR-V-203 LIQUID EXCHANGER	100 SQ FT 0.5 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-301	STRIPPER OVERHEAD CONDENSER	1,350 SQ FT 4.5 MMBTU/HR	SHELL: C.S. TUBES: C.S.	
E-302	STRIPPER OVERHEAD TRIM CONDENSER	500 SQ FT 1.01 MMBTU/HR	SHELL: C.S. TUBES: C.S.	

**Table 8.4 (Concluded)**  
**ATMOSPHERIC RESIDUE CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**MAJOR EQUIPMENT**

CAPACITY: 3,424 MILLION LB/YR (1,549,1000 T/YR)  
HDT ATMOSPHERIC RESIDUE  
AT 0.95 STREAM FACTOR

EQUIPMENT NUMBER	NAME	SIZE	MATERIAL OF CONSTRUCTION	REMARKS
PROCESS FURNACES				
F-101	FEED HEATER	11.8 MMBTU/HR	316 SS	
TANKS				
T-101A,B	AR STORAGE TANK	1,890,000 GAL	C.S.	
T-301	WILD NAPHTHA TANK	73,000 GAL	C.S.	
T-302A,B	HYDROTREATED VGO FCC	2,001,000 GAL	C.S.	
PRESSURE VESSELS				
V-101	FEED SURGE DRUM	9,250 GAL	C.S.	
V-102	MAKE-UP H2 KNOCK OUT DRUM	500 GAL	C.S.	
V-103	MAKE-UP H2 KNOCK OUT DRUM	400 GAL	C.S.	
V-104	MAKE-UP H2 KNOCK OUT DRUM	460 GAL	C.S.	
V-201	HOT HIGH PRESSURE SEPARATOR	13,600 GAL	C.S.	
V-202	COLD HIGH PRESSURE SEPARATOR	15,300 GAL	C.S.	
V-203	COLD LOW PRESSURE SEPARATOR	1,200 GAL	C.S.	
V-204	HOT LOW PRESSURE SEPARATOR	15,000 GAL	1.25 CR-0.5 MO	
V-301	STRIPPER REFLUX DRUM	750 GAL	C.S.	
SPECIAL EQUIPMENT				
S-101A,B	FEED FILTERS		CARBON STEEL	
S-201	EXPANDER	582 KW	2.25 CR-1 MO	
PACKAGE UNITS				
G-101	CATALYST REPLACEMENT	CARBON STEEL	8,600 LB FRESH CATALYST/WEEK ADDED; 12,700 LB/WEEK SPENT CATALYST REMOVED	
G-102	HDM CATALYST FILL	190,000 LB	HDM CATALYST	
G-103	HDS CATALYST FILL	674,000 LB	HDS CATALYST	
G-301	AMINE UNIT		CARBON STEEL	MDEA ABSORPTION
PUMPS				
	SECTION	OPERATING	SPARES	OPERATING BHP
	100	6	2	2,108
	200	2	1	112
	300	6	3	85



**Table 8.5**  
**ATMOSPHERIC RESIDUE CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**UTILITIES SUMMARY**

CAPACITY: 3,424 MILLION LB/YR (1,549,1000 T/YR)  
HDT ATMOSPHERIC RESIDUE  
AT 0.95 STREAM FACTOR

	<b>UNITS</b>	<b>BATTERY LIMITS TOTAL</b>	<b>SECTION 100</b>	<b>SECTION 200</b>	<b>SECTION 300</b>
<b>AVERAGE CONSUMPTIONS</b>					
COOLING WATER	GPM	6,070	--	1,337	4,733
ELECTRICITY	KW	11,933	10,060	306	1,567
NATURAL GAS	MM BTU/HR	28	28	--	--
STEAM, 50 PSIG	M LB/HR	48	--	--	48
STEAM, 150 PSIG	M LB/HR	3	--	--	3
STEAM, 150 PSIG	M LB/HR	-44	--	-44	--
<b>PEAK DEMANDS</b>					
COOLING WATER	GPM	7,284	--	1,604	5,680
ELECTRICITY	KW	12,525	10,652	306	1,567
NATURAL GAS	MM BTU/HR	31	31	--	--
STEAM, 50 PSIG	M LB/HR	58	--	--	58
STEAM, 150 PSIG	M LB/HR	4	--	--	4

The process flow diagram for the conventional hydrotreater, Figure 8.1 (in Appendix E) is divided into three sections:

- Section 100—Reaction
- Section 200—Gas Recovery
- Section 300—Product Recovery

### **Section 100 - Reaction**

Atmospheric residue feedstock from the crude unit is pumped to surge drum V-101. A small amount of make-up hydrogen is injected before the first of a series of heat exchangers that preheat the feed. After heating by the feed-stripper product exchanger (E-101), the feed is heated by exchange with vapor from the hot high pressure separator (V-201) in E-102 and then by the liquid from that separator in E-103. The last of the preheat exchangers in E-104, the feed-reactor effluent exchanger. Feed furnace F-101 heats the feed to the desired first reactor's inlet temperature.

Temperature of the reactor is controlled by a hydrogen quench stream. The moving bed first reactor (R-101) is primarily a HDM reactor. Fresh catalyst for the moving bed reactor is charged by the catalyst replacement unit (G-101). This unit also removes an equal volume of metal laden spent catalyst for reclamation. Effluent from the top of R-101 is quenched with hydrogen prior to flowing into the second reactor (R-102). Although this fixed bed reactor is removes metals escaping the HDM reactor, it is primarily a HDS reactor. The second reactor's effluent is quenched with hydrogen and flows into the third reactor, also a fixed bed reactor.

The final hydrotreated effluent stream is cooled in the feed-reactor effluent heat exchanger (E-104) and flows to the Gas Recovery Section.

### **Section 200 - Gas Recovery**

In the Gas Recovery Section, a set of four separators removes vapors and gases from the hydrotreated reactor effluent to produce relatively clean hydrogen recycle gas. The cooled and partially condensed effluent from the final reactor flows into the hot, high pressure separator (V-201). The liquid is then expanded (S-201) and cooled by heat exchange with the fresh feed (E-103). Vapor from V-201 is also cooled, first by heat exchange with the make-up hydrogen in E-201 and with the fresh feed (E-102). The stream is still hot enough to generate steam in boiler E-202. Direct cooling next occurs when the wash water is injected. Air cooled condenser E-203 and trim condenser E-204 condense almost all the water and partially condense the hydrocarbons. The mixture is separated in V-202, the cold, high pressure separator. Almost all of the ammonia dissolves into the water. The water flows to the refinery's sour water scrubber. Hydrogen rich gas from V-202 is amine treated (G-201) to remove H<sub>2</sub>S. A portion of the treated gas is purged to remove noncondensable gases from the hydrogen recycle loop. The remainder is compressed (K-201) and recycled mainly as quench gas to the reactors.

The liquid hydrocarbon stream from V-202 is reduced in pressure and flows into the cold, low pressure separator, V-203. Partially condensed vapors (from E-205) from the cold, low pressure separator (V-204) also flow to V-203. Offgas from V-203 flows offsite to the refinery's sour gas scrubber. The liquid from V-203 is heated by heat exchange with vapor from the hot, low pressure separator, V-204, as it flows to the Product Separation Section. Liquid from V-202 that flowed through the expander S-201 and was cooled in E-103 is the source of the vapor leaving V-204.

Hydrotreated atmospheric residue from separator V-204 is the main stream flowing to the Product Recovery Section.

### **Section 300 - Product Recovery**

Hydrotreated atmospheric residue from separator V-204 contains naphtha and dissolved gases that is separated by steam stripping in C-301. Liquid streams from V-203 and V-204 are fed to the bottom of the stripper along with the stripping steam. Stripper overhead vapors are partially condensed by air condenser E-301 and trim condenser E-302. Condensate and condensed naphtha are separated from each other and the vapor and gases in the stripper receiver, V-301. The sour water is sent to the refinery's sour water system. A portion of the naphtha is returned to the column (C-301) as reflux; the balance is the wide boiling wild naphtha product.

The stripper bottom product is the hydrotreated atmospheric residue FCC feedstock. It is cooled by exchange with the fresh feed (E-101) and pumped hot to the FCCU.

### **PROCESS DISCUSSION**

The on stream factor of 0.95 is conservative since usual experience is higher. The conditions given are generally for the start-of-run. At end-of-run conditions, the reactor inlet temperatures will have been raised to the maximum. The reactor pressure drops are often larger than at the start of run.

The designs are not fully optimized, especially for energy utilization. Our goal is to derive a reasonable process for cost estimating within our  $\pm 25\%$  accuracy. The model should be considered as a preliminary design that should serve as a good starting point for performing more detailed process design. Hydrotreater units are customized to meet feedstock flexibility, catalyst conditions and owner preferences. Process licensors and contractors have decades of experience to draw upon in designing specific plants.

The basic design of the conventional hydrotreater is a generic flowsheet with feedstock and yields obtained from reported information [214A530]. Additional information was from our literature review in Sections 5 and 6.

### **Feedstock**

The feedstock is atmospheric residue obtained from Arabian Heavy crude oil. The assumed feedstock is characterized in Table 8.3. Filtering the feed by a set of two continuously backwashed filters (S-101A, B) is generally recommended to remove particulates greater than 25 microns to minimize the fixed bed pressure drop buildup. Because of the high viscosity of the feedstock, it should be filtered after the feed-V-201 vapor exchanger (E-102). Filtering temperature of 450°F (232°C) is suggested [214A560].

### **Section 100 - Reaction**

The first reactor is a moving bed reactor whose main purpose is to remove metals from the feed to protect the HDS catalyst in the second and third reactors. The second and third reactors are both trickle-bed reactors. The moving bed vessel is 12 ft. diameter by 65 ft tall tangent-to-tangent (T-T) including 10 ft. for internals. The catalyst bed is 55 ft deep. The moving bed should expand about 3% (about 1.7 ft) when charging and discharging catalyst. The size is based upon the feedstock metals load, the assumed HDM catalyst's metal capacity (48%) and bulk density, and the LHSV. Similarly, the second reactor contains a single catalyst bed 58 ft deep and is 13 ft.

diameter by 68 ft tall tangent-to-tangent. The third reactor is also 13 ft in diameter by 70.5 ft (T-T) containing a catalyst bed of 60.5 ft high.

Since the compositions and properties of commercial catalysts are proprietary, the HDM and HDS catalyst system was assumed to be NiMo on alumina of reported typical catalytic metals content [214A560].

### **Section 200 - Gas Recovery**

The Gas Recovery Section is very similar to that of the conventional VGO hydrotreater discussed in Section 7. In order to maximize the recovery of heat, the fresh feed is exchanged with both the vapor and liquid from the hot high pressure separator (V-201). The wash water rate is in agreement with reported values [214A576].

### **Section 300 - Product Recovery**

The stripper operation is aided by the naphtha contained in the feed stream, thus potentially reducing the amount of stripping steam. The bottom temperature of the stripper is a function of the feed temperature, the hotter the better to keep water out of the bottoms product. Although the FCCU can tolerate some water in the feed, the drier the feed the less potential for flow problems.

