HYDROTREATING HEAVY OILS OVER A COMMERCIAL HYDRODEMETALLATION CATALYST

by

Seokhwan Kwak

A dissertation to the faculty of The University of Utah in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemical and Fuels Engineering The University of Utah August 1994
ABSTRACT

A Uinta Basin bitumen was hydrotreated over a sulfided Ni-Mo on alumina commercial hydrometallation catalyst. The catalyst was on-stream continuously for more than 1,000 hours. The data were obtained with the reactor operating as a fixed bed reactor in the upflow mode to ensure complete wetting of the catalyst and nearly isothermal operation.

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This dissertation has been read by each member of the following supervisory committee and by majority vote has been found to be satisfactory.

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To the Graduate Council of the University of Utah:

I have read the dissertation of Seokhwan Kwak in its final form and have found that (1) its format, citations and bibliographic style are consistent and acceptable; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the supervisory committee and is ready for submission to The Graduate School.

Date: June 15, 1994

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CHAPTER 1

INTRODUCTION

Heavy oils and bitumens are known for their high molecular weight and high concentrations of heteroatomic species such as nitrogen, sulfur and oxygen and metals such as Ni, V. and As. The heteroatomic species are a cause for environmental concern since they form SO$_x$ and NO$_x$ during combustion. Both metals and heteroatomic species are a concern in refinery processes such as catalytic cracking, hydrocracking and reforming by poisoning the catalysts.

In catalytic upgrading, heteroatoms are removed as H$_2$S and NH$_3$ via desulfurization and denitrogenation; however, in hydrodemetallation (HDM), metals are deposited on the catalyst as sulfides and cause irreversible fouling of the catalyst. This catalyst deactivation has a serious impact on the economics of residuum hydroprocessing because catalysts poisoned by metal deposition must be replaced whereas coked catalysts can be reused after regeneration. Therefore metals which are concentrated in the high molecular weight resin and asphaltene fractions ultimately determine the lifetime of the catalyst. Recent hydrotreating processes for upgrading heavy feedstocks have focused on catalysts having a low tendency toward coke formation and catalysts which can tolerate higher metal deposition [1].

A commercial hydrodemetallation catalyst which had a large pore diameter and volume was used in this study due to the nature of the Whiterocks bitumen: high molecular weight and high residuum content. These
characteristics of heavy feeds may cause maldistribution of the feedstock over the surface of the catalyst bed in conventional trickle-bed laboratory reactor operation. The resulting coning in the inlet region of the reactor and the consequent incomplete wetting of the catalyst may lead to the determination of erroneous apparent kinetic parameters and to misleading conclusions regarding the influence of process variables on conversion and product distribution and yields. Furthermore, lower superficial velocities in laboratory reactors at the same space velocity relative to the commercial reactor could lead to partial wetting of the catalyst. Therefore, the kinetic parameters for heteroatom removal and residuum conversion for bitumen and bitumen-derived heavy oil were determined in an reactor which operated upflow in the plug-flow mode.

The objective of this study was to determine the influence of process operating variables, temperature, pressure and residence time or space velocity on denitrogenation, desulfurization and residuum conversion and on product distributions and yields. The determination of apparent kinetic parameters was also undertaken.
CHAPTER 2

LITERATURE SURVEY

Origin of Bitumen

The potential hydrocarbon resource that occurs in oil sand deposits have been variously estimated on a worldwide basis as being in excess of 3 trillion \((3 \times 10^{12})\) barrels of petroleum equivalent and the oil sand resource for the United States has been estimated to be in excess of 52 million barrels [2].

Oil sand is a general term for any rock material, loose or consolidated, that contains the bitumen in pores or fractures. It is usually composed of 85 wt% of rock matrix which is mostly quartz or carbonate sand-sized particles and the heavy oil called bitumen [3]. The bitumen has a reddish brown to black color and exists in semisolid under natural reservoir conditions due to its high viscosity. It contains more heteroatoms and metals and less volatiles than conventional petroleum crude oil. This bitumen must be recovered from the oil and upgraded to produce high quality hydrocarbon values.

Bitumen Separation Technologies

Bitumen can be recovered from oil sands by either in-situ thermal enhanced oil recovery processes or by aboveground recovery processes.
**In-Situ Processes**

In-situ thermal enhanced oil recovery processes can be divided into three types: 1) heating alone to reduce the viscosity of bitumen to release it from the rock, 2) solvent (or chemically active solution) injection to flush the bitumen from the rock and 3) combinations of heating and solvent injection.

Steam or hot water injection [4,5] and in-situ combustion (fire flooding) [6] belong to the first category. In steam injection processes minor changes occur in bitumen properties except for pour point and viscosity reduction [4,5]. However, when steam is introduced into the formation at high pressures, cracking may occur to some extent in addition to distillation. In-situ combustion usually causes significant physical and chemical changes in bitumen due to the coking and combustion of a portion of the bitumen to provide heat to mobilize bitumen and/or the bitumen-derived heavy oils. In-situ combustion includes a number of options: forward and reverse and wet and dry combustion [6].

Chemical processes which use chemicals or chemically active solutions for mobilizing bitumen result in minor changes in bitumen properties other than viscosity. In these processes, the chemical should be recovered and cleaned up for reuse in view of the high cost of the injected chemicals.

**Aboveground Processes**

The first step in all aboveground processes is mining or quarrying followed by size-reduction. The size and quantity along with the cost of this equipment are all enormous.

There are ways of recovering bitumen-derived heavy oils from oil sands after mining or quarrying: extraction using water and/or chemical solvents [7,8,9] and pyrolysis or thermal processing [10]. The extraction processes do not significantly influence the physical and chemical properties of bitumen; however,
the final mineral-free product is little different from the original reservoir fluid [7,8,9]. Pyrolysis or thermal processing results in significant physical and chemical changes to the bitumen-derived liquids recovered from the oil sands relative to the bitumen. A sufficient heat should be introduced in this type of processes to volatilize a portion of bitumen, thus, being separated from the oil sand; at the same time the heavier or higher boiling fractions of the bitumen will be thermally decomposed [10].

The alternative schemes for production of a refinery feedstock from oil sands are summarized in Figure 2.1.

**Chemical Composition of Bitumen and Petroleum Resids**

Definitions of heavy oils are usually based on the API gravity or viscosity at reservoir conditions and are frequently quite arbitrary [11]. The term “heavy oil” has often been used to describe conventional petroleum crude oils which have API gravities of less than 20 °API and which require thermal stimulation to induce mobility in the reservoir. The bitumen in oil sands which require surface mining followed by extraction or pyrolysis to recover hydrocarbon values are also defined to be heavy oils. Heavy oils are generally darker than conventional crudes and may even black.

Speight [2] classified the heavy oils according to the following density-gravity system:

- **Heavy crude oil**
  - Density-gravity range from 1,000 kg/m³ to more than 934 kg/m³
    
    (10 °API to < 20 °API)

- **Extra heavy crude oil** (may also include atmospheric residua (boiling range 613 K to 923 K))
Figure 2.1

Alternative Schemes for Production of a Refinery Feedstock from Oil Sands
RECOVERY

IN SITU
Steam Drive
Steam Soak
Oxygen/Air Injection
Hot Water Injection
Combustion
Combinations of the Above

CRACKING
Bitumen or Bitumen-Derived Heavy Oil
Via Bore Hole

Hydropyrolysis
Hydrocracking

HYDROTREATING
Cracked Products
Metals & Coke

Nitrogen & Sulfur

MINING OR QUARRYING
Tar
Sand

SOLVENT OR WATER EXTRACTION PROCESS
Bitumen

Hydropyrolysis
Hydrocracking

HYDROTREATING
Cracked Products
Metals & Coke

Nitrogen & Sulfur

CONVENTIONAL REFINERY FEEDSTOCK
- Density-gravity greater than 1,000 kg/m³ (<10 °API)
- Maximum viscosity of 10,000 mPa s (cp)

- Oil sand bitumen or natural asphalt (may also include vacuum residua (boiling range>783 K)):
  - Density-gravity greater than 1,000 kg/m³ (<10 °API)
  - Viscosity greater than 10,000 mPa s (cp).

Beaton [12] defined residuum as the bottom fraction that remains after atmospheric or vacuum distillation of a crude oil. The atmospheric and vacuum residuum differs in their nominal initial boiling points which are 617 K (650°F) and 811 K (1000°F), respectively. Asphaltene constituents and vanadium and nickel organometallic compounds distinguish residuum from the lighter fractions of crude oils. Residuum must undergo significant upgrading as they are generally less valuable in their natural state than lighter crude fractions.

Beaton and Bertolacini [1] demonstrated that sulfur contents vary between 1% to 6%, with 4% typical in the petroleum residuum and the typical residuum contains 20% oils (the most catalytically reactive fraction), 65% resin (intermediate reactive fraction), and 15% asphaltenes (the least reactive fraction). Most studies on the composition of residuum begin with fractionation of the materials into several compound-type classes by techniques such as gel permeation and liquid chromatography.

The bitumen in oil sands differs from crude oil in heteroatom concentrations and in the proportions of hydrogen and carbon. Bitumens have higher nitrogen and oxygen concentrations and lower hydrogen-to-carbon ratios than conventional crude oils due to the heavier, complex hydrogen-deficient constituents. These differences are reflected on the high Conradson carbon residue (CCR) and asphaltene contents of bitumen. These chemical differences
are reflected in physical properties: high viscosity, high specific gravity, and high pour point [10,13-17].

The properties of a conventional crude oil, a Canadian bitumen, a Utah bitumen and an atmospheric petroleum resid are compared in Table 2.1.