### **Hydrogen System**

Makeup hydrogen supplied is assumed to be vendor provided 99.55 mol% pure hydrogen. Makeup hydrogen replaces hydrogen consumed by reaction to form  $H_2S$  and ammonia and to saturate aromatics and olefins as well as losses through venting to the fuel gas system and small leaks.

Each hydrogen compressor load is split between two compressors in parallel to increase reliability and safety at the cost of a slightly lower efficiency and slightly higher capital cost than a single compressor. It is assumed package reciprocating compressor units are used that include lubricating systems and controls.

The compressors are generally sized for start-of-run (SOR) conditions. At the end-of-run (EOR), the pressure drop across the first reactor could well be higher, resulting in lower pressure in the stripper column and the gas recovery train to the amine unit.

### **Materials of Construction**

The presence of  $H_2S$  and  $H_2$  requires chrome-molybdenum or stainless steel clad vessels and exchanger shells and stainless steel exchanger tubes. The reactors and down stream vessels and exchanger shells that operate above 500°F (260°C) are either 2¼ Cr 1 Mo or 1¼ Cr ½ Mo. Stainless steel is used for the furnace tubes. The piping around the reactors is also Cr-Mo steel. Unless noted in the equipment list (Table 7.6 and 7.7), all other equipment is carbon steel.

Ammonia in the presence of  $H_2S$  forms ammonium hydrosulfide salt that deposits on heat exchanger surfaces. The salt is very water soluble, but the solution is very corrosive to carbon steel tubes. Besides the exchangers, the sour water must be steam stripped, another corrosive location. For the same reason, the stripper condenser is an extremely corrosive environment where titanium can be necessary [214A571].

## **Waste Treatment and Disposal**

Wastes from the hydrotreater include sour water, sour gas and spent catalysts. H<sub>2</sub>S is recovered by amine scrubbing. The H<sub>2</sub>S rich stream from the amine unit is sent to the refinery's sulfur recovery unit, typically a Claus-type process with tail gas treater, for recovery as elemental sulfur. Sulfur recovery is reviewed in PEP Report 216 "Acid Gas Treatment and Sulfur Recovery" (1997). The sour water is treated and the ammonia recovered. Oily condensate is sent to the refinery's gravity settler (API settler). Oil is recovered and the water is further purified in the refinery's wastewater treatment system.

The U.S. Environmental Protection Agency now lists hydrotreating catalysts as Hazardous Wastes (K171 and K172). Some European agencies are reviewing the disposal of spent hydrotreating catalyst [214A588]. Landfilling is increasingly becoming unattractive. Spent HDS catalyst is usually sent offsite to a metals reclaimer for processing to recover the valuable metals, as discussed in Section 5, which is the option we assume.

## **COST ESTIMATES**

We present here the capital investment and production cost estimates for hydrotreating atmospheric residue oil to produce FCC feedstock. Allowance for interest on funds spent during construction is not included (i.e. overnight construction). The location is the U.S. Gulf Coast. Construction begins in the second quarter of 2006.

Equipment costs and production costs are estimated primarily using the PEP COST database, version 3.1.5, developed by PEP [PEP Report 162].

### **Capital Costs**

Capital costs at a PEP Cost Index of 718 (mid 2006) are developed for hydrotreating 30,000 BPSD of a vacuum gas oil feedstock.

Table 8.6 shows the Total Fixed Capital (TFC) investment is \$203 million. The Battery Limits Investment (BLI), which includes PEP's contingency of 15%, is \$146 million. The Battery Limits Installed cost is \$128 million. This installed cost includes \$3.9 million for the initial reactor fill of the catalysts (added to the capital costs calculated without the catalyst). The investment cost of the amine unit only includes the absorption and amine regeneration section [PEP Report 216]. The sulfur recovery sections are excluded since the refinery's existing Claus unit is assumed to be used. The Battery Limits Investment of \$146 million coincidentally equals a published estimate also of \$146 million estimate for a hydrotreater of 70,000 B/D capacity when adjusted for size using an exponent of 0.71 and inflation to 2006 using the PEP COST Indices [214A530]. The off-sites utility and tankage investment is \$10.6 million. Allotments for general services and waste treatment bring the total offsites investment to \$49.3 million including a 15% contingency. The costs of each section are shown in Table 8.7.

**Table 8.6**  
**ATMOSPHERIC RESIDUE CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

<b>TOTAL CAPITAL INVESTMENT</b>			
CAPACITY: 3,424 MILLION LB/YR (1,549,1000 T/YR)			
HDT ATMOSPHERIC RESIDUE			
AT 0.95 STREAM FACTOR			
PEP COST INDEX: 718			
	<b>COST</b>	<b>CAPACITY</b>	
	<b>(\$1,000)</b>	<b>EXPONENT</b>	
		<b>UP</b>	<b>DOWN</b>
BATTERY LIMITS EQUIPMENT, F.O.B.			
REACTORS	42,000	0.93	0.87
COLUMNS	68	0.42	0.33
VESSELS & TANKS	1,405	1.01	0.77
HEAT EXCHANGERS	1,833	0.90	0.70
FURNACES	546	0.82	0.82
COMPRESSORS	8,036	0.76	0.76
SPECIAL EQUIPMENT	345	0.95	0.95
PUMPS	803	0.77	0.73
TOTAL	55,036	0.90	0.85
DIRECT INSTALLATION COSTS	18,645	0.85	0.65
PACKAGE UNIT	14,937	0.68	0.60
INDIRECT COSTS	27,928	0.79	0.70
UNSCHEDULED EQUIPMENT, 10%	11,192	0.84	0.75
BATTERY LIMITS, INSTALLED	127,737	0.84	0.75
CONTINGENCY, 15%	18,467	0.84	0.75
BATTERY LIMITS INVESTMENT	146,202	0.84	0.75
OFF-SITES, INSTALLED			
CLARIFIED WATER	426	0.51	0.00
COOLING WATER	1,356	0.92	0.92
PROCESS WATER	278	0.62	0.34
BOILER FEED WATER	757	0.17	0.00
STEAM	1,734	0.00	0.00
TANKAGE	6,061	0.65	0.65
UTILITIES & STORAGE	10,612	0.57	0.46
GENERAL SERVICE FACILITIES	31,363	0.83	0.73
WASTE TREATMENT	7,310	0.84	0.75
TOTAL	49,284	0.78	0.67
CONTINGENCY, 15%	7,393	0.78	0.67
OFF-SITES INVESTMENT	56,677	0.78	0.67
TOTAL FIXED CAPITAL	202,879	0.83	0.72

**Table 8.7**  
**ATMOSPHERIC RESIDUE CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**CAPITAL INVESTMENT BY SECTION**

CAPACITY: 3,424 MILLION LB/YR (1,549,100 T/YR)  
HDT ATMOSPHERIC RESIDUE  
AT 0.95 STREAM FACTOR

PEP COST INDEX: 718

	REACTION SECTION			GAS RECOVERY SECTION			PRODUCT RECOVERY SECTION		
	COST (\$1,000)	CAPACITY EXPONENT		COST (\$1,000)	CAPACITY EXPONENT		COST (\$1,000)	CAPACITY EXPONENT	
		UP	DOWN		UP	DOWN		UP	DOWN
BATTERY LIMITS EQUIPMENT, F.O.B.									
REACTORS	42,000	0.93	0.87	--	--	--	--	--	--
COLUMNS	--	--	--	--	--	--	68	0.42	0.33
VESSELS & TANKS	118	0.50	0.42	1,267	1.05	0.82	20	0.33	0.27
HEAT EXCHANGERS	1,051	0.89	0.67	698	0.94	0.74	84	0.62	0.61
FURNACES	546	0.82	0.82	--	--	--	--	--	--
COMPRESSORS	7,676	0.76	0.76	277	0.76	0.76	83	0.76	0.76
SPECIAL EQUIPMENT	--	--	--	345	0.95	0.95	--	--	--
PUMPS642	0.80	0.80	44	0.65	0.55	117	0.58	0.47	--
TOTAL	52,032	0.90	0.85	2,631	0.98	0.80	372	0.59	0.52
DIRECT INSTALLATION COSTS	14,051	0.87	0.65	3,522	0.87	0.76	1,072	0.49	0.37
PACKAGE UNIT	7,304	0.82	0.79	--	--	--	7,633	0.57	0.48
INDIRECT COSTS	22,864	0.82	0.74	2,040	0.85	0.72	3,010	0.50	0.40
UNSCHEDULED EQUIPMENT, 10%	9,163	0.87	0.79	819	0.90	0.77	1,209	0.55	0.45
BATTERY LIMITS INSTALLED	105,414	0.87	0.79	9,013	0.90	0.77	13,296	0.55	0.45
CONTINGENCY, 15%	15,118	0.87	0.79	1,352	0.90	0.77	1,994	0.55	0.45
BATTERY LIMITS INVESTMENT	120,532	0.87	0.79	10,365	0.90	0.77	15,290	0.55	0.45
OFFSITES, INSTALLED									
CLARIFIED WATER	--	--	--	86	0.51	0.00	340	0.51	0.00
COOLING WATER	--	--	--	299	0.92	0.92	1,057	0.92	0.92
PROCESS WATER	--	--	--	61	0.62	0.34	217	0.62	0.34
BOILER FEED WATER	--	--	--	--	--	--	757	0.17	0.00
STEAM--	--	--	--	--	--	1,734	0.00	0.00	
TANKAGE	2,886	0.65	0.65	--	--	--	3,175	0.65	0.64
UTILITIES & STORAGE	2,886	0.65	0.65	446	0.81	0.61	7,280	0.51	0.38

The cost of the initial catalyst fill may well be low for the latest catalysts. As discussed in Section 4, the price of catalysts can vary widely with the cost of the metals. The cost of the second batch of catalyst is included as an operating materials expense. For our estimate, the HDS treatment catalyst is priced at 5.83 \$/lb determined from the cost of metals (3.5% NiO/12.5% MoO<sub>3</sub> was assumed) plus a base charge of \$4.00/lb.

The BLI costs in Tables 8.6 and 8.7 include factors for indirect costs and unscheduled equipment. Indirect costs include such items as equipment rental (scaffolding and lifting for example), testing, freight, and sales taxes and insurance. The indirect cost also includes labor overhead expenses, engineering and contractor's profit. Indirect costs are discussed in Appendix B. We apply the unscheduled equipment allowance factor of 10% to the sum of equipment cost, direct installation costs, package unit costs and indirect costs. Licensing or royalty fees are regarded as proprietary and are not included in these costs.

Some tankage is required for handling upsets and for good product quality control. Off-site utilities and tankage installed investments totaled about \$10.6 million. Of this total, tankage for three days feedstock and three hours production cost \$6.0 million.

An allowance of \$31 million is made for investment in general services facilities, which includes items such as roads, parking, fences, administrative offices, craft shops, fire and safety equipment, plant communications and warehouses. A \$7.3 million allowance is made for investments expanding or providing waste treatment facilities. The off-sites investment totals \$56.7 million for the unit with the inclusion of the general services facilities, waste treatment investments and 15% contingency.