**Uinta Basin Oil Sands**

Although the United States does not have oil sand deposits which comparable in size with those of Canada and Venezuela, there are several large deposits in the state of Utah.

As can be seen in Table 2.1., the Uinta Basin bitumen has a higher hydrogen content and contains about three times as much nitrogen, but only about one-tenth as much sulfur, as the Athabasca bitumen [14]. It also has a lower vanadium content, but slightly higher nickel content [16-18]. The Uinta Basin bitumens originated in a non-marine environment (lacustrine) thus they are richer in saturates than Athabasca bitumens which originated in a marine environment [17]. The bitumens usually differ not only in depositional environment, but in age. The bitumens that had lower saturate molecular weight distributions were reported to be older [18]. The higher concentrations of mono-, di- and tricyclic saturates in Athabasca bitumen [19] may simply be the result of greater degradation of higher molecular weight saturates in the bitumen. These results are consistent with the high H/C ratio of Whiterocks oil sands bitumen [20].

The distinguishing property of the Uinta Basin oil sand bitumens are the viscosities. The Uinta Basin bitumens are at least one to two orders of magnitude more viscous than the Athabasca bitumen [21]. This high viscosity affects recovery and upgrading process and makes handling of the primary bitumen difficult.
## Table 2.1

Comparison of Athabasca and Uinta Basin Bitumens with Petroleum Resid and Conventional Crude Oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Conventional Crude Oil</th>
<th>Athabasca Bitumen</th>
<th>Uinta Basin Bitumen</th>
<th>Safaniya Atmospheric Residuum (617 K*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>[13]</td>
<td>[14]</td>
<td>[10]</td>
<td>[15]</td>
</tr>
<tr>
<td>Gravity, API</td>
<td>25-37</td>
<td>7.4</td>
<td>10.3</td>
<td>13.9</td>
</tr>
<tr>
<td>Conradson carbon, wt%</td>
<td>1-2</td>
<td>12.7</td>
<td>13.0</td>
<td>13.2</td>
</tr>
<tr>
<td>Ash, wt%</td>
<td>0.0</td>
<td>0.9</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td><strong>Elemental analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C, wt%</td>
<td>86</td>
<td>83.1</td>
<td>85.0</td>
<td>84.9</td>
</tr>
<tr>
<td>H, wt%</td>
<td>13.5</td>
<td>9.8</td>
<td>11.4</td>
<td>11.1</td>
</tr>
<tr>
<td>N, wt%</td>
<td>0.2</td>
<td>0.4</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>S, wt%</td>
<td>0.1-2.0</td>
<td>4.5</td>
<td>0.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Ni, ppm</td>
<td>-</td>
<td>68</td>
<td>75 [17]</td>
<td>24.3</td>
</tr>
<tr>
<td>V, ppm</td>
<td>-</td>
<td>234</td>
<td>2 [17]</td>
<td>86.0</td>
</tr>
<tr>
<td>Fe, ppm</td>
<td>2-10</td>
<td>408</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H/C Atomic Ratio</td>
<td>1.9</td>
<td>1.4</td>
<td>1.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>
The physical and chemical properties of bitumens extracted from Utah oil sands are presented in Table 2.2 [10].

**Heavy Oil Upgrading Technology**

The decline in demand for residual fuel oils and the increase in heavier crude supplies worldwide indicates that the development of heavy oil upgrading technologies for converting heavy residuum to lighter and/or more valuable materials are necessary [22-24].

There are several ways to categorize heavy oil upgrading technology [25,26]. Traditionally upgrading processes have been classified according to whether carbon is rejected from or hydrogen is added to the feedstock. Carbon rejection aims to remove asphaltene and carbon residues in the form of coke, pitch, or extra heavy, aromatic oils by thermal cracking whereas hydrogen addition is intended to increase hydrogen/carbon ratio via hydrotreating.

Upgrading processes can be grouped as follows:
- catalytic processes (hydrotreating (HT), hydrocracking)
- noncatalytic processes (hydrovisbreaking, donor-solvent processes, hydropyrolysis)
- catalytic cracking (FCC); and
- thermal processes (visbreaking, coking)

Finally there are other non-refining processes in which heavy oils and residuum can be utilized:
- combustion
- partial oxidation
- steam reforming
- solvent deasphalting (SDA)
Table 2.2

Properties of Extracted Bitumen from Utah Oil Sands [10]

<table>
<thead>
<tr>
<th>Property</th>
<th>PR Spring Rainbow I</th>
<th>Sunny-side</th>
<th>Whiterocks</th>
<th>Asphalt Ridge</th>
<th>Circle Cliffs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen Content, wt%</td>
<td>14.1</td>
<td>8.5</td>
<td>8.0</td>
<td>10.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Gravity, °API</td>
<td>7.8</td>
<td>5.5</td>
<td>10.3</td>
<td>14.4</td>
<td>14.3</td>
</tr>
<tr>
<td>Conradson Carbon, wt%</td>
<td>14.0</td>
<td>14.8</td>
<td>13.0</td>
<td>-</td>
<td>23.3</td>
</tr>
<tr>
<td>Ash, wt%</td>
<td>3.3</td>
<td>2.4</td>
<td>0.8</td>
<td>0.04</td>
<td>0.10</td>
</tr>
<tr>
<td>Pour Point, K</td>
<td>372</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>332</td>
</tr>
<tr>
<td>Viscosity, cps</td>
<td>8269a</td>
<td>7373b</td>
<td>29245c</td>
<td>2015d</td>
<td>23012e</td>
</tr>
<tr>
<td>Simulated Distillation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatility, wt%</td>
<td>39.9</td>
<td>32.4</td>
<td>22.1</td>
<td>-</td>
<td>31.2</td>
</tr>
<tr>
<td>IBP-478K, wt%</td>
<td>1.3</td>
<td>0.9</td>
<td>0.9</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>478K-617K, wt%</td>
<td>5.1</td>
<td>7.3</td>
<td>3.3</td>
<td>-</td>
<td>3.4</td>
</tr>
<tr>
<td>617K-811K, wt%</td>
<td>25.6</td>
<td>24.0</td>
<td>18.8</td>
<td>-</td>
<td>27.8</td>
</tr>
<tr>
<td>&gt;811 K Residue, wt%</td>
<td>68.1</td>
<td>67.6</td>
<td>77.9</td>
<td>-</td>
<td>68.8</td>
</tr>
<tr>
<td>Elemental analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C, wt%</td>
<td>84.7</td>
<td>83.3</td>
<td>85.0</td>
<td>85.2</td>
<td>83.2</td>
</tr>
<tr>
<td>H, wt%</td>
<td>11.2</td>
<td>10.8</td>
<td>11.4</td>
<td>11.7</td>
<td>9.8</td>
</tr>
<tr>
<td>N, wt%</td>
<td>1.3</td>
<td>0.7</td>
<td>1.3</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>S, wt%</td>
<td>0.5</td>
<td>0.6</td>
<td>0.4</td>
<td>0.6</td>
<td>4.9</td>
</tr>
<tr>
<td>Atomic H/C Ratio</td>
<td>1.60</td>
<td>1.56</td>
<td>1.61</td>
<td>1.65</td>
<td>1.42</td>
</tr>
<tr>
<td>MW, g/mol</td>
<td>702.0</td>
<td>1042.0</td>
<td>-</td>
<td>668.0</td>
<td>744.0</td>
</tr>
<tr>
<td>Gradient elution chromatography</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturates, wt%</td>
<td>9.5</td>
<td>13.2</td>
<td>15.3</td>
<td>10.0</td>
<td>13.4</td>
</tr>
<tr>
<td>MNA/DNA Oils, wt%</td>
<td>10.2</td>
<td>21.0</td>
<td>8.5</td>
<td>11.4</td>
<td>21.1</td>
</tr>
<tr>
<td>PNA Oils, wt%</td>
<td>11.4</td>
<td>5.9</td>
<td>11.9</td>
<td>4.4</td>
<td>9.1</td>
</tr>
<tr>
<td>Soft Resins, wt%</td>
<td>13.9</td>
<td>13.9</td>
<td>16.7</td>
<td>18.4</td>
<td>9.5</td>
</tr>
<tr>
<td>Hard Resins, wt%</td>
<td>1.1</td>
<td>5.6</td>
<td>2.6</td>
<td>1.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Polar Resins, wt%</td>
<td>2.0</td>
<td>1.7</td>
<td>2.7</td>
<td>3.7</td>
<td>3.8</td>
</tr>
<tr>
<td>Asphaltenes, wt%</td>
<td>31.3</td>
<td>29.8</td>
<td>31.2</td>
<td>39.9</td>
<td>33.0</td>
</tr>
<tr>
<td>Noneluted Asphaltenes, wt%</td>
<td>20.6</td>
<td>8.9</td>
<td>11.1</td>
<td>11.1</td>
<td>6.5</td>
</tr>
</tbody>
</table>

a  Measured at 373 K
b  Measured at 338 K
c  Measured at 347 K
d  Measured at 493 K
e  Measured at 363 K
• olefin processes (non-tubular, tubular)

The various heavy oil and residuum upgrading process schemes are summarized in Figure 2.2.

Catalytic hydroprocessing includes hydrotreating and hydrocracking. Hydrotreating includes hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetallation (HDM). Co/Mo catalysts are recommended where HDS is the primary objective because Co exhibits better selectivity for desulfurization than Ni and Ni/Mo catalysts are more suitable in applications where mild hydrogenation or nitrogen removal is required because Ni exhibits better hydrogenation than Co.

Since the initial developments for the production of low-sulfur fuel oil (LSFO) in the late 1960s catalytic residuum hydroprocessing has played an important role in producing low-sulfur fuel oil in accordance with environmental regulations. It should be noted that these restrictions have become stricter since the 1970s. Quann et al. [27] reported that the capacity of residuum hydrotreating is increasing with the total free world capacity has increased from approximately 200,000 barrels per stream day (BPSD) in 1970 to 1,200,000 BPSD in 1986 [27].

In residuum desulfurization processes the distillate and naphtha yields are low even though conversion of gas-oils to light products occurs. Recently high severity residuum hydrotreater operations have been used to attain 80 to 95% sulfur conversion [28-30]. Thus, the current trend in catalytic residuum hydrotreating is to use an HDM catalyst at severe operating conditions rather than using an HDS catalyst at moderate conditions [1].
Figure 2.2

Summary of Heavy Oil Upgrading Processes
HYDROPROCESSES

Catalytic Hydroprocesses

Hydrotreating
- Chevron RDS or VRDS
- Exxon RESIDfining
- Gulf RDS
- Shell RDS
- UNOCAL Unicracking/RDS
- UOP RCD/BOC Unibon

Hydrocracking
- LC-Fining
- CANMET
- HR Dynacracking
- H-Oil
- LC-Fining
- Exxon M-Coke
- UOP Aurabon

Non-Catalytic Hydroprocesses

Donor Solvent Processes
- CANMET
- VEBA
- Lurgi

Hydropyrolysis
- Delayed Coking
- Fluid Coking
- Flexicoking
- Eureka
- ART

Thermal Conversion

Visbreaking
- University of Utah
- University of Erlangen
- Dynacracking (HRI)

Non-HYDROPROCESSES

Catalytic Conversion

HOC (Heavy Oil Cracking)
- RCC (Resid Catalytic Cracking)
- Total RC (Resid Fluid Catalytic Cracking)

Non-tubular
- Solvahl-Asvahl SDA
- LEDA (Low-Energy Deasphalting)
- Solvent Decarbonizing
- ROSE (Residuum Oil Supercritical Extraction)
- Demex
- RSR (Residue Solvent Refining)

Tubular
- Sand Cracker
- Fluidized Coke/Flow Cracking
- Ube Process
- KK Process (Coke-Heat-Carrier Process)
- ACR (Advanced Cracking Reactor)
- Partial Combustion Cracking
- TRC (Thermal Regenerative Cracking)
- COSMOS (Cracking Oil by Steam and Molten Salts)
- Pacca

OTHER PROCESSES

Combustion
- SGP (Shell Gasification Process)
- Texaco Process

Partial Oxidation
- THR-R (Total Hydrocarbon Reforming)

Steam Reforming
- Non-tubular

Solvent Deasphalting
- Tubular

Olefin Processes
- Two-Stage Heavy Oil Cracking
Typical residuum hydrotreating operating conditions are a temperature range of 623-713 K (350-440°C), a pressure range of 5.2-20.7 MPa (750-3000 psi) and a space velocity range of 0.1-2 h⁻¹ LHSV. Hydrogen consumptions range from 550 to 2500 [scf/bbl] [27]. Beaton and Bertolacini [1] reported operating temperatures between 672-728 K (750-850°F, about 400-450°C), hydrogen partial pressures from 9.7 to 17.2 MPa (1400-2500 psi), and liquid hourly space velocities ranging from 0.1 to 0.5 h⁻¹ for residuum hydrotreating.

Chevron RDS or vacuum residuum desulfurization (VRDS) [22], Exxon RESIDfining [31], Gulf RDS [32], Shell RDS [33], UNOCAL Unicracking/RDS [34], and UOP reduced crude desulfurization/black oil conversion (RCD/BOC) Unibon [35] are the current commercial residuum hydrotreating processes. The combination of two processes exhibits advantages over single processes. The combination of residuum hydrotreating-fluidized catalytic cracking (FCC) [36] and residuum hydrotreating-delayed coking [37] are typical examples. The residuum hydroprocessing-coking combination produces higher yields of upgraded liquid products which are lower in heteroatoms and higher in hydrogen-to-carbon ratio with less coke formation than the coking process alone. This makes these products superior feedstocks to the downstream process. In this process the effective catalyst lifetime and tolerance is more important than high activity of the catalyst. The produced coke is of a higher quality and can be used in the production of high-value anode-grade coke.

In residuum hydroprocessing the boiling range reduction is accompanied by heteroatom removal. The main difference between residuum hydrotreating and hydrocracking processes is the boiling range reduction. In the residuum hydrotreating, heteroatom removal occurs to improve the quality of petroleum liquid and boiling range conversions below 25% are achieved whereas in residuum hydrocracking boiling range reduction is commonly about 50%. 
Hydrocracking processes differ from catalytic cracking in a variety of feedstocks relative to catalytic cracking and in its incorporation of a metal sulfide catalyst and hydrogen at a total pressure of 5.5-17.2 MPa (800-2500 psig). Commercial heavy oil hydrocracking processes include LC-Fining [38], H-Oil [39], VEBA-Combi [40], CANMET [41], UOP Aurabon [42], HFC [43], M-Coke [44], and Chiyoda asphaltenic bottom cracking (ABC) [45]. Operating variable ranges include temperatures of 703-743 K (430-470°C), pressures of 7.6-20.7 MPa (1100-3000 psig), LHSV’s of 0.5-1.0 h⁻¹ and hydrogen consumptions of 500-1500 [scf/bbl] [25].

**Noncatalytic Hydroprocessing**

Noncatalytic hydroprocessing includes hydrovisbreaking, donor-solvent processes, and hydropyrolysis.

The basic concept in hydrovisbreaking is to increase the solubility of hydrogen in oil with temperature and pressure. Hydrovisbreaking gives better conversions and paraffin/olefin ratios than visbreaking and operates in the same temperature-time range as hydrocracking.

Donor-solvent processes involve the dehydrogenation of the feed with solvent and the formation of hydrogen radicals which are then available for cracking reactions. The licensors for this process include Lurgi (Donor Solvent Visbreaking (DSV)) [46], Gulf (Chevron) (Donor Refined Bitumen (DRB)) [47], and Exxon (Hydrogen Donor Visbreaking (HDDV)) [48].

Hydropyrolysis upgrades the feedstock by hydrogen addition with little or no coke formation. Hydropyrolysis operates at temperatures of 773-973 K (500-700°C), pressures of 4.1-12.4 MPa (600-1800 psig), and retention times below 1 minute. This hydropyrolysis process has been used at the University of Erlangen [49] and HRI (Dynacracking) [50] to upgrade petroleum residuum.
Most of these hydroprocessing processes are not still available at the commercial scale.

**Thermal and Nonhydrogen Processes**

The carbon/hydrogen ratio of petroleum feed can be upgraded by thermal processes through the formation of coke or unsaturated/aromatic hydrocarbons (hydrogen disproportionation). Thermal processes have the advantage of flexibility of feed selection over catalytic processes which require higher quality feeds due to the catalytic deactivation. The disadvantages of the thermal processes are related to the production of significant amounts of unsalable products. Thermal conversion processes for heavy oil upgrading including Visbreaking [51], Delayed Coking [52], Fluid Coking [53], Flexicoking [54], and Eureka [55] are in commercial operation. The catalytic nonhydrogen processes, heavy oil cracking (HOC) [56], residual catalytic cracking (RCC) [57], and total residuum cracking (RC) [58] are in commercial operation.

**Other Processes**

Other processes include combustion, partial oxidation, steam reforming, and solvent deasphalting. Heavy oils are frequently used as refinery fuels. Noncatalytic partial oxidation process is used in generation of synthesis gas by producing an additional hydrogen source [59]. One of the typical steam reforming process for producing synthesis gas from heavy oil is THR-R (Total Hydrocarbon Reforming) developed by Toyo Engineering Co. [60]. ASHVAL's Solvahl-asvahl solvent deasphalting (SDA) [61], Foster Wheeler's low-energy deasphalting (LEDA) [62], Kellogg's Solvent Deasphalting [63], Kerr-McGee's residuum oil supercritical extraction (ROSE) [64], UOP's Demex [65], Lummus
Crest's residue solvent refining (RSR) [66] are the representative processes for solvent deasphalting.

**Reactors in Residuum Hydroprocessing**

The most common reactor designs for residuum hydroprocessing include fixed beds, ebulliated or expanded beds and slurry beds, and moving-bed reactors. The types of reactors used in resid hydroprocessing are tabulated in Table 2.3.

**Hydroprocessing Catalysts**

Hydrotreating catalysts were developed primarily for processing petroleum feedstocks and typically contain 1 to 8 wt% and 3 to 20 wt% of a group VIII and VIB metal oxides on a support having a high-surface-area such as alumina. The metal oxides have been used as the active phase either in combination or alone in either supported or unsupported forms. In particular Co-Mo, Ni-Mo, Ni-Co-Mo and Ni-W have focused wide applications. The individual catalyst properties such as pore volume, pore size distribution, metal loading atomic ratio and surface area play important roles in the catalyst's activity, deactivation and stabilization [67].