The BLI in Tables 8.6 and 8.7 includes PEP's contingency of 15% for established refinery processes. The major licensors and engineering contractors have experience building many types of hydrotreaters. With a 25% contingency, the BLI becomes \$152.4 million and the TFC rises to \$211.5 million with an off-sites investment of \$59 million.

## **Production Costs**

Table 8.8 shows our production cost estimate for a 30,000 BPSD atmospheric residue oil hydrotreating unit along with estimates for 15,000 BPSD and 60,000 BPSD units. The feedstock, product and utility values are based on mid-year 2006 prices for the U.S. Gulf Coast. The feedstock was valued at 10.25 ¢/lb (35.40 \$/B or 0.843 \$/gal). The hydrotreated FCC feedstock was valued as low sulfur fuel oil at 15.63 ¢/lb (51.27 \$/B or 1.221 \$/gal). In the table, all variable costs are expressed as ¢/lb of the FCC feedstock product. Gross raw materials cost 13.37 ¢/lb. By-products are shown as credits (negative). The by-product credit is 0.81 ¢/lb due to the purge gas and off gas. No value was given to the H<sub>2</sub>S stream. Net total utilities cost 0.24 ¢/lb. The costs of a replacement batch of each catalyst is included assuming a two year catalyst life for the fixed bed reactors. Fresh catalyst for the moving bed reactor is charged batchwise at 24,150 lb per week. The fixed bed catalyst life estimate may be conservative. Variable costs total 12.80 ¢/lb.

Labor costs are based upon 4 operators per shift (one control room, three outside) at the total compensation rate, including benefits, of \$41.50/H each. Maintenance labor is estimated as 3%/yr of battery limits investment. Since many of the analyses are derived from the online control instrumentation, control laboratory labor is estimated at 20% of direct operating labor costs. Labor costs total 0.18 ¢/lb.



**Table 8.8**  
**ATMOSPHERIC RESIDUE CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

<b>PRODUCTION COSTS</b>				
PEP COST INDEX: 718				
<b>VARIABLE COSTS</b>				
	<b>UNIT COST</b>	<b>CONSUMPTION PER LB</b>		<b>¢/LB</b>
	-----	-----		-----
RAW MATERIALS				
HYDROGEN	81.04 ¢/LB	0.028967 LB		2.35
ATMOSPHERIC RESIDUE FEED	10.25 ¢/LB	1.04919 LB		10.75
HDS CATALYST	583 ¢/LB	0.000103 LB		0.06
DEA	84.4 ¢/LB	0.00002 LB		NEGL
HDS/HDN CATALYST	642 ¢/LB	0.000103 LB		0.07
HDM CATALYST	366 ¢/LB	0.000323 LB		0.12
SPENT CATALYST FEE	39 ¢/LB	0.000529 LB		0.02
				-----
GROSS RAW MATERIALS				13.37
BY-PRODUCTS				
PURGE GAS	28.42 ¢/LB	-0.014706 LB		-0.42
OFF GAS (SEPARATOR)	12.72 ¢/LB	-0.002664 LB		-0.03
WILD NAPHTHA	28.15 ¢/LB	-0.010351 LB		-0.29
OFF GAS (STRIPPER)	9.841 ¢/LB	-0.007296 LB		-0.07
				-----
TOTAL BY-PRODUCTS				-0.81
	<b>UNIT COST</b>	<b>CONSUMPTION PER LB</b>	<b>CONSUMPTION PER KG</b>	
	-----	-----	-----	
UTILITIES				
COOLING WATER	10.66 ¢/MGAL	0.885 GAL	7.39 LITERS	0.01
STEAM, 150 PSIG	8.4 \$/MLB	0.0174 LB	0.0174 KG	0.01
ELECTRICITY	5.76 ¢/KWH	0.029 KWH	0.0639 KWH	0.17
NATURAL GAS	6.74 \$/MMBTU	67.4 BTU	37.5 KCAL	0.05
				-----
TOTAL UTILITIES				0.24

**Table 8.8 (Concluded)**  
**ATMOSPHERIC RESIDUE CONVENTIONAL HYDROTREATING**  
**30,000 BPSD**

**PRODUCTION COSTS**

PEP COST INDEX: 718

<b>CAPACITY (MILLION LB/YR)*</b>	<b>1,712</b>	<b>3,424<sup>#</sup></b>	<b>6,848</b>
INVESTMENT (\$ MILLIONS)			
BATTERY LIMITS (BLI)	87.1	146.2	262.5
OFFSITES	35.7	56.7	97.1
TOTAL FIXED CAPITAL (TFC)	122.8	202.9	359.6
SCALING EXPONENTS	0.72	0.83	
PRODUCTION COSTS (¢/LB)			
RAW MATERIALS	13.37	13.37	13.37
BY-PRODUCTS	-0.81	-0.81	-0.81
UTILITIES	0.24	0.24	0.24
VARIABLE COSTS	12.80	12.80	12.80
OPERATING LABOR, 4/SHIFT, \$41.5/HR	0.08	0.04	0.02
MAINTENANCE LABOR, 3%/YR OF BLI	0.15	0.13	0.11
CONTROL LAB LABOR, 20% OF OPER LABOR	0.02	0.01	NEGL
LABOR COSTS	0.25	0.18	0.13
MAINTENANCE MATERIALS, 3%/YR OF BLI	0.15	0.13	0.11
OPERATING SUPPLIES, 10% OF OPER LABOR	0.01	NEGL	NEGL
TOTAL DIRECT COSTS	13.21	13.11	13.04
PLANT OVERHEAD, 80% OF LABOR COSTS	0.20	0.14	0.10
TAXES AND INSURANCE, 2%/YR OF TFC	0.14	0.12	0.11
PLANT CASH COSTS	13.55	13.37	13.25
DEPRECIATION, 10%/YR OF TFC	0.72	0.59	0.53
PLANT GATE COSTS	14.27	13.96	13.78
G&A, SALES, RESEARCH	0.08	0.08	0.08
NET PRODUCTION COST	14.35	14.04	13.86
ROI BEFORE TAXES, 26.8%/YR OF TFC	1.92	1.59	1.41
PRODUCT VALUE	16.27	15.63	15.27

\* OF HDT ATMOSPHERIC RESIDUE

# BASE CASE

Maintenance materials are estimated at 3%/yr of the battery limits investment; operating supplies at 10% of operating labor costs. Adding maintenance materials and supplies to the variable materials and labor costs produces a total direct operating cost of 13.11 ¢/lb or 43.00 \$/B of hydrotreated FCC feedstock.

Our production cost estimates includes charges for plant overhead (80% of labor costs), property taxes and insurance (2%/yr of total fixed cost) and depreciation (10%/yr, straight line). Adding the overhead and taxes and insurance costs to the total direct operating cost gives a plant cash cost of 13.37 ¢/lb. Depreciation further adds 0.59 ¢/lb to bring the plant gate cost to 13.96 ¢/lb or 45.785 \$/B.

General and administrative expenses (G&A), sales, and research and development (R&D) expenses add 0.08 ¢/lb since the product is usually used within the refinery. With G&S, sales and R&S expenses, the net production cost is 14.04¢/lb or 46.05 \$/B.

With a before tax return on investment (ROI) of 26.8%, total product value of the hydrotreated FCC feedstock is 15.63 ¢/lb or 51.26 \$/B, the market price. With a before tax return on investment (ROI) of 25%, a frequently used project screening value, the total product value of the hydrotreated FCC feedstock is 15.52 ¢/lb or 46.21 \$/B.

Economy of scale benefits the product value as illustrated in Table 8.8 in cases of units of one-half and double the capacity of the base case unit.

### Profitability

The value of hydrotreated VGO FCC feedstock was 15.63 ¢/lb or 51.27 \$/B. With this product value, the before tax return on investment (ROI) is 26.8% for the base capacity hydrotreater, essentially equaling the 25% frequently used to screen projects.

The atmospheric residue feedstock value was determined by applying a 25% discount to the average of values reported by Platts for mid 2006 (May thru August) [214A583 through 214A586]. This resulted in a value of 47.20 \$/B after adjusting for sulfur content. The discount was taken for the relatively high carbon residue and metals content of this feedstock. Sensitivity of ROI to feedstock costs is shown in Table 8.9.

**Table 8.9**  
**SENSITIVITY OF ROI TO FEEDSTOCK COSTS**

<u>% Discount<sup>a</sup></u>	<u>Value, \$/B AR</u>	<u>Value, ¢/lb AR</u>	<u>ROI<sup>b</sup>, %</u>
15	40.12	11.62	2.6
20	37.76	10.93	14.6
25 <sup>c</sup>	35.40	10.25	26.8
30	33.04	9.57	38.8
50	23.60	6.83	87.3

<sup>a</sup> From 47.20 \$/B.

<sup>b</sup> At 15.63 ¢/lb value of hydrotreated AR FCC feedstock.

<sup>c</sup> Used for determining production costs shown in Table 8.8

**Appendix A**  
**PATENT SUMMARY TABLES**

**Table A.1**  
**HEAVY OIL HYDROTREATING CATALYSTS**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 5444033	Cosmo Research Institute and Cosmo Oil Co., Ltd.	6/6/94
Catalysts containing active metals from Groups VIB (preferably molybdenum) and VIII (preferably cobalt or nickel) of the Periodic Table are at a higher concentration in the center of the catalyst particles than on their surface. This allows desulfurization activity to be maintained for a longer time than with conventional catalysts. The metals are added to the carrier by a specified impregnation procedure. The catalyst can be used for hydrotreating a variety of oils including residues.		
US 5484755		8/22/94
High activity slurry catalysts for hydrotreating heavy oils are produced from Group VIB metal (preferably molybdenum) compounds by sulfiding an aqueous mixture of the metal compound with from greater than about 8 to about 14 SCF of hydrogen sulfide per pound of Group VIB metal. Preferably adding a Group VIII metal (i.e., cobalt or nickel) improves the denitrogenation capability of the catalyst.		
US 5676822	Texaco Inc.	3/9/95
A hydrotreating process particularly advantageous for treating FCC feedstock uses a catalyst comprising zinc and one or more non-noble Group VIII metals (cobalt, iron and preferably nickel) and one or more metals of Group VIB (molybdenum, chromium and preferably tungsten) on an activated carbon support. Feedstocks may be gas oil, vacuum gas oil, residua, shale oils, tar sand oils, coal liquids and mixtures. The addition of zinc to the catalyst formulation significantly increases the hydrodearomatization activity and seems to improve the hydrodenitrification activity some. Under conditions necessary to significantly saturate aromatics, both the HDS and HDN conversions approach 100%.		
US 5677259		6/10/93
A hydrotreating catalyst allows deep desulfurization of gas oil without changing the reaction temperature, pressure or liquid hourly space velocity (LHSV). The catalyst contains at least one of molybdenum or tungsten, at least one of cobalt or nickel and at least one of rhenium or iridium. Reaction temperature is between 572 to 734°F (300 to 390°C), pressure preferably from 427 to 711 psi (30 to 50 kg/cm <sup>2</sup> ) and LHSV preferably from 2 to 4 H <sup>-1</sup> .		