The Co-Mo supported on gamma alumina catalyst has been widely used in hydrodesulfurization of petroleum liquids due to its activity and selectivity. Richardson [68] reported that Co-Mo catalyst on alumina is superior in HDS and that the activity varies with the concentration of metals with an apparent optimum Co-Mo weight ratio of 1/5. Conventional HDS catalysts contain 3% CoO, 14% MoO₃ metal oxides and is supported on gamma alumina which has surface areas as high as 200-300 m²/g and small pore diameters in the range 80-120 Å.
Table 2.3

Types of Reactors in Residuum Hydroprocessing [25,69]

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Bed</td>
<td>Chevron RDS and VRDS [22]</td>
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<td>Exxon RESIDfining [31]</td>
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<td>UNOCAL Unicracking/RDS [34]</td>
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<td>UOP RCD/BOC Unibon [35]</td>
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<td>Ebulliated Bed</td>
<td>H-Oil [39]</td>
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<td>Expanded Bed</td>
<td>C-E Lummus/Cities Service LC-Fining</td>
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<td>licensed by AMOCO [38]</td>
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<td>Slurry Reactor</td>
<td>Canadian DOE CANMET [41]</td>
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<td>UOP Aurabon [42]</td>
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<td>Moving Bed or Bunker Reactor</td>
<td>Shell RDS [25]</td>
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The Ni-Mo catalyst is well known for its hydrogenation activity and has been used in hydrodenitrogenation of petroleum feedstocks. Phosphorous has been used as a promoter in hydrotreating process.

Hydrodemetallation catalysts typically contain larger pore diameters (180-250 Å in meso pore range) and lower surface areas of 150 m²/g than HDS catalysts. The HDM catalysts have lower metal contents than HDS catalysts with the intention of demetallation and maintaining catalyst activity [70].

Noncylindrical extrudates such as quadralobes exhibit better diffusion characteristics, improved activities and lower pressure drops across the catalyst bed than cylindrical, non-shaped catalysts [71].

Precipitation and impregnation are two typical methods for preparing hydrotreating catalysts [72]. In precipitation, solutions of the desired components are mixed with a precipitation agent and dried in air at 339-478 K. They are then extruded or pelleted, calcined and activated. The precipitation agent is used to promote the formation of either a coprecipitate or a gel, depending upon conditions. In impregnation, solutions of the desired constituents are in contact with either a dried porous support or a wet precipitate or gel and the excess solution is removed. The catalyst is subsequently dried and calcined. The calcination temperature, generally in the range 589-1033 K, may affect the structure and activity of the catalyst [68]. Pellet size and pore structure of the support are also important [73].

**Particle Size and Reaction Rate**

Catalyst size and shape are important considerations in optimizing catalyst performance considering that HDM reactions are typically diffusion limited. For large particle size residuum hydrotreating catalysts, the reaction rates are controlled by intraparticle diffusion. The factor controlling intraparticle
diffusion is the rate of heteroatomic species diffusion since the rate of hydrogen in the oil is known to be greater than that of heteroatoms in the catalyst [74]. Arey et al. [75] observed no effect of increasing the bulk-liquid flow rates on desulfurization rates and reported that diffusion of hydrogen through the liquid phase was not limiting. They also found that desulfurization was markedly improved by reducing particle size and they attributed it to the increased utilization of the interior region of the catalyst.

Kato et al. [76] investigated the relation between catalyst size and the rate constant for desulfurization of Khafji atmospheric residuum. When the volume of the catalyst bed was constant, the rate constant, $k$, increased in proportion to $1/d$ for values of $1/d$ up to approximately 1 where $d$ is the average diameter of the catalyst particle. When $1/d$ exceeded 1, the influence of catalyst particle size significantly diminished.

Shah and Paraskos [77] observed no difference in desulfurization rate for catalysts having particle sizes of 0.5 to 0.6 mm and 0.8 mm when 50% Kuwait atmospheric reduced crude oil was hydrotreated in a down-flow fixed bed reactor. Particles smaller than 0.8 mm (1/32 in.) are typically not used in commercial fixed-bed reactors because of excessive pressure drop or the potential for plugging of the catalyst bed by particulates found in residuum feeds [78]. Therefore the optimum catalyst should compromise physical properties such as surface area, pore radius, pore volume with feedstock characteristics [79].

**Surface Area, Pore Structure and Pore Size Distribution**

The catalyst surface area, pore volume, pore size distribution and the ratio of molecular size to pore size are considered to be significant factors
influencing hydrotreating. These properties influence the diffusivity of the liquid feed whereas reactivities of metal compounds influence the reaction kinetics.

Riley [80] reported a general classification of catalysts according to median pore diameters: 1) small pore catalysts have median pore diameters less than 100 Å; 2) intermediate pore catalysts have median pore diameters between 100-150 Å; and 3) large pore catalysts have median pore diameters above 150 Å. Physical properties of the catalysts reflect the properties of the support. Bulk densities range from 0.4 to 0.7 g/ml, whereas pore volumes vary from 0.4 to 1.5 ml/g and surface areas typically range from 50 to 300 m²/g. The average pore diameters of hydrotreating catalysts range from 40 to 400 Å but catalysts with bimodal pore structures may contain some pores as large as 1000 to 10,000 Å [27].

Residuum Hydroprocessing Catalysts

Since residuum typically contains a significant amount of high molecular weight resins and asphaltenes as well as nitrogen, sulfur, and metal containing species, the catalyst used to hydrotreat residuum must have optimum physical properties to permit the activity to be maintained over a long period even when excessive amounts of coke and metals deposit. In other words, the physical properties should be appropriate to the reaction environment in addition to the activity, selectivity, and stability required of the catalyst in the residuum hydrotreating catalyst [67].

Richardson and Alley [81] reported that when hydroprocessing a residuum containing 12% of its sulfur in the asphaltene fraction, the refractoriness of the feed was determined by the asphaltenic sulfur for the sulfur conversion levels above 90%. This refractoriness was attributed to the small pores of the catalyst. The refractoriness for desulfurization at lower conversion
levels was attributed to sterical hindrance involving aromatic sulfur compounds such as substituted thiophene, benzothiophenes, and dibenzothiophenes. Schuit and Gates [82] reported the effectiveness factor of two cylindrical catalysts (1.6 mm diameter) which had mean pore diameters of 78 Å and 103 Å in their study of hydrodesulfurization of a Middle East residuum. The effectiveness factor of the former was estimated to be 0.4 and that of the latter to be 0.8.

Inoguchi et al. [83] investigated the influence of catalyst physical properties on desulfurization of Khafji atmospheric residuum and have shown that pores having diameters less than 40 Å did not affect activity while pores having diameters of 100 Å or larger did affect the activity. Desulfurization conversions of 60 to 70% were obtained with catalysts having pore sizes of 100 to 150 Å.

**Hydrodemetallation Catalysts**

In residuum hydrotreating processes, catalysts which have a tendency for low coke formation and high metal deposition tolerance are required. When the metal species permeate the catalyst pore structure, maximum metals tolerance can be obtained even though the metal deposition would still poison the active site of the catalyst. However, when metal penetration is shallow due to fast reaction or controlled pore size, the pore mouth would soon be plugged by metal deposition leaving active sites unused in the inner portions of the catalyst [84].

When the run-length is limited by the metals capacity of catalyst, the HDM catalyst which allows maximum metal-bearing molecule penetration and uniform metal deposition is preferred. However, when the run-length is not controlled by catalyst metal capacity, catalysts with high activity for HDM and moderate activity for HDS and Ramsbottom carbon conversion are desirable. High-activity HDM
catalysts which also have high HDS and Ramsbottom carbon removal activities are usually used for the feeds which contains low-metals [85]. Catalyst surface activity may be manipulated to alter the ratio of HDM activity to metal compound diffusivity with a predictable impact on optimum pore size. The increase of Ni and V penetration into the HDM catalyst can be accomplished by lowering the intrinsic surface activity. This is done by varying the quantity, chemical composition, or distribution of active catalytic metals.

Plumail et al. [86] determined that the optimum pore diameter for demetallation of Boscan crude on a unimodal pore size catalyst was 150 to 200 Å. Hydrodesulfurization activity was highest on catalysts with pores of 100 Å, suggesting a difference in molecular size between the sulfur- and vanadium-bearing molecules. Riley [15] reported that pore structure controlled Ni and V removal in hydrotreating a Safaniya atmospheric residuum. Metals removal activity increased with increasing pore size from 100 to 150 Å in narrow-pore-size distribution CoMo/Al₂O₃ catalysts.

Catalysts prepared by Hardin et al. [87] contained two pore regimes: large interparticle pores corresponding to intergranular voids with diameters of 10,000 Å and larger and intragranular pores of diameter 500 Å and smaller. Catalysts characterized by median pore diameters of 200 Å exhibited maximum activity for Ni and V removal from Athabasca bitumen. This observation was explained on the basis of catalyst surface area. As pore size increases, the catalyst surface area decreases and as does the number of active sites. Decreasing the pore size increases the surface area but also increases the diffusional resistance to the sites. Bimodal catalysts having micropore diameters ranging from 100 to 320 Å and macropores of 1000 Å and greater also exhibit maxima in hydrodevanadation (HDV) activity in the range 150 to 200 Å average pore diameter, similar to the unimodal catalyst. HDV activity over bimodal catalysts is
markedly enhanced, up to 50%, relative to the unimodal catalysts. The introduction of macropores increases asphaltene accessibility to the micropores of the catalyst, enabling conversion by depolymerization and cracking and by demetallation.

The pore structure of the catalyst is the controlling parameter for metals removal for large pore size catalysts. Vanadium removal is somewhat easier to accomplish than nickel removal which implies that either the vanadium is in a smaller molecular species than the nickel or the nickel is more tightly held by the molecule [27]. Apparently the selectivity for vanadium removal with small pore catalysts is independent of pore size [80]. Howell et al. [85] reported that Ni compounds in both Arabian Heavy and Maya feedstocks penetrated more deeply and deposit more uniformly than V counterparts.