**Table A.1 (Continued)**  
**HEAVY OIL HYDROTREATING CATALYSTS**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 5928499	Texaco Inc	12/29/95
<p>A heavy feedstock hydrotreating process utilizes a heterogeneous catalyst having a specified pore size distribution, median pore diameter by surface area and pore mode by volume. Among the catalyst characteristics is 22.0 to 33.0% of the total pore volume is macropores greater than 250 Å and 67.0 to 78.0% of total pore volume is micropores of diameter less than 250 Å. The process reduces sediment make and provides improved levels of conversion of components boiling greater than 1000°F (538°C). Hydrodesulfurization is improved, especially from the converted 650-1000°F (343-538°C) and unconverted heavier fractions. Also improved are the levels of carbon residue reduction and of demetalization (Ni and V).</p>		
US 6162350	Exxon Research and Engineering Company	1/15/99
<p>A hydrotreating process uses a catalyst composition comprising a nickel species of nickel molybdate. At least a portion but less than all of the molybdenum is replaced by tungsten, the nickel species being represented by the formula: <math>(\text{Ni})_b(\text{Mo})_c(\text{W})_d\text{O}_z</math> wherein the molar ratio of b to (c + d) ranges from 0.5/1 to 3/1 and the molar ratio of c to d is greater than or equal to 0.01/1, and <math>z = (2b + 6)/2</math>. The catalyst provides enhanced hydrodenitrogenation activity compared to unsubstituted Ni-Mo phase catalyst.</p>		
US 6203695	Institut Francis du Petrole	3/17/2000
<p>A hydrotreating process for heavy feedstocks uses a catalyst comprised of an alumina-based extruded support having a plurality of juxtaposed agglomerates. Each agglomerate is partly in the form of packs of flakes and partly needles that are uniformly dispersed. Different pore distributions are possible that modifies the hydrodesulfurization and hydrodemetalization proportions.</p>		
US 6267874	Tonen General Sekiyu K.K.	11/17/98
<p>A hydrotreating catalyst for high sulfur feedstocks such as vacuum gas oil has improved tolerance to the inhibiting effects of H<sub>2</sub>S, high desulfurization activity and notable effects for deep desulfurization (sulfur reduced to 0.05 wt% or lower). The catalyst is composed of a silica-alumina or silica-alumina-third component (such as phosphorus) carrier in which the silica is highly dispersed. The carrier has a Bronsted acid content of at least 50 micromol/g (preferably 80 micromol/g or more). The active metals (Groups 6 and 8 of the Periodic Table) are preferably molybdenum or tungsten with cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum. The active metals are finely dispersed due to the highly dispersed silica.</p>		

**Table A.1 (Continued)**  
**HEAVY OIL HYDROTREATING CATALYSTS**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6306289	Tonen Corporation	3/16/99
A heavy oil hydrotreating catalyst comprises a specified silica-alumina carrier and one or more highly dispersed hydrogenation-active metals of Groups VI and VIII (preferably molybdenum or tungsten and cobalt, nickel, ruthenium, rhodium, palladium, iridium or platinum respectively). When a silica layer formed on the alumina surface is the carrier under controlled solid acidity, an increase in silicon-aluminum bonds and the uniform development of a number of uniformly acidic solid acid sites is facilitated. High desulfurization and denitrogenation activity results that is excellently maintained.		
US 6383975	Instituto Mexicano del Petroleo	7/1/99
A preparation procedure produces a catalyst with high catalytic activity and selectivity for hydrodenitrogenation along with good hydrodesulfurization and hydrodemetalization of preferably middle and heavy oils. Metals from Groups VIB (preferably molybdenum) and VIII (preferably nickel) of the Periodic Table are solution impregnated on a porous refractory oxide. The carrier is an oxide of metals of Groups IIIA and IVA. The support also includes an oxide additive of Group IVB (preferably titanium) to promote physical and chemical stability and uniformly distributing the active metals. The catalyst is activated by presulfiding.		
US 6398950	Idemitsu Kosan Co., Ltd.	6/4/99
A Mo-Ni, Mo-Co on alumina or the like heavy oil hydrotreating catalyst is used once and regenerated to a specified x-ray diffraction pattern to provide specific properties and composition so it can be reused as a hydrogenation catalyst.		
US 6436870	Tonen Corporation	8/31/2000
US 6451198		10/7/1999
A hydrotreating catalyst particularly suitable for heavy vacuum distillates and residues as well as bitumen, shale oil and coal-liquefied oils contains a specified refractory inorganic oxide support uniformly dispersed with active metals in high homogeneity. The active metals include at least one Group 6A metal (molybdenum is most preferred) and/or at least one of a Group 8 metal (cobalt and nickel are most preferred) plus optionally an element selected from Groups 1B, 2B and 7A (including copper, zinc, manganese and rhenium).		

**Table A.1 (Continued)**  
**HEAVY OIL HYDROTREATING CATALYSTS**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6509291	Akzo Nobel N.V.	4/11/2000
<p>A specified process activates hydrotreating catalyst with increased activity by applying an organic liquid prior to or during hydrogen treatment. The catalyst contains at least one hydrogenation metal of Group VI (includes molybdenum, tungsten or chromium) or Group VIII (includes nickel, cobalt and iron) of the Periodic Table and a sulfur containing organic additive. The additive is more preferably a mercaptocarboxylic acid (HS-R<sub>1</sub>-COOR, where R<sub>1</sub> is a divalent C<sub>1-10</sub> and R is a H atom, alkali metal, an alkaline earth metal, ammonium or linear or branched C<sub>1-10</sub>). The organic liquid is preferably white oil, gasoline, diesel, gas oil or mineral lube oil. To simplify startup, conducting the sulfiding ex situ is preferred. Suitable hydrotreating feedstocks include heavy gas oils, vacuum gas oil and residues.</p>		
US 6667271	Haldor Topsoe A/S	8/23/2001
<p>A heavy oil hydrotreating catalyst support is in the shape of angular extrudate with rounded edges. In ebullating beds, this support provides higher mechanical strength without changing the ebullating bed characteristics since the geometry is close to the usual cylindrical extrudates.</p>		
US 6712955	ExxonMobil Research and Engineering Company	8/22/2001
<p>A slurry residual oil hydrotreating process uses a bulk multimetallic catalyst comprising at least one Group VIII metal and at least two Group VIB metals. The preferred metals are the combinations: nickel, molybdenum and tungsten or nickel, cobalt, molybdenum and tungsten. The ratio of Group VIB metal to Group VIII metal is about 10:1 to about 1:10.</p>		
US 6780817	Japan Energy Corporation	12/2/99
<p>A hydrogenation active hydrorefining catalyst has a porous refractory support with a median pore diameter of 8 to 20 nm, a pore volume of 0.56 cm<sup>3</sup>/g or greater and a pore volume of pores with a pore diameter of 50 nm or larger of 0.32 cm<sup>3</sup>/g or greater. Both the demetalization activity and metal deposition (nickel and vanadium) capacity when demetallizing heavy oil are high.</p>		
US 6821412	Cosmo Oil Co., Ltd.	8/24/2000
<p>A gas oil hydrotreating catalyst contains specified amounts of platinum, palladium and a inorganic oxide support containing crystalline alumina with a crystal diameter of from 20 to 40 Å. Gas oils containing sulfur that is unsusceptible to conventional desulfurization can be practically hydrotreated with this catalyst to produce a high quality, low aromatic gas oil having 10 ppm sulfur or less.</p>		



**Table A.1 (Continued)**  
**HEAVY OIL HYDROTREATING CATALYSTS**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6855653	Indian Oil Corporation Limited	11/26/2003
A process for preparing a hydrotreating catalyst produces active metals in the nanoparticle range (less than 50A) on a carrier of phosphated alumina and an ultra stable Y zeolite. The metals are a Group VIB metal (molybdenum) and a Group VIII metal (cobalt or nickel) and reside mostly on the alumina. The catalyst produces desulfurized gas oil of less than 50 ppm sulfur from gas oil feedstocks containing greater than 1 wt% sulfur under typical commercial operating conditions.		
US 6872678		4/10/2001
A specified process activates hydrotreating catalyst with increased activity by applying an organic liquid prior to or during hydrogen treatment. The catalyst contains at least one hydrogenation metal of Group VI (includes molybdenum, tungsten or chromium) or Group VIII (includes nickel, cobalt and iron) of the Periodic Table and a sulfur containing organic additive. The organic liquid is preferably white oil, gasoline, diesel, gas oil or mineral lube oil. Suitable hydrotreating feedstocks include heavy gas oils, vacuum gas oil and residues.		
US 6930219	ABB Lummus Global Inc.	12/6/2002
A process suitable for heavy oil hydrotreating uses a catalyst having a carrier composition with both mesopores (2 to 50 nm) and micropores (less than 2 nm). A substantially mesoporous silica containing at least 97% by volume of pores having a pore size ranging from about 15 to about 30 and having a micropore volume of at least about 0.01 cc/g, wherein the mesoporous structure has at least about 0.02% by weight of at least one catalytically active metal. For hydrotreating, the active metals are selected from Ni, Mo, Co, W, Pt, Pd and their combinations.		
US 20050201920		4/8/2005
A catalyst composition for hydrotreating of preferably residual oils containing high metals, sulfur and nitrogen has a substantially mesoporous silica support having at least 97 vol% of pores from about 15 to 30 A and a micropore volume of at least about 0.01 cc/g. At least 0.02 wt% of active heteroatoms (from a group including Mo, Co and Ni) is incorporated into the support.		
US 20060052234		8/5/2005
A process for hydrotreating of preferably residual oils containing high metals, sulfur and nitrogen uses a catalyst with a substantially mesoporous silica support having at least 97 vol% of pores from about 15 to 30 A and a micropore volume of at least about 0.01 cc/g. At least 0.02 wt% of active heteroatoms (from a group including Mo, Co and Ni) is incorporated into the support.		