The selection of the optimum HDM catalyst should be determined by residuum feed properties, process operating conditions, and product quality requirements [88]. A compensation effect is operative between the increase in activity due to an increase in surface area and the decrease due to diffusional resistance; hence, the existence of an optimum pore size.

**Bench Scale Hydrotreating Reactor**

**Effect of Liquid Holdup and Catalyst Wetting**

Satterfield [89] reported that the liquid holdup is a measure of the effectiveness of contact between liquid and solid catalyst and can be defined as the ratio of the volume of liquid present in the reactor to the volume of the empty reactor. The liquid present in the catalysts pores accounts for the internal holdup while that present outside the catalyst pellets is responsible for the external holdup.
Satterfield and Way [90] proposed that the external liquid holdup can be correlated in terms of the superficial velocity and viscosity of the fluid. According to Koros [91] complete catalyst wetting cannot be attained in a pilot-plant scale reactor whereas it may be attained in a commercial reactor.

Schwartz et al. [92] used tracers to make liquid holdup measurements in trickle bed reactors. The observed liquid holdups were 45-60% and 25-40% with porous and nonporous packing; respectively, for liquid fluxes in the range 0.3 to 5 kg/m² s. The general trend observed was an increase in liquid holdup with increasing liquid flow rate. Mears [93] proposed a model based on incomplete catalyst wetting and suggested it was a better criterion for assessing the effects of dynamic conditions in the reactor. In narrow diameter laboratory reactor, as well as in large commercial units, the liquid trends to migrate towards the wall resulting in partial wetting of the catalyst bed. Satterfield and Ozel [94] provided visual evidence for non-uniform wetting of the catalyst particles in packed beds. Also, diluting the pilot-scale catalyst bed with fine inert material such as silicon carbide (SiC) had a minimal effect on reducing axial dispersion and channeling, and did not improve the catalyst wetting at normal operating conditions with a bitumen-derived coker gas-oil [95].

Yui and co-workers [95,96] studied the kinetics of HDS, HDN and mild hydrocracking (MHC) in pilot-scale trickle-bed reactors. Yui et al. [96] reported that plug-flow was not attained with catalyst dilution and proposed that the plug-flow model used for reaction kinetics should be modified by including a power term for space velocity, \( \text{WHSV}^\alpha \), to compensate for nonplug-flow. Yui et al. [96] also proposed that the effect of hydrogen partial pressure should be represented by a power-rate law term, \( p_{\text{H}_2}^\beta \).

The empirical power, \( \alpha \), has been determined in pilot-scale reactors [95,96] to be between 0.3 to 1.0. Various values of alpha have been reported in
the literature for undiluted trickle-bed reactors; 0.6 [97], 0.68 [93], 0.5 to 0.9 [98]. Yui et al. [99] also reported the power term for space velocity to be 1.0 for HDS and HDN and 0.5 for mild hydrocracking (MHC) for bitumen-derived coker and hydrocracker heavy gas-oils.

Montagna and Shah [79] reported that for catalyst particles of 20/30 mesh size the liquid holdup or catalyst wetting effects are negligible in explaining the hydrotreating kinetics for 56% reduced crude. Henry and Gilbert [97] reported that at constant process operating conditions the increased utilization of catalyst achieved by decreasing the catalyst particle size can be attributed to an increase in liquid holdup.

**Axial and Radial Dispersion and Backmixing in Packed Beds**

Axial liquid dispersion was investigated by Scott [100] who reported that a height to column diameter ratio (H/D) of 25 to 1 was necessary to minimize axial dispersion problems in packed towers.

The model widely used for explaining the axial mixing in fixed beds is the one parameter piston diffusion (PD) model which superimposed plug-flow with a "Fick's diffusion" type of process [101]. The Peclet number (Pe) is the parameter by which the residence distribution of the liquid is described:

\[
P_e = \frac{D_p \cdot u}{E}
\]  

(2-1)

where, \(D_p\) is the particle diameter, \(u\) is the linear liquid velocity in the interstices and \(E\) is the dispersion coefficient. When this parameter is based on the particle diameter, it is called the Bodenstein number (Bo):
\begin{align*}
Bo &= \frac{d_s \cdot u}{D_a} \quad (2-2)
\end{align*}

where, \( d_s \) is the spherical catalyst particle diameter and \( D_a \) is the axial eddy diffusivity [102]. Many investigators have shown that the Bodenstein number can be correlated by the Reynolds number (Re):

\begin{align*}
Re &= \frac{D_p \cdot u \cdot \rho}{\mu} \quad (2-3)
\end{align*}

where, \( \rho \) is the density, and \( \mu \) is the viscosity of the liquid [103-105]. In most instances the investigations have taken place in the Reynolds number range from 1 to 100 whereas small-scale trickle-flow reactor experiments typically operate at in the Reynolds number range from 0.001 to 0.1 [102].

Satterfield [106] states that liquid and gas radial dispersion attains a constant value above a particle Reynolds Number of about 100 and axial dispersion attains a constant value above a Reynolds Number of about 10. Small-scale laboratory experiments normally fall well below the critical Reynolds Number of 100 for radial dispersion unless special provisions are taken to ensure that the criterion is met.

Schwartz and Roberts [107] indicate that radial distribution problems may exist in trickle-flow reactors. Although they define the concept as "contacting efficiency" they did not present a method for prediction of their contacting efficiency but suggest an experimental program to determine the efficiency and develop a correlation.

The deviation from plug-flow as a function of Reynolds number has been quantified by Mears in terms of a minimum value for Peclet number [93,108].
The following criterion was suggested to determine the minimum \( \frac{h}{d_p} \) ratio required to establish the reactor length within 5% of that needed for plug-flow:

\[
\frac{h}{d_p} > \frac{20n}{Bo} \ln \frac{C_o}{C_f}
\]

where \( h \) is the catalyst bed length, \( d_p \) is the catalyst particle diameter, \( n \) is the reaction order and \( C_o \) and \( C_f \) are the inlet and outlet reactant concentrations. Mears applied the criterion to bench scale hydrotreating units processing a straight run gas-oil feed at a temperature of 644 K (700°F), a pressure of 10.3 MPa (1500 psia) and a LHSV of 2.0 h\(^{-1}\). A minimum \( \frac{h}{d_p} \) of 350 was calculated.

**Comparisons of Upflow with Downflow Operation**

There may be a deviation in the test data of the pilot-plant relative to the results of commercial operation even when they are obtained under same conditions of temperature and space velocity. This is due to the low superficial mass velocities in a test unit which result in poor liquid-solid contact along with low rate constants which vary with the catalyst bed length and liquid velocity [93,97]. Satterfield [89] showed that under commercial conditions the effectiveness of catalyst wetting is ideal only if a sufficiently high superficial liquid mass velocity is used. Although criteria on wetting and back-mixing for bench-scale catalyst testing units were met [71,109] in diluted downflow experiments with shaped catalysts it was reported that downflow experiments in bench-scale gave poor reproducibility and the method of catalyst packing changed reaction orders. This indicates ineffective catalyst wetting and liquid maldistribution [110]. Catalyst testing in the upflow mode can be used to overcome these problems in some instances [79,89].
A comparison of a bench-scale reactor operated in the upflow versus downflow mode for desulfurization of a heavy coker gas-oil by Takematsu and Parsons [111] indicated that the upflow mode gave superior performance and more consistent kinetics for desulfurization. This was attributed to the fact that upflow maximized the residence time of the heavy liquid fractions.

De Wind et al. [110] reported that close to 100% effective wetting of catalyst with liquid and good liquid distribution were obtained at low mass velocities using the upflow mode and concluded that upflow testing does improve catalyst wetting. The small scale reactor data and catalyst wetting efficiency were comparable to commercial downflow hydrotreaters. Thus, they recommend the upflow mode operation in bench-scale evaluation of hydrotreating catalysts in small units and at low space velocities. Testing in the upflow mode indicated that catalyst wetting efficiency was independent of space velocity and that at the conversions obtained in the upflow mode, dilution has no beneficial effect on catalyst utilization.

The upflow mode may also provide other benefits. If a catalyst gradually becomes deactivated by the deposition of polymeric or heavy materials, the upflow reactor may maintain activity longer by more effectively washing off these deposits. Heat transfer between liquid and solid may also be more effective in upflow than in downflow operation. This is of particular importance if reaction is rapid and highly exothermic. If reactants are present in both the gas and liquid phases over a range of operating conditions in which pores of the catalyst pellets are filled with liquid, an upflow reactor would be expected to exhibit a lower reaction rate than a partially-wetted trickle bed or one in which the solid catalyst is deliberately designed so as not to be wetted by the liquid phase. Some upflow reactor designs may lead to fluidization of the catalyst unless the catalysts are held in place by mechanical means [89].
Trickle-bed operation has several advantages. Pressure drop through the bed is less which reduces pumping costs and in the downflow operations the catalyst bed remains in place.

**Chemistry and Reaction Mechanisms of Hydroprocessing**

The presence of sulfur and nitrogen species in residuum reduces the quality of the refined products and poses environmental concerns due to the formation of SO\textsubscript{2} and NO\textsubscript{x} emissions during combustion. The heteroatoms (S, N) also act as catalyst poisons, causing rapid deactivation in catalytic conversion steps such as catalytic cracking and reforming [112]. Typical organosulfur compounds, organonitrogen compounds (both basic and nonbasic) and porphyrin type nickel analogs are shown in Figure 2.3.

**Hydrodenitrogenation**

The nitrogen in petroleum residuum, bitumens, coal-derived liquid, and shale oils can be divided into two types; heterocyclic aromatic compound and nonheterocyclic organonitrogen compounds such as aliphatic amines and nitriles. The former are dominant in heavy oils and are more difficult to denitrogenate than the latter and thus play a significant role in hydrodenitrogenation (HDN) processes involving heavy feeds [113].

Nitrogen is more difficult to remove than other heteroatoms such as sulfur or oxygen because of wider variations in adsorptivity and reactivity [114]. These variations are attributed to the two types of nitrogen species in petroleum: pyridinic and pyrrolic. These two classes of nitrogen heterocyclics have different electronic configurations. The pyridinic ring containing nitrogen compounds (six-membered) exhibit a strong basic nature since the unshared pair of electrons
Figure 2.3

Typical Heteroatom Species Present in Petroleum.
ORGANOSULFUR COMPOUNDS

- Thiophene
- Benzo thiophene
- Dibenzothiophene
- Thianthrene
- Benzonaphtho thiophene

ORGANONITROGEN COMPOUNDS

- Basic Compounds [Six-Membered-Compounds]
  - Pyridine
  - Piperidine
  - Quinoline
  - Tetrahydroquino line
  - Acridine
  - Benzoquino line

- Non-Basic Compounds [Five-Membered-Compounds]
  - Pyrrole
  - Indole
  - Indoline
  - Carbazole
  - Aniline

NICKEL ANALOGS OF MODEL METALLOPORPHYRRINS

- Ni-octaethylporphyrin (Ni-OEP)
- Ni-etio porphyrin (Ni-EP)
- Ni-tetraphenylporphyrin (Ni-TPP)
- Ni-tetra(3-methylphenyl)porphyrin (Ni-T3MPP)
associated with the nitrogen are not involved in the $\pi$ cloud and therefore available to share with acids. The basic nitrogen can therefore accept surface protons from the acidic site on the catalyst (Brönsted acidity) or donate unpaired electrons to electron-deficient surface sites (Lewis acidity). However, the pyrrolic ring type nitrogen heteroaromatics (five-membered) exhibit nonbasic characteristics since the extra pair of electrons on nitrogen is involved in the $\pi$ cloud of the ring so that they can not interact with acids [115,116].

Typical catalysts used to accomplish HDN include Ni-Mo/Al$_2$O$_3$. The reaction chemistry for heterocyclic organonitrogen species removal indicates that the nitrogen atom containing ring must be hydrogenated before the hydrogenolysis of the carbon-nitrogen bond [113]. This is because hydrogenation of the heteroring facilitates carbon-nitrogen bond scission by reducing the bond energy of the carbon-nitrogen bond [116]. Large HDN rates can be obtained by increasing the equilibrium concentrations of saturated heteroring compounds with high hydrogen partial pressure [117].

The reactions in which nitrogen is removed from aniline derivatives are important in the denitrogenation networks because the pathways involving these reactions are those requiring the lowest hydrogen consumption. Investigations of the HDN of anilines indicate that both direct hydrogenolysis and HDN via hydrogenated intermediates may occur [118,119]. The hydrogen consumption depends strongly on the extent of hydrogenation of the aromatic rings.

Generally kinetics govern the removal of nitrogen rather than thermodynamics at reaction conditions currently used for commercial hydrotreating. Deep removal of nitrogen from moderately-refractory feedstocks can generally be achieved when a sufficiently long reaction time is used [114]. The reaction pathways for HDN of pyridine [120] and quinoline [119] are shown in Figure 2.4.
Figure 2.4

Possible Reaction Pathways for HDN of Pyridine [120] and Quinoline [119]
Reaction Pathways for Pyridine HDN Proposed by Hanlon [120]

\[
\text{Pyridine} \rightarrow \text{N}^+ \text{H} \quad + \quad \text{NH}_2 \quad \rightarrow \quad \text{NH}_3
\]

Slow

\[
\text{N}^+ \text{H} \quad + \quad \text{NH}_2 \quad \rightarrow \quad \text{NH}_3
\]

Reaction Network for Quinoline HDN Proposed by Satterfield and Yang [119]

\[
\text{Quinoline} \leftrightarrow \text{Quinolinium} \rightarrow \text{Quinoline} \quad + \quad \text{NH}_3
\]

\[
\text{Quinolinium} \rightarrow \text{Quinoline} \quad + \quad \text{NH}_3
\]

\[
\text{Quinoline} \rightarrow \text{Quinolinium} \rightarrow \text{Quinoline} \quad + \quad \text{NH}_3
\]

\[
\text{Quinoline} \rightarrow \text{Quinolinium} \rightarrow \text{Quinoline} \quad + \quad \text{NH}_3
\]

\[
\text{Quinoline} \rightarrow \text{Quinolinium} \rightarrow \text{Quinoline} \quad + \quad \text{NH}_3
\]

\[
\text{Quinoline} \rightarrow \text{Quinolinium} \rightarrow \text{Quinoline} \quad + \quad \text{NH}_3
\]
Hydrodesulfurization

Hydrodesulfurization (HDS) has been used not only for removing sulfur from naphtha reformer feedstocks but also for reducing the sulfur contents of heavy oils used as fuel refinery feedstocks and as power plant feedstocks.

Gates et al. [112] reported on the chemistry of thiophenic compound conversion since these are the least reactive organosulfur compounds in petroleum and other fossil fuels. Beaton and Bertolacini [1] showed that like the metals, about 73% of the total sulfur is distributed in the resin fraction of a typical vacuum residuum. Bar Vise and Whitehead [121] reported that sulfur-containing compounds are more volatile than metal-bearing compounds. More than 20% of the sulfur appears in 773 K minus fraction, with less than 50% of the sulfur occurring in the 923 K plus fraction.

Unlike nitrogen removal which requires the heteroatom ring hydrogenation before the hydrogenolysis of the carbon-nitrogen bond, sulfur removal occurs either with or without hydrogenation of the heterocyclic ring. Also, thermodynamics would govern the HDS pathways involving prior hydrogenation of the ring since hydrogenation of the sulfur-containing rings of organosulfur compounds is equilibrium-limited at practical HDS temperatures [117]. The HDS of organosulfur compounds is exothermic and essentially irreversible under the reaction conditions employed industrially (e.g., 613-698 K (340-425°C) and 5.6-17.2 MPa (55-170 atm)) [122]. Reaction pathways for HDS of thiophene [112], benzothiophene [123] and dibenzothiophene [124] are presented in Figure 2.5.

Hydrodemetallation

Heavy oil feedstocks contain not only heteroatoms but also the trace metals in the form of organometallic compounds [125]. The metals in heavy oils poison the catalyst in hydrotreating processes and the resulting metal deposition
Figure 2.5

Possible Reaction Pathways for HDS of Thiophene [112],
Benzothiophene [123] and Dibenzothiophene [124]
Thiophene reaction pathways suggested by Gates et al. [112]

Reaction network for benzothiophene proposed by Van Parijs et al. [123]

Reaction network for dibenzothiophene proposed by Houalla et al. [124]
ultimately determines the catalysts' useful operating lifetime because the metal contaminants can not be removed as gases \( \text{H}_2\text{S} \) and \( \text{NH}_3 \) as in desulfurization and denitrogenation, respectively. For example, reducing metal content via HDM is essential when heavy oils are fed to the fluid catalytic cracking unit because it would poison the cracking catalyst and erode the furnace linings and turbine blades.

Metals are usually present in the 811 K plus (1000°F*) fraction of the heavy oils whereas sulfur and nitrogen are distributed over the entire boiling range. The abundance of nickel and vanadium compounds in heavy oils have stimulated the interest in residuum hydroprocessing.

**Metal Compounds**

Unlike sulfur and nitrogen compounds in petroleum which are distributed in the aromatic, resin and asphaltene fractions, more than 85% of the nickel and vanadium compounds are found in the resin and asphaltene fractions [126]. Beaton and Bertolacini [1] showed that nickel and vanadium reside primarily in the resin and asphaltene fractions of the residuum fractions.

There are two main types of nickel and vanadium compounds in petroleum feedstocks: one is metal porphyrins and the other is nonporphyrin metal species. The metal porphyrins differs from nonporphyrin metal species in properties such as polarity, molecular weight and structure. The nonporphyrin metals have higher polarities, higher molecular weights and lower volatility than the metal porphyrins. Dean and Whitehead [127] have shown that most Ni and V appeared as nonporphyrins in 923 K plus (650°C*) fraction of Middle East crudes and only 5% of the metals in the asphaltenes are present as metalloporphyrins. This indicated that nonporphyrin metals associate with the highly polar asphaltene fraction. Sugihara et al. [128] also observed that the
nonporphyrin metals are associated with the asphaltene due to high polarity in his study of metal porphyrins in Boscan asphaltenes using gel permeation chromatograph (GPC) and other techniques.

The basic form of porphyrin is called porphrite \( (C_{20}H_{14}N_4) \) which has four pyrrole groups in a closed ring and connected to the \( \alpha \)-carbon by methine-carbon atoms. The metalloporphyrins are also divided into two categories, a deoxophyloerythroetioporphyrin (DPEP) and an etioporphyrin (Etio) series [128-130].

The basic skeleton of nonporphyrin metal compounds has not been well identified. It is reported that they are composed of various forms of metals from inorganic to polar organic compounds [128]. Two main types of nickel and vanadium compounds have been proposed by Yen [129]: one includes arylporphyrins, hydroporphyrins, and porphyrin-degraded products and the other includes tetradeionate-mixed ligands in Ni and V complexes.