**Table A.1 (Concluded)**  
**HEAVY OIL HYDROTREATING CATALYSTS**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 20060054536		12/17/2003
<p>Ultra-deep desulfurization of gas oil is obtained without requiring more severe operating conditions than conventional hydrotreating. A specified heterogeneous catalyst contains 10 to 40 wt% of oxides of Group 6 metals such as molybdenum, 1 to 15 wt% of Group 8 metals (cobalt or nickel) oxides, 1.5 to 8 wt% phosphorous oxide plus 2 to 14 wt% of carbon. Catalyst specific surface area is 150 to 300 m<sup>2</sup>/g, pore volume is 0.3 to 0.6 ml/g and the average pore diameter is 65 to 140 Å. In addition, the catalyst has a certain NO adsorption FT-IR spectrum after sulfidation.</p>		
US 20060128555		2/8/2006
<p>A process for treating hydrocarbon feeds, including hydrotreating, uses a catalyst containing microporous zeolites supported on a mesoporous inorganic oxide such as silica or silicate. A variety of zeolites can be used such as zeolites Y, L, beta and various ZSM zeolites (for example 5 and 11) as well as SAPO's and ALPO's. The material advantageously facilitates the transport of reactants to active catalyst sites. Activity is about 2.5 times the activity of the zeolite used alone, depending upon the specific application.</p>		
US 20060264318		6/2/2006
<p>A catalytic material composition suitable for hydrotreating catalyst contains microporous zeolites supported on a mesoporous inorganic oxide such as silica or silicate. A variety of zeolites can be used such as zeolites Y, L, beta and various ZSM zeolites (for example 5 and 11) as well as SAPO's and ALPO's. The material advantageously facilitates the transport of reactants to active catalyst sites. Activity is about 2.5 times the activity of the zeolite used alone, depending upon the specific application.</p>		
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**Table A.2**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 5569434	Amoco Corporation	10/10/94
<p>The superficial liquid velocity distribution in a slurry-type or ebullated bed resid hydrotreating reactor is improved by use of specified inlet sparger assemblies. The spargers dampen or redirect feedstock having undesired momentum components. The discharged feedstock impinges on a surface of a baffle oriented in a plane that is non-parallel to the direction of the unwanted momentum.</p>		
US 5591325	Catalysts & Chemicals Industries Co., Ltd.	
<p>In a hydrotreater process, heavy oil is fed in series to one or more fixed bed catalytic reactors operated under mild conditions to remove easily hydrotreated impurities having high reactivities with hydrogen such as those contained in resin. The effluent from the last fixed bed reactor is charged to a suspended-bed reactor where impurities having low reactivity with hydrogen such as asphaltenes are reacted at severe conditions. The deactivation of the fixed bed hydrotreating catalyst is suppressed so replacing the catalyst is not necessary for a prolonged period of time.</p>		
US 5624642	Amoco Corporation	10/14/94
<p>A slurry-type or ebullated bed reactor is improved by using a liquid-gas separator system that transfers gas bearing liquids to a reactor vapor space through one or more specified, non-linear conduits or risers constructed and oriented to enhance gas separation from the liquid. The separator includes a conical recycle pan located above the reactor liquid zone and below the vapor space.</p>		
US 5779992	Catalysts & Chemicals Industries Co., Ltd.	8/15/96
<p>In a hydrotreater apparatus, heavy oil is fed in series to one or more fixed bed catalytic reactors operated under mild conditions to remove easily hydrotreated impurities having high reactivities with hydrogen such as those contained in resin. The effluent from the last fixed bed reactor is charged to a suspended-bed reactor where impurities having low reactivity with hydrogen such as asphaltenes are reacted at severe conditions. The deactivation of the fixed bed hydrotreating catalyst is suppressed so replacing the catalyst is not necessary for a prolonged period of time.</p>		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 5837130	Catalytic Distillation Technologies	10/22/96
<p>A process for hydrotreating petroleum fractions employs catalyst prepared as components of distillation structures or as contained beds of catalyst in atmospheric distillation columns and or side draw columns. For example, a crude oil is hydrotreated by taking side streams from the atmospheric distillation column and the vacuum gas oil from a vacuum distillation column which are individually fed to separate, preferably distillation column reactors containing a hydrodesulfurization catalyst. The overhead from each of the distillation reactors is returned to the atmospheric column where it assists with stripping and the bottoms from each distillation column reactor is withdrawn as hydrotreated product. Preferably hydrodesulfurization occurs at low total pressures (0 to 200 psig), low hydrogen partial pressure (0.01 to 70 psi) and temperatures in the range of 400 to 800°F (204 to 427°C). The upflowing hydrogen helps strip the H<sub>2</sub>S produced in the distillation reactor, shifting the equilibrium reactions.</p>		
US 5841678	Phillips Petroleum Company	1/17/97
<p>A method for computer modeling and simulation of a hydrotreating reactor is particularly useful for evaluating crude oils to aid in selecting an economical crude oil slate for a refinery. The program uses a data base of reaction kinetic parameters for hydrotreating sulfur and metals in residua and gas oils. The data base also includes parameters and physical properties for these feedstocks that are obtained from several locations. A set of equations that are functions of catalysts, reactor and feedstock composition models the reaction by predicting yields, H<sub>2</sub> consumption, contaminant levels and product physical properties. Kinetic parameters are adjusted for reactor conditions such as temperature, catalyst activity, time-on-stream, space velocity.</p>		
US 5863416	Nalco/Exxon Energy Chemicals, L. P.	10/18/96
<p>The method prevents fouling and coke formation on the high temperature sections of processing equipment such as found in hydrotreaters that comes in contact with the oil. High temperature surfaces are passivated by a vapor phase additive is added to a carrier (air, steam or mixtures) prior to the carrier contacting the high temperature surface. The additives are tri-tertiary-butylphenol phosphate esters or aromatic compounds having specified structures and are commercially available.</p>		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 5871635	Exxon Research and Engineering Company	12/3/96
<p>A heavy oil such as vacuum gas oil is hydroprocessed in a reactor containing a captive hydrotreating catalyst with a flow-through catalyst added to the feedstock. The flow-through catalyst is typically a fresh or regenerated FCC catalyst or a hydrocracking catalyst, an isomerization catalyst or a catalyst that promotes ring opening. The flow-through catalyst increases the conversion of heavy oils and enhances the performance of the hydrotreating catalyst by converting the feed into molecular structures that are more readily hydrogenated, desulfurized and denitrified. It is desirable that the hydrotreating catalyst sufficiently saturates some of the aromatic rings to more easily form crackable naphthene rings as well as saturate olefins and diolefins to paraffins. The reactor may be a fixed bed, slurry or ebullating bed. The presence of the flow-through catalyst improves the conversion of heavy oil, the hydrogenation, desulfurization and denitrification.</p>		
US 5958218	The M. W. Kellogg Company	1/22/96
<p>Two hydroprocessing reactors are operated in parallel with two feedstocks. Hydrogen flowing in series first to one reactor with recycle hydrogen rich gas flowing to the other reactor. A first feedstock, preferably a light vacuum gas oil, is fed to the first reactor; a second feedstock, preferably a heavy vacuum gas oil, is fed to the second reactor. The first reactor may be a hydrocracker; the second reactor is a hydrotreater. The parallel reactors operate at different hydrogen partial pressures, but the capital and operating costs for compression are reduced compared to conventional configurations.</p>		
US 5972202	Petro-Canada	3/13/97
<p>A process retards the coating of additive or catalyst particles by asphaltenes and retards subsequent agglomeration during the hydrotreatment of heavy oils. A slurry feed of the heavy oil and coke-inhibiting additive particles or catalyst plus hydrogen gas is passed upwardly through a hydrotreater reactor. The effluent is separated into a gaseous stream and a liquid stream of heavy hydrocarbons and particles. At least part of the liquid is recycled. An aromatic oil, typically a gas oil, is added to the hydrotreater in an amount sufficient to inhibit adsorption of asphaltenes on the particles and subsequent agglomeration. Apparently the affinity of the resins and aromatic oils for asphaltenes is shared by the fine particles. The adsorption of the asphaltenes is reversible and can be adjusted by addition of the aromatic oil. The process allows for the more efficient use of the particles, controls the particles agglomeration, allows higher gas rates in the reactor, and recycles a higher proportion of the particles since no purge is required to control agglomeration. Metals from the feedstock have a higher probability of adsorbing on the particles in the reactor.</p>		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 5980730	Institut Francais du Petrole	10/1/97
<p>Heavy oils with large amounts of metals, high carbon residue and sulfur are treated (&gt;80% demetalized, &gt;80% desulfurized and the Conradson carbon residue ≤8%) to produce FCC feedstock. The feed is first hydrotreated first over a at least one three-phase reactor containing at least one ebullated bed hydrotreating catalyst to reduce the metal, sulfur and Conradson carbon residue. Normally all the hydrotreater liquid effluent is atmospherically distilled into a distillate and a residue. At least a portion of the atmospheric residue is vacuum distilled with the residue sent to a solvent deasphalter. Preferably all the deasphalted oil, along with at least a portion of the vacuum distillate, is hydrotreated to reduce the metals, sulfur and Conradson carbon residence. The effluent is atmospherically distilled. The heavier liquid fraction is sent to a residue fluid catalytic cracker or, if the carbon residue is &lt;3%, to a conventional FCCU.</p>		
US 5980732	UOP LLC	8/26/97
<p>In an integrated hydrotreating process for desulfurizing vacuum residue (a 50% boiling point greater than 500°F (260°C)), the feedstock flows with hydrogen through at least two reactors in series, the first reactor containing a hydrotreating catalyst. The effluent from the next to last reactor is separated into a gaseous stream (light hydrocarbons, H<sub>2</sub>S and H<sub>2</sub>) and a liquid stream. The liquid is passed into a fractionator and/or a carbon rejection zone, such as a solvent deasphalter, where asphaltenes are concentrated into a high boiling residue stream and the remaining oil is a distillate. Gas oils and the distillate is passed through the last hydrotreating reactor and a product having a 50% boiling point above 500°F (260°C) is recovered.</p>		
US 6007703	Institut Francais du Petrole	10/1/97
<p>Heavy oils with large amounts of metals, high carbon residue and sulfur are treated (&gt;80% demetalized, &gt;80% desulfurized and the Conradson carbon residue ≤8%) to produce FCC feedstock. The feed is first hydrotreated first over a at least one fixed hydrodemetalization catalyst bed and then a hydrodesulfurization catalyst bed. Normally all the hydrotreater liquid effluent is atmospherically distilled into a distillate and a residue. Normally all the atmospheric residue is vacuum distilled with the residue sent to a solvent deasphalter. Preferably all the deasphalted oil, along with at least a portion of the vacuum distillate, is hydrotreated in at least one three-phase ebullating bed reactor to reduce the metals, sulfur and Conradson carbon residence. The effluent is atmospherically distilled. The heavier liquid fraction is sent to a residue fluid catalytic cracker or, if the carbon residue is &lt;3%, to a conventional FCCU.</p>		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6017441	Institut Francais du Petrole	10/1/97
<p>Heavy oils with large amounts of metals, high carbon residue and sulfur are treated (&gt;80% demetalized, &gt;80% desulfurized and the Conradson carbon residue ≤8%) to produce FCC feedstock. The feed is first hydrotreated first over at least one three-phase reactor containing at least one ebullated bed hydrotreating catalyst to reduce the metal, sulfur and Conradson carbon residue. Normally all the hydrotreater liquid effluent is atmospherically distilled into a distillate and a residue. At least a portion of the atmospheric residue is vacuum distilled with the residue sent to a solvent deasphalter. Preferably all the deasphalted oil, along with at least a portion of the vacuum distillate, is hydrotreated in at least one three-phase, ebullated bed reactor to reduce the metals, sulfur and Conradson carbon residence. The effluent is atmospherically distilled. The heavier liquid fraction is sent to a residue fluid catalytic cracker or, if the carbon residue is &lt;3%, to a conventional FCCU.</p>		
US 6070128	Eutech Engineering Solutions Limited	4/9/97
<p>A method, preferably applicable to hydrotreating, determines or predicts a value <math>P_x</math> of a property (e.g. octane number) of a material X (or a property of a product of a process from the material or yield of the process) using the near IR spectra. The method comprises measuring the absorption <math>D_{ix}</math> of the material at more than one wavelength in the region 600-2600 nm, comparing the signals of the absorptions or a derivative with signals of absorptions <math>D_{im}</math> or derivatives at the same wavelength for a number of standards, S, in a bank for which the property or yield P is known. From the bank at least one standard <math>S_m</math> with property <math>P_m</math> choosing the standard having the smallest average value of the absolute difference at each wavelength i between the signal for the material and the signal for the standard <math>S_m</math> to obtain <math>P_x</math>. The properties or yields <math>P_m</math> are averaged when more than one standard <math>S_m</math> is chosen. If desired, the method can be used to control the process by comparison of <math>P_m</math> with the desired value and adjustment of the process to minimize deviations from <math>P_m</math>. In an alternative process, the signal (or function thereof) of the standard(s) with the smallest average value of the absolute difference may be used directly to control the process. The method may determine more than one property at once or control to maintain more than one property substantially constant. The method avoids the problems of needing a strong correlation between the spectrum and the property and dealing with synergy between components contributing to that property.</p>		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6117306	Institut Francais du Petrole	10/1/97
<p>Heavy oils with large amounts of metals, high carbon residue and sulfur are treated (&gt;80% demetalized, &gt;80% desulfurized and the Conradson carbon residue ≤8%) to produce FCC feedstock. The feed is first hydrotreated first over at least one fixed hydrodemetalization catalyst bed and then a hydrodesulfurization catalyst bed. Normally all the hydrotreater liquid effluent is atmospherically distilled into a distillate and a residue. Normally all the atmospheric residue is vacuum distilled with the residue sent to a solvent deasphalter. Preferably all the deasphalted oil, along with at least a portion of the vacuum distillate, is hydrotreated to reduce the metals, sulfur and Conradson carbon residence. The effluent is atmospherically distilled. The heavier liquid fraction is sent to a residue fluid catalytic cracker or, if the carbon residue is &lt;3%, to a conventional FCCU.</p>		
US 6123835	Process Dynamics, Inc.	6/24/98
<p>A hydrotreating process eliminates circulation of gaseous H<sub>2</sub> through the reactor by mixing or flashing the feedstock with H<sub>2</sub> in the presence of a solvent or diluent that has a high solubility for H<sub>2</sub> relative to the feedstock. All the hydrogenation required can be supplied to the reactor by the choice and amount of solvent/diluent added and reactor conditions. Since gaseous H<sub>2</sub> is not present, the reactor is simplified and reduced in size. Packed reactors operate as plug flow reactors and trickle bed operation is avoided. The reactor temperature is controlled by recycling reactor effluent. When operated at supercritical solution conditions, there is no solubility limit. Since there is always sufficient hydrogen available from the solvent/diluent, coking is greatly minimized and longer catalyst life obtained, which leads to lower operating and maintenance costs. Eliminating the H<sub>2</sub> recycle compressor and the use of smaller reactors reduces the capital cost.</p>		
US 6171471	Exxon Research and Engineering Company	4/30/99
<p>Heavy oil such as vacuum residua is upgraded to FCC feedstock by hydrotreating in a slurry-type reactor using a finely dispersed heterogeneous catalyst. The molybdenum catalyst is added so that the metal levels is at or below 300 ppmw relative to the feed, i.e., &lt;300 ppm Mo. The slurry reactor is a single stage vessel of sufficient residence time, temperature (between 725 and 850°F, 385 to 454°C) and pressure for hydrotreating. The hydrotreating catalyst may be prepared in-situ by contacting the feed with phosphomolybdic acid. The metals and microcarbon residue in the hydrotreated oil is then reduced in a solvent deasphalter.</p>		



**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6179995	Chevron U.S.A. Inc.	1/8/99
Residuum is hydrotreated and the desulfurized effluent is fractionated; the distillate is then hydrocracked to produce high quantities of high quality middle distillate fuels. At least a portion of the hydrocracked VGO may be recycled, along with a portion of hydrotreated VGO, to the hydrocracker. Hydrotreating reduces asphaltene content of the residue, a portion of which is recycled to the hydrotreater and the remainder sent to other refinery processes or blended into fuel oil. Hydrocracker catalyst fouling from heavy aromatics present in the hydrotreated products is minimized. The hydrotreater and hydrocracker are further integrated by a single hydrogen supply, recovery loop and purification, which increases savings in cost and energy usage.		
US 6207041	Institut Francais Du Petrole	10/14/98
A process for hydrotreating heavy oil (vacuum distillate to residue oil with an end point of 1112°F (600°C) or even 1292°F (700°C)) first hydroconverts the oil in at least one three-phase reactor containing an ebullating bed of catalyst. At least a portion of the three-phase effluent is sent to at least one fixed bed hydrotreater reactor. A portion of the effluent from a hydrotreater reactor is distilled at least into a diesel cut and/or a heavier fraction. A portion of the diesel cut and/or the heavier fraction is recycled to at least one three-phase hydrotreating reactor or at least one fixed bed hydrotreating reactor. The heavier product is a catalytic cracker feedstock.		
US 6291391	IFP North America, Inc.	11/12/98
Residuum hydrotreating catalyst, either fresh or regenerated, is presulfided, conditioned and activated by exposing the catalyst to H <sub>2</sub> S and H <sub>2</sub> rich streams within the hydrotreating unit to at least partially convert the metal oxide to a metal sulfide. The catalyst is then conditioned by passing it through a liquid hydrocarbon stream. Catalyst is added on stream intermittently or continuously without interrupting the continuous hydrotreater operation. The process maximizes the catalyst activity.		
US 6299759	Mobil Oil Corporation	2/13/98
A temperature profile and pressure drop control method along successive hydroprocessing catalyst beds comprises injecting H <sub>2</sub> containing gas and a portion of liquid feed onto the first bed and feeding a portion of the liquid feed into at least one quench zone after the bed. For each successive bed, quench gas is injected into each quench zone. A portion of the liquid feed and the quench gas each are injected in a sufficient amount to control the reactor's temperature profile and pressure drop.		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6406615		5/25/99
<p>When a deactivated hydrotreating catalyst is regenerated and optimally combined with fresh catalyst, the combined catalyst system is still effective for hydrogenation of heavy oil. When the catalyst is regenerated in a manner that controls the amount of impurities adhering to the regenerated catalyst and controls the physical properties with a specified range, the process is especially effective. Heavy oil feed is hydrogenated via passing through at least a layer containing regenerated catalyst. Heavy oil is hydrogenated, hydrodesulfurized and hydrodenitrogenified by passing through a bed containing regenerated catalyst and then a bed of fresh catalyst. The conditions can be those used in ordinarily hydrotreating the heavy oil with fresh catalysts. Efficient utilization of used catalysts is achieved.</p>		
US 6409912	Texaco, Inc.	1/11/2000
<p>Deasphalted oil or other heavy oil feedstock is hydrotreated producing a hydrogen rich gas and treated liquid product. The reactor effluent is stripped with steam or nitrogen to remove volatiles from the liquid. The asphaltene rich stream recovered from the solvent deasphalter is gasified to H<sub>2</sub> and CO. The H<sub>2</sub> is used in the hydrotreater.</p>		
US 6428686	Process Dynamics, Inc.	6/22/2000
<p>A hydrotreating process eliminates circulation of gaseous H<sub>2</sub> through the reactor by mixing or flashing the feedstock with H<sub>2</sub> in the presence of a solvent or diluent that has a high solubility for H<sub>2</sub> relative to the feedstock. All the hydrogenation required can be supplied to the reactor by the choice and amount of solvent/diluent added and reactor conditions. Since gaseous H<sub>2</sub> is not present, the reactor is simplified and reduced in size. Packed reactors operate as plug flow reactors and trickle bed operation is avoided. The reactor temperature is controlled by recycling reactor effluent. When operated at supercritical solution conditions, there is no solubility limit. Since there is always sufficient hydrogen available from the solvent/diluent, coking is greatly minimized and longer catalyst life obtained, which leads to lower operating and maintenance costs. Eliminating the H<sub>2</sub> recycle compressor and the use of smaller reactors reduces the capital cost.</p>		
US 6436279	Axens North America, Inc.	11/8/2000
<p>A hydrotreating process for heavy vacuum gas oil and deasphalted oil feeds employs an ebullated bed reactor having a high length-to-diameter ratio enabling more high catalyst loading per total reactor volume and enhanced conversion and hydrodesulfurization performance. The ebullated bed is operated at a minimum degree of expansion such that catalyst withdrawal is feasible while maintaining stable operation. Recycle liquid rate is low, in the range of 0.67 to 1.5 times the fresh feed rate compared to the conventional rate of 2-3 times. The low degree of expansion and the low recycle rate enhance the kinetics since a closer approach to plug flow is obtained. Product quality is uniform with time.</p>		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6676828	Intevep, S. A.	7/26/2000
<p>Vacuum gas oil and diesel feed are sequentially hydrotreated in a process that utilizes a stripping and washing step to separate at high pressure and high temperature an intermediate feedstock. The wash liquid is a diesel, light vacuum gas oil or their mixtures either from the process or an external source. The hydrodesulfurization and hydrotreating reactors along with the stripper/washer separator are operated at substantially the same pressure and preferably substantially the same temperature. This avoids the need for intermediate compression and/or reheating the feed to the hydrotreating stage. The stripper/washer is operated at a pressure within about 50 psig of the reactor feed pressure.</p>		
US 6716339	Corning Incorporated	3/30/2001
<p>Catalyst and reactor efficiency for hydrodesulfurization are substantially improved over pellet catalysts in trickle bed reactors by using a parallel channel monolith honeycomb catalyst. Uniformly distributing gas and liquid to each channel significantly reduces partial wetting and stagnant fluid areas, increasing the overall catalyst volumetric efficiency.</p>		
US 6733659	Nippon Mitsubishi Oil Corporation and Petroleum Energy Center	12/21/2000
<p>A reactor for hydrotreating suitable for heavy oils contains a plurality of catalyst layers packed with hydrotreating catalysts and exhibits total desulfurization activity higher than prior art along with a long catalyst life. The hydrotreating catalysts satisfy the following relationship: <math>S_n \leq S_{n+1}</math>, <math>1.15 V_n \geq V_{n+1}</math> where <math>S</math> is the surface area per cubic meter of catalyst, <math>V</math> is the pore volume per cubic meter of catalyst and <math>n</math> is the number of the catalyst layer.</p>		
US 6740226	Saudi Arabian Oil Company	1/16/2002
<p>Hydrogen partial pressure in the hydrotreating reactor is increased by absorbing <math>H_2S</math>, methane and higher hydrocarbons from the recycle hydrogen stream. Flash gases from the high pressure overhead separator are counter-currently contacted with lean solvent to produce a overhead gas of typically 90 to 98% or higher purity hydrogen. The rich solvent is flashed to release the absorbed <math>H_2S</math> and hydrocarbons thereby regenerating the lean solvent. The solvent is predominantly <math>C_4</math> to <math>C_5</math> hydrocarbons. Prior art teaches that the inventory of lean solvent can be maintained and stabilized by controlling the temperature. Thus the volume of solvent lost due to equilibrium at absorber conditions is made equal to the amount of <math>C_4</math> to <math>C_5</math> components in the flash separator gas. At steady state, no make-up solvent is needed. The <math>H_2S</math> is removed from the flashed regenerator gases by a significantly smaller amine unit than required to treat the high pressure separator overhead gas stream.</p>		