**Catalytic Hydrodemetallation**

Hung and Wei [131] reported that total metal removal was less than the overall disappearance of feed porphyrins in their study of hydrodemetallation of porphyrins. This observation was attributed to the production of intermediate (hydrogenated metalloporphyrin termed metallochlorin) during the hydrotreating process.

Agrawal and Wei [74] found that vanadium removal is much faster than the nickel removal in their kinetic study of hydrodemetallation of nickel and vanadium porphyrins. The fast vanadium removal is due to its reactive moieties and concentration at the surface of the catalyst. However, nickel species are distributed more evenly over the catalyst than vanadium and this resulted in lower removal. They also proposed that an initial reversible hydrogenation
would be followed by terminal hydrogenolysis step in hydrodemetallation process.

Galiasso et al. [132] reported that the depolymerization of asphaltene structures followed by transport of metal species to catalytic sites is rate controlling in reactions of porphyrinic and nonporphyrinic molecules during hydrodemetallation of heavy crude oils rather than the intrinsic demetallation chemistry.

Proposed demetallation reaction pathways for Ni-etioporphyrin (a) and Ni-tetra (3-methylphenyl) porphyrin (b) [133] are presented in Figure 2.6.
Possible Reaction Pathways for HDM of Ni-etioporphyrin and Ni-tetra (3-methylphenyl) porphyrin [133].
DEMETALLATION REACTION PATHWAYS [133]

(a) Ni-etioporphyrin

(b) Ni-tetra(3-methylphenyl)porphyrin
CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

Feedstock Preparation

Ore Acquisition

The bitumen prepared for this study was obtained by solvent extraction of the Whiterocks oil sand. The oil sand ore was obtained from the Northeast section of the Fausett quarry on the Whiterocks deposit in the Uinta Basin. The mined oil sand ore was transported in polyethylene lined, 209 liter (55 gallon) drums to the Oil Sand Research Laboratory at the University of Utah. The drums were sealed to minimize oxidative degradation of the bitumen. The ore was crushed and sieved prior to extraction.

Solvent Extraction

Bitumen was separated from the oil sand by toluene extraction. Three 5-liter and five 4-liter Soxhlet extractors were used to extract the bitumen. Whatman cellulose extraction thimbles (90 mm diameter x 200 mm length) were completely filled with 800 to 1,000 g of fresh oil sands. Filter paper covers were placed on top of each thimble to prevent sand from being transferred from the thimbles into the solvent reservoir. Toluene (ACS grade, EM Science) was used as a extracting solvent. Approximately 2,000-2,500 cm³ of toluene was poured into the solvent reservoir until the toluene level was about 2.5 cm above the top of the Glas-Col heating mantle. Four or five boiling chips were placed in the
solvent reservoir to prevent bumping and the outer wall of the thimble was cleaned. Each thimble was then wrapped with sharkskin filter paper to filter fines and the thimble and sharkskin filter paper were placed in an extractor. The assembled extractor containing fresh oil sand was wrapped with aluminum foil and the reboiler temperature controller set point was set to 55% of full scale. The extractor was checked frequently until condensed toluene started to drip from the condenser onto the top of the extraction thimble. Approximately 12 hours were required to complete the extraction. During extraction, water was collected and separated from the toluene in the trap mounted between the extractor and the water cooled condenser to produce a water-free bitumen-toluene solution.

The extent of bitumen extraction was determined by monitoring the color of toluene dripping from the thimble. When the toluene solution was clear it was determined that extraction was complete. The heating mantle switch was turned off and the aluminum foil was removed. The water and toluene were drained from the trap. The sharkskin and thimble cover were dried and placed in an appropriate disposal vessel. The extracted sand in the thimble was dried and stored in the designated receptacle for disposal. These procedures were repeated until the eighth extraction was completed.

After the eighth extraction, the extractor was cooled to room temperature and the toluene-bitumen solution was poured into 5-gallon plastic containers which were sealed and stored for rotary-evaporation and distillation. The extractor was cleaned completely with toluene and the procedure was repeated. Sufficient toluene-bitumen solution was collected to produce 57 liters (15 gallons) of solvent-free bitumen. Approximately five drums of the crushed Whiterocks oil sand ore were extracted during a 4-month period to produce the toluene-bitumen solution. The toluene-bitumen solution was allowed to stand for
3 days to permit mineral fines to settle from the solution before evaporation and recovery of the toluene.

Safety precautions were rigorously followed during the extraction procedure:

- Safety glasses, gloves and laboratory apron were worn to avoid contact with the solvent when handling toluene, toluene-wetted thimbles and sand.
- The handling of thimbles and extracted sand was done in the hood.
- The assembly and disassembly of the extractor were done cautiously due to the fragile nature of the glass extractors.
- The presence of fines in the toluene-bitumen solution was avoided as they might cause bumping of the solution in the reboiler.

**Rotary Evaporation**

Toluene was removed from the toluene-bitumen solutions by rotativeaporation followed by batch distillation. A Büchi EL 131 rotary evaporator with a Büchi 460 water bath was used to remove the solvent. A Precision Scientific vacuum pump (Model S35) was connected to the evaporator to evaporate toluene at sub-atmospheric conditions. This was done to facilitate solvent recovery. The pump operated at 100-150 torr and the evaporator speed and water-bath temperature were 120 rpm and 353 K, respectively. The previous study revealed that about 6-8 wt% toluene still remained in the bitumen after rotary evaporation [18]. This residual toluene was removed by vacuum distillation.
Distillation

A Semi-Cal high temperature distillation apparatus (Series 3650) by Reliance Glass Works, Inc. and a Precision Scientific vacuum pump were used for vacuum distillation. This tilting-funnel fractionating column was filled with Heli-Pak packing (stainless steel wire-coil packing; Podbielniak Inc.). The 12-liter kettle was filled with 8 liters of the toluene-bitumen solution to allow sufficient vapor space for disengagement of liquid. The kettle temperature was monitored by J-type thermocouples and the heating mantle was controlled with three variable transformers. The kettle pressure was monitored with a mercury manometer. The reflux ratios were varied with a solenoid valve timer.

The column and kettle were purged with argon to prevent air oxidation of the bitumen during distillation. The system was evacuated and the kettle heater was activated. It has been reported that bitumen would thermally crack when the kettle temperature reaches 620-650 K (347-377°C) [18]. Two methods have been proposed to avoid cracking the bitumen in the kettle at the termination of the distillation process. The first was to shut down the heating mantle when the kettle temperature reached 595 K (322°C). This method assumed a 25°C temperature overshoot might occur in the kettle. The second method was to stop heating the kettle when the desired reflux temperature was reached. Two assumptions were made to calculate the target reflux temperature at which distillation should be stopped. The first was that the lightest material in the Whiterocks bitumen is C_{11} naphthene which has the same vapor pressure properties as hexylcyclopentane. The second was that the toluene used in the extraction contained impurities like xylene. Therefore, a 50/50 mixture of xylene and hexylcyclopentane was used with the Antoine equation and Raoult’s law to calculate the end point temperature at a specified system pressure. This temperature was considered as the final reflux temperature.
The system pressure during the distillation was held between 60-80 torr which was sufficient to distill the toluene while maintaining the kettle temperature below the bitumen thermal cracking temperature. The reflux ratios were selected based on a compromise between efficient and rapid separation. The initial reflux ratio was 5; it was increased to 10 near the end of the distillation and was 20 at the end point to give a sharp separation. Approximately 15 batch distillations were made to remove the solvent from the bitumen-solvent solution.

The kettle and reflux temperatures and the cumulative amount of the overhead liquid collected were measured during the distillation. The reflux temperature and the reflux ratios versus the volume of liquid distilled are plotted in Figure 3.1.

The concentrated bitumen was analyzed by simulated distillation to determine residual toluene concentration. The overhead product was also examined to determine the amount of light ends distilled overhead. The toluene in the residual bitumen and the light ends in the overhead fraction were less than the detectable limits (< 0.1 wt%) indicating that toluene removal was complete and that the bitumen was characteristic of the reservoir fluid.

The solvent-free bitumen was collected and stored in a 15-gallon drum. Due to the bitumen viscosity, the drum was wrapped with a Brisk Heat Drum Heater (Model DHCH 11) and heated to 373 K when transferring bitumen to the liquid feed burettes. The bitumen was blanketed with nitrogen to prevent air oxidation during storage.
Figure 3.1

Reflux and Kettle Temperatures versus Volume of Liquid Distilled
• Reflux Temperature [K]

○ Kettle Temperature [K]
Experimental Equipment

The hydrotreating reactor system used in this study consisted of four distinct sections; the liquid feed system, the hydrogen feed system, the catalytic reactor and the product recovery and sampling system. The hydrotreater was designed for both upflow and downflow operating modes by placing three-way manifold valves at the reactor inlet and outlet. The hydrogen and liquid feeds were fed to the reactor in the upflow mode in this study. The product gases and liquids were separated in a high pressure vapor-liquid separator. The gases were withdrawn through a back pressure regulating valve (BPRV) and the liquid product was withdrawn through the high pressure separator liquid level control valve (Annin valve). The process flow diagram for the hydrotreating unit and a schematic of the control panel are presented in Figures 3.2 and 3.3, respectively.

Liquid Feed System

Two heat traced Ace Glass, Inc. Instatherm burettes were used as feedstock reservoirs and to meter the bitumen feed rate to the hydrotreating unit. The smaller burette had a capacity of 500 cm$^3$ (110 volts, 2 amps maximum), and was used during mass balances and to set feed rates to the unit. The larger burette had a capacity of 4,000 cm$^3$ (120 volts, 5 amps maximum) and was used as a feed reservoir for overnight, unattended operation. A Model 52 Proportional Controller (Love Controls Co.) was used to control the temperature of the fluids in the burettes.