**Table A.2 (Continued)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 6787025	Chevron U.S.A. Inc.	12/17/2001
Typically the middle distillate from VGO hydrotreating does not meet the smoke point, cetane number or aromatic specification and is further hydrotreated in a separate hydrotreater. In this patent, middle distillate is hydrotreated in the same high pressure loop as a vacuum gas oil hydrotreater reactor. Investment cost is reduced and/or utilities are saved since a separate middle distillate hydrotreater is not required.		
US 6855246	Institut Francis du Petrole	2/12/2001
A gas oil is desulfurized in a first catalytic zone with the H <sub>2</sub> S is at least partially eliminated. One or more additional desulfurization steps are then conducted. The distribution of catalyst in each step selected to maximize the catalytic activity thus minimizing the volume of catalyst required for the unit at fixed operating temperature and pressure while producing a low sulfur gas oil of less than 30 ppm or even less than 10 ppm.		
US 2005 0133411		2/23/2005
This process reduces sulfur and polyaromatic hydrocarbons (PAH) in FCC feedstock by cooling the effluent containing H <sub>2</sub> rich gas from a main hydrotreater and contacting the effluent over a hydrotreating catalyst in a small post-treatment reactor. The PAH content is reduced in the post reactor due to more favorable equilibrium conditions. Only slightly more investment in reactor volume is required without reduction in run length. The crackability of the FCC feedstock is improved by the reduction in PAH.		
US 2005 0167333		1/30/2004
A heavy oil supercritical cracking process having high sulfur, nitrogen and metals removal is followed by hydrotreating to further reduce the sulfur, nitrogen and carbon residue. Oil boiling above 1000°F (538°C) is mixed with a solvent at a weight ratio of solvent to oil of at least 2:1. Examples of solvents include light and heavy naphtha, distillates and gas oils. Hot fluidized solids such as refractory oxides (alumina or silica for examples) supply heat and are regenerated and recycled.		
US 2006 0042999		8/30/2004
A process upgrades and demetallizes heavy oils and bitumens by solvent extraction of asphaltenes followed by FCC using a low conversion catalyst to remove metals prior to hydrotreating for upgrading to a synthetic crude product. The asphaltene fraction can be gasified to produce hydrogen, which can be supplied to the hydrotreater. An optional coker can convert excess asphaltenes or decant oil to naphtha, distillate and gas oil, which can also be fed to the hydrotreater.		

**Table A.2 (Concluded)**  
**HEAVY OIL HYDROTREATING PROCESSES**

**PATENT SUMMARY**

<b>Reference Number</b>	<b>Assignee</b>	<b>Earliest Date Shown</b>
US 2006 0163115	ENI s.p.a., Snamprogetti s. p. a. and Enitechologie s. p. a.	12/12/2003
Heavy oil feedstocks are converted by hydrotreatment in a slurry reactor, distillation and solvent deasphalting (SDA). The heavy feedstock and asphaltenes from SDA are mixed with a hydrotreating catalyst and hydrotreated. The hydrotreated effluent is separated at high pressure into light and heavy fractions. The heavy hydrotreated product containing the catalyst is distilled or flashed and at least part of the distillation residue containing dispersed catalyst is recycled to the SDA. The SDA unit produces deasphalted oil and asphaltene rich product streams. A fraction of the asphaltene stream (flushing stream) is treated with a solvent to separate the product into a solid fraction and a liquid fraction from which the solvent is subsequently removed.		
US 2006 0175229	ENI s.p.a., snamprogetti s. p. a. and Enitechologie s. p. a.	12/12/2003
Heavy oil feedstocks are converted by hydrotreatment in a slurry reactor, distillation and solvent deasphalting (SDA). The heavy feedstock and asphaltenes from SDA are mixed with a hydrotreating catalyst and hydrotreated. The hydrotreated effluent is separated at high pressure into light and heavy fractions. The heavy hydrotreated product containing the catalyst is distilled or flashed and at least part of the distillation residue containing dispersed catalyst is recycled to the SDA. The SDA unit produces deasphalted oil and asphaltene rich product streams.		
US 2006 0231455		7/13/2004
An integrated process produces and upgrades heavy and extra-heavy crude oil by reforming to produce H <sub>2</sub> , CO <sub>2</sub> and steam. The H <sub>2</sub> is separated into a H <sub>2</sub> rich fraction that is used to hydrotreat and hydrocrack the oil, either downhole or at an upgrading facility, in one step to reduce the oil's viscosity.		
US 2006 0254956	Saudi Arabian Oil Company	5/10/2006
High sulfur heavy crude oil is catalytically hydrotreated under low pressure (preferably 500-1500 psi) hydrogen to produce a lower sulfur, lighter, lower density oil and a heavier crude oil residue. The residue oil is further hydrotreated in a second reactor. The low pressure catalyst may contain a transition metal, more preferably selected from molybdenum, iron cobalt, nickel or mixtures.		

**Appendix B**

**DESIGN AND COST BASES**

## DESIGN AND COST BASES

### DESIGN CONDITIONS

Design and cost calculations are based on an assumed plant location along the U.S. Gulf Coast at Houston, Texas. Particular temperature assumptions are:

Dry bulb air temperature	100°F (38°C)
Wet bulb air temperature	80°F (27°C)
Groundwater temperature	80°F (27°C)
Cooling water temperature	85°F (29°C)
Cooling water temperature rise	20°F (11°C)
Chilled water temperature	50°F (10°C)
Chilled water temperature rise	up to 20°F (11°C)

Columns and vessels were sized respectively for 80% of flooding.

The usual definitions of terms relating to yield are used in this report. They are as follows:

Conversion	Ratio of material reacted to material fed, stated as a percentage or fraction.
Selectivity	Ratio of product desired to material reacted, stated as a percentage or fraction of material reacted
Yield per pass	Ratio of product desired to material fed, stated as a percentage or fraction of material fed, = Conversion x Selectivity

### COST BASES

Below, we outline the criteria for calculating capital investment and production costs, and the effect of the operating level on production costs.

#### Capital Investment

Equipment costs are estimated primarily from correlations using the PEP Cost database, version 3.1.5 (Program PC-3-2006) [PEP Reports 145 *Battery Limits Cost Estimating* (April 1982) and 162 *Computer Program for Estimating Plant Investment* (March 1985)] developed by PEP and supplemented occasionally by vendors' estimates. If an equipment item is specialized or contributes substantially to the cost of the facility, a vendors' quote has been obtained if possible. When necessary, the costs are corrected to a PEP Cost Index of 718 (midyear 2006).

Direct installation costs are estimated by a modular method developed by PEP; the details are described in detail in PEP Report 145, *Battery Limits Cost Estimating* (April 1982). The indirect costs in capital investment are estimated by adding allowances for engineering, field expenses, overhead, purchasing, and contractor's profit. The bases for the estimation of these allowances are detailed in Section 7 of PEP Report 162, *Computer Program for Estimating Plant*

*Investment* (March 1985). These indirect cost estimates are then added to the direct investment (FOB costs plus direct installation costs) to get the overall installed costs.

Investment in utilities is computed for the entire plant and allocated to each major operation according to use. Indirect costs for utilities and off-site tankage (generally raw material and product storage) are assumed to be 20% of the direct utilities investment.

General service facilities not directly associated with process operations are shown as an allowance. General services facilities includes items such as roads, parking, fences, administrative offices, craft shops, fire and safety equipment, plant communications and warehouses. An allowance is also made for investments to expand or provide waste treatment facilities, including ground water collection and treatment. These allowances are determined prior to the addition of contingencies to the installed costs.

The total fixed capital for the facility includes total investment in battery limits, utilities and tankage, general service facilities, and a contingency. Usually the contingency for large generic petroleum refinery processes is taken as 15% each of the battery limits investment and the off-site investment. All of the above investment estimates have been calculated with the aid of SRI Consulting's PEPCOST II computer program.

In comparing SRI Consulting's estimates with actual plant costs or contractors' estimates, the following should be borne in mind:

- The processes may be the same generally but differ enough in detail to affect costs significantly. Proprietary process information or designs may be used.
- The estimates may not be strictly comparable because of omission of process sections (for example, by-product recovery) in one or another of the designs.
- Actual plants are frequently over designed for reasons unique to the particular situations.
- During periods of rapid escalation of equipment costs, and when long delivery times are anticipated, cost indexes probably are not an accurate reflection of actual costs.
- During periods of depression in chemical plant construction, equipment vendors and engineering contractors will provide goods and services at little or no profit.

## **Production Costs**

The operating labor wages are based on estimated prevailing rates in Houston, Texas. The base rate is derived from U.S. national average rates in industrial chemical plants, corrected to the Houston area on a relative basis for production workers. With an allowance for fringe benefits and a 10% shift overlap assumed, the effective total rate is \$41.50 per hour. The operating labor requirements have been estimated subjectively on the basis of the number of major equipment items in the process. A completely computer automated plant with a central control room is assumed where several smaller units may be controlled by one operator. The number of men per shift includes the working foremen. Control laboratory labor is assumed to be 20% of operating labor. The cost of staff supervision—such as the assistant operating department manager, etc.—is assumed to be included in our allowance for plant overhead.

Plant overhead has arbitrarily been assumed at 80% of total labor. It includes all staff personnel located at the plant site, and services directly associated with plant operations and maintenance.

G&A, sales, and research costs are assumed for each product by making allowances for the stage of process development in estimating research expense, and for the character of marketing channels and technical service requirements in estimating selling expense. These estimates are



customarily assigned a percentage of the sales value of the product, generally in the range of 5-30% for specialty plants, but lower or even negligible for large commodity plants such as petroleum refineries. When actual prices are unknown, we base the G&A, sales, and research expense on the calculated product value (total production cost plus 25%/yr pretax return on fixed capital).

The cost of taxes and insurance is calculated at 2% of total fixed capital. Depreciation is based on 10%/yr of fixed capital.

### **Effect of Operating Level on Production Costs**

Variations in production costs with plant capacity and with operating rate are based on the following assumptions:

- The annual costs of process plant operating labor, control laboratory labor, and operating materials are invariant with plant capacity. Also, the entire process plant labor force remains on the payroll when the plant is operating at reduced capacity or is shut down.
- Investment-related items, including maintenance labor, maintenance materials, taxes, and depreciation, are directly proportional to investment, and their annual cost remains constant with reduced operating rate.
- Corporate overhead charges are constant to various plant capacities, and the annual allocation is also constant, regardless of plant operating rate.
- Production costs generally do not include any allowance for packaging or shipping; i.e., they represent bulk costs, FOB plant.
- Working capital is not included in the fixed capital cost, nor are start-up costs. Interest on working capital is not included in the production cost or in the product value.
- Royalties are not included in any of the estimates. Royalties for any given licensed process may vary considerably, depending on terms of the agreement, geographic location, etc. Initial payments or paid-up royalties may be substantial, and they should be considered in specific estimates.
- Annual costs for raw materials and utilities are directly proportional to the annual plant production.

In accordance with the last assumption, unit costs for raw materials and utility consumptions do not change with either plant capacity or operating rate.

**Appendix C**  
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ABB Lummus Global Inc.	US 6930219
Akzo Nobel N.V.	US 6509291
Amoco Corporation	US 5569434
	US 5624642
Axens North America, Inc.	US 6436279
Catalysts & Chemicals Industries Co., Ltd.	US 5591325
	US 5779992
Catalytic Distillation Technologies	US 5837130
Chevron U.S.A. Inc.	US 6179995
	US 6787025
Corning Incorporated	US 6716339
Cosmo Oil Co., Ltd.	US 6821412
Cosmo Research Institute and Cosmo Oil Co., Ltd.	US 5444033
Eni s.p.a., snamprogetti s. p. a. and Enitechologie s. p. a.	US 2006 0175229
	US 2006 0163115
Eutech Engineering Solutions Limited	US 6070128

<b>Assignee</b>	<b>Patent Number</b>
Exxon Research and Engineering Company	US 5871634
	US 5871635
	US 5997723
	US 6162350
	US 6171471
	US 6712955
Haldor Topsoe A/S	US 6667271
Idemitsu Kosan Co., Ltd.	US 6398950
IFP North America, Inc.	US 6291391
Indian Oil Corporation Limited	US 6855653
Institut Francais du Petrole	US 5980730
	US 6007703
	US 6017441
	US 6117306
	US 6207041
	US 6203695
	US 6855246
Instituto Mexicano del Petroleo and Instituto Mexicano Del Petroleo	US 6383975
Japan Energy Corporation	US 6676828
Mobil Oil Corporation	US 6299759
Nalco/Exxon Energy Chemicals, L. P.	US 5863416
Nippon Mitsubishi Oil Corporation and Petroleum Energy Center	US 6733659
Petro-Canada	US 5972202
Phillips Petroleum Company	US 5841678
Process Dynamics, Inc.	US 2005 0082202
	US 6123835
	US 6428686
	US 6881326
Saudi Arabian Oil Company	US 2006 0254956
	US 6740226

<b>Assignee</b>	<b>Patent Number</b>
Texaco Inc.	US 5676822
	US 5928499
	US 6409912
The M. W. Kellogg Company	US 5958218
Tonen Corporation	US 6306289
	US 6436870
Tonen General Sekiyu K.K.	US 6267874
UOP LLC	US 5980732



**Appendix E**  
**PROCESS FLOW DIAGRAMS**

Figure 7.1  
CONVENTIONAL HYDROTREATING VACUUM GAS  
OIL FOR FCC FEED

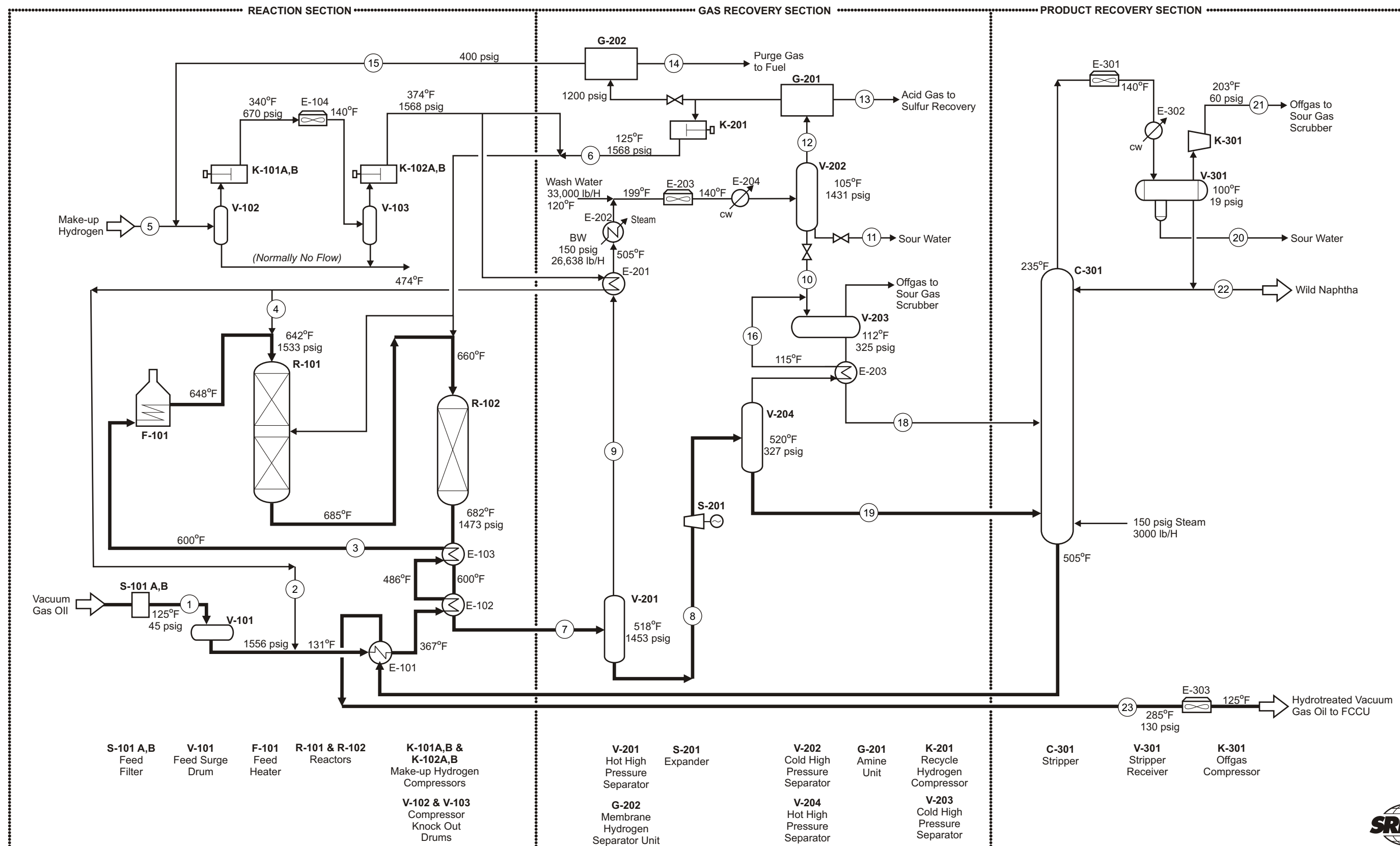


Figure 7.2  
ISOTHERMING™ TYPE HYDROTREATING VACUUM  
GAS OIL FOR FCC FEED

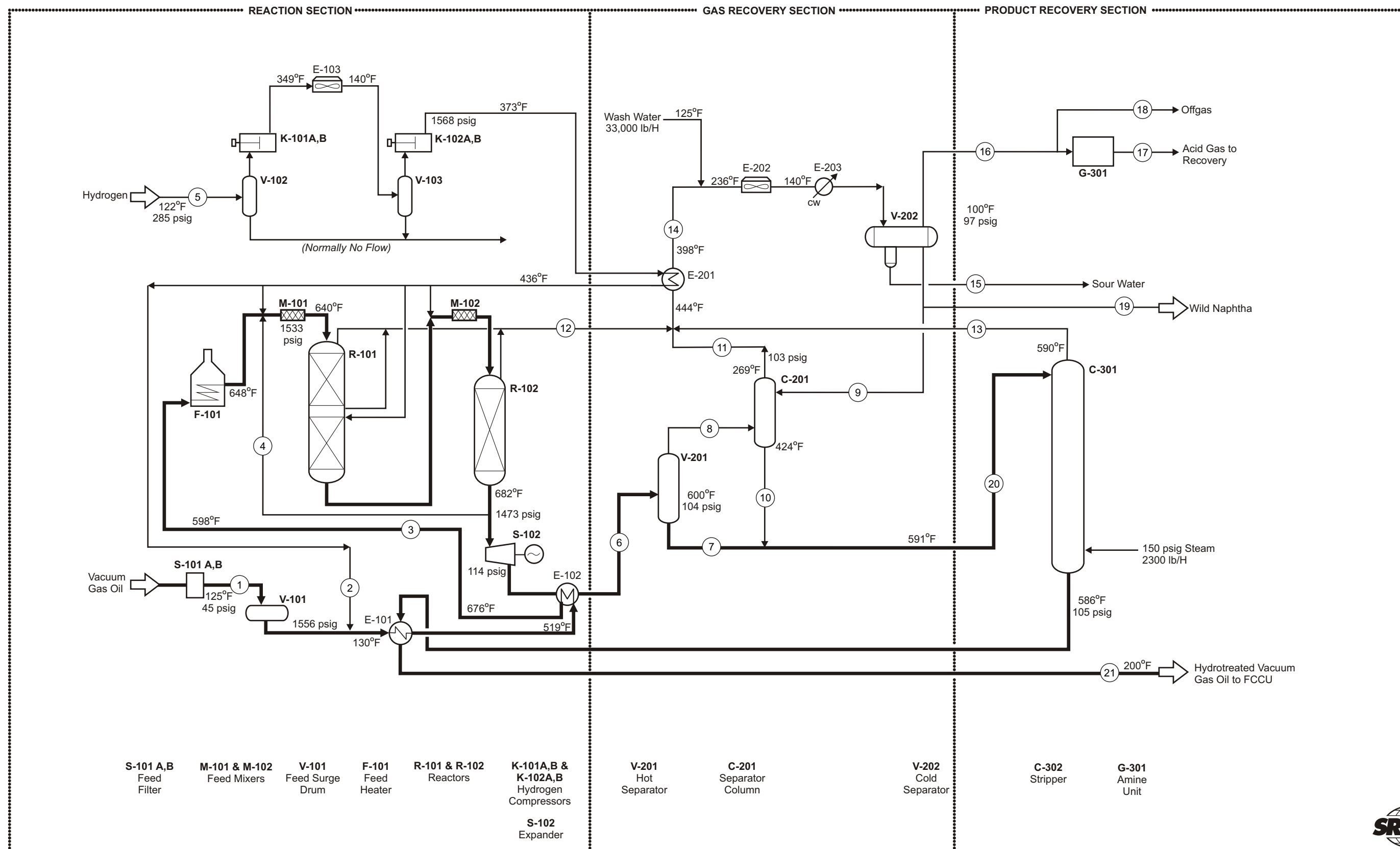


Figure 8.1  
HYDROTREATING ATMOSPHERIC RESID FOR  
FCC FEED