The specific gravity of the bitumen in the heated burettes was measured at 417 K (144°C) with a Streamline Hydrometer (H-B Instrument Co.; 19-31 °API range). The specific gravity was calculated according to the following equation:
Figure 3.2

Process Flow Diagram of the Hydrotreating Unit
Figure 3.3
Diagram of Hydrotreating Unit Control Panel
Valve #1: Manifold #1 to Manifold #2

Valve #2: Compressor to Manifold #2

Valve #3: Always Closed

Valve #4: Nitrogen to Manifold #1

Valve #5: Hydrogen to Manifold #1

Valve #7: Manifold #2 to BPRV

Valve #6: Manifold #1 to Compressor

Pressure Indicator

Temperature Indicator

Pressure Indicator Channel

Temperature Indicator Channel

#1: Manifold #2 to Mass Flow Controller
#2: Outlet of Compressor
#3: Top of Reactor
#4: Bottom of Reactor
#5: Vapor-Liquid Separator (Inlet of BPRV)
#6: Back Pressure Regulating Valve
#7: Dosing Volume Pressure
#8: Checking Atmosphere

Manifold #2 to Dosing Volume
Dosing Volume to Aim
Pressure
Temperature

Mass Flow Controller

Buret Temperature Controller
Heat Tracing Line Controller
Liquid Level Controller

Top
Middle
Bottom

Furnace Temperature Controller
The API gravity and the specific gravity were 23.3 °API and 0.9144 g/cc, respectively, at 417 K (144°C). A Durcometer U Type proportioning pump (Duriron Company, Inc.) was used to pump the bitumen from the burettes to the reactor at the desired flow rate. A standard digital stroke adjustment, graduated in percent of stroke length, permitted reproducible setting of the stroke. The maximum operating discharge pressure of the pump was 34.3 MPa (5,000 psig) and the minimum flow rate was 20 cm³/h at 13.8 MPa (2,000 psig).

The pump was primed using the valve at the outlet of the pump. Check valves were installed between the pump and the pump outlet manifold to prevent back flow of hydrogen into the liquid feed system. A pressure relief valve was installed at the pump outlet to avoid damage if the heat tracing failed and the transfer lines between the pump and the reactor inlet plugged with bitumen.

**Heat Tracing Lines**

The Whiterocks bitumen has a viscosity of about 10,000 cp at room temperature and about 1,500 cp at 361 K (190°F) [18]. Liquid transfer lines, valves, and the pump head were heat traced with 25 gauge Nichrome wire to heat the bitumen and lower its viscosity. The liquid product sampling line was also heat traced. This precaution permitted uninterrupted operation and circumvented plugging of transfer lines due to cold spots. The Nichrome wire had a resistivity of 0.83 ohm/cm (2.1 ohm/in) and was coated with glass fabric to avoid shorting on metal surfaces. Fiberglass tape was used to attach the wire to the system.
A proportional controller was used to control temperature of the heat traced lines. The heat tracing was divided into two sections; section A (lines A1 through A13), which included the lines from the pump to the reactor inlet and section B (lines B1 through B14), which included the lines from the reactor outlet to the liquid product recovery system. These two sections were connected in parallel. The spacing of the wire in each section was determined by the nature of the fluids flowing in the section.

The resistance of the heat-trace wires in each section is indicated in Table 3.1. Typical temperatures of heat traced lines for the base case operating condition at a controller setting was 343 K (70°C) are reported in Table 3.2. A schematic of heat traced sections A and B is presented in Figure 3.4.

**Hydrogen Feed System**

Hydrogen was compressed to the reactor inlet pressure by a Whitey Laboratory Compressor (Model LC10) whose maximum output pressure was 20.7 MPa (3,000 psig). The sealed diaphragm construction of this compressor was ideally suited for pumping hydrogen since leaks could not be tolerated. The compressor power supply was designed to turn the compressor off if the inlet pressure fell below 1.38 MPa (200 psig) to prevent damage since the inlet pressure limit was 0.35 MPa (50 psig). The regulator pressure and the compressor outlet pressure were controlled to provide a fixed hydrogen supply of 890 m³/m³ (5,000 scf/bbl) to the reactor. Typically the hydrogen supply pressure to the compressor inlet was 3.4 to 5.5 MPa (500-800 psig).

The initial hydrogen cylinder pressures were 13.8 MPa (2,000 psig). When the cylinder pressure fell below 5.5 MPa (800 psig), the hydrogen cylinders were changed. The hydrogen cylinder exchange was done in such a way that the lines were purged of air.
<table>
<thead>
<tr>
<th>Section</th>
<th>Segment</th>
<th>Resistance (Ohms)</th>
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</thead>
<tbody>
<tr>
<td><strong>A Section</strong></td>
<td>A1-A2</td>
<td>9.5</td>
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<tr>
<td></td>
<td>A3-A4</td>
<td>22.5</td>
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<td></td>
<td>A5-A6</td>
<td>5.6</td>
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<td>22.5</td>
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<tr>
<td></td>
<td>A9-A10</td>
<td>2.1</td>
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<tr>
<td></td>
<td>A11-A12</td>
<td>5.5</td>
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<tr>
<td></td>
<td>Total in A Section</td>
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<tr>
<td><strong>B Section</strong></td>
<td>B1-B2</td>
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</tr>
<tr>
<td></td>
<td>B3-B4</td>
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<td>8.7</td>
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<tr>
<td></td>
<td>B11-B12</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>Total in B Section</td>
<td>82.0</td>
</tr>
</tbody>
</table>
Table 3.2

Typical Temperatures of Heat Traced Lines at the Base Case Condition

<table>
<thead>
<tr>
<th>Temperature Indicator</th>
<th>Section Description</th>
<th>Temperatures [K]</th>
</tr>
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<tbody>
<tr>
<td>#1</td>
<td>Catalyst Bed Temperature</td>
<td>642</td>
</tr>
<tr>
<td>#2</td>
<td>Pump-Reactor Inlet Transfer Line</td>
<td>402</td>
</tr>
<tr>
<td>#3</td>
<td>Three-Way Valve at Reactor Inlet</td>
<td>420</td>
</tr>
<tr>
<td>#4</td>
<td>Vapor-Liquid Separator</td>
<td>352</td>
</tr>
<tr>
<td>#5</td>
<td>Annin Valve</td>
<td>380</td>
</tr>
<tr>
<td>#6</td>
<td>Room Temperature</td>
<td>289</td>
</tr>
</tbody>
</table>
Figure 3.4

Schematic of Heat Traced Lines
**Calibration of Mass Flow Controller**

Hydrogen flow was controlled with a Brooks mass flow controller (Emerson Electric Co.). The mass flow controller valve was located between the compressor outlet and the reactor inlet manifold valves. Check valves were installed in the gas inlet lines to the reactor to prevent the backflow of liquid into the mass flow controller. Pressure relief valves were installed on the outlet of the compressor and on the inlet of the mass flow controller to protect the controller in the event of system overpressurizing.

The mass flow controller was calibrated at 13.7 MPa by measuring the hydrogen flowrate from the reactor in the absence of hydrogen consumption. Hydrogen flowrate was measured with a wet testmeter at different mass flow controller settings. The calibration curve for the mass flow controller is presented in Figure 3.5.

**Reactor**

A packed-bed tubular reactor was used in this study to simulate a refinery reactor. This type of reactor is superior to a batch autoclave even though both are governed by the same kinetics [89]. The reactor held 100 cm³ of catalyst and was rated for operation at 20.7 MPa (3,000 psig) hydrogen at 773 K (500°C). The bitumen was fed into the reactor in the upflow mode to ensure complete wetting of the catalyst and to permit isothermal operation.

The reactor was made of seamless 316 stainless steel tubing which had an inside diameter of 2.54 cm (1 in) and a wall thickness of 0.95 cm (0.37 in). A 0.32 cm (0.13 in) outside diameter thermowell which held a movable thermocouple was located on the centerline of the reactor. The reactor was flanged at each end and sealed by copper and aluminum gaskets.
Figure 3.5

Mass Flow Meter Reading versus Volumetric Hydrogen Flow Rate
Mass Flow Meter Display Reading

H₂ Volumetric Flow Rate [liter STP H₂ / h]
The copper gasket was used to seal the bottom (inlet) flanges because the inlet gas contained no hydrogen sulfide (H$_2$S) or ammonia (NH$_3$). The aluminum gasket was used to seal the top (outlet) flanges because copper might interact with the hot H$_2$S and/or NH$_3$ leaving the reactor and aluminum is corrosion resistant. The aluminum gaskets showed no signs of corrosion even after 1,000 hours at temperatures in the range 620-685 K (656-775°F) in the presence of ammonia, hydrogen sulfide and water.

A 0.95 cm (0.38 in) stainless steel tube was welded in the center of the inlet and outlet cap-flanges to serve as the feed inlet and product outlet lines.

**Reactor Temperature Control System**

A three-zone Lindberg furnace was used to provide the heat to the reactor. Three UDC 2000 Mini-Pro Universal Digital Controllers were used to control the temperature of each section. The reactor temperature was monitored by DP 285J temperature display, Omega Engineering Co., using a movable thermocouple.

The catalyst was located in the middle (30.5 cm (12 in)) furnace zone. The bottom zone (15.2 cm (6 in)) served as the preheater and the top zone (15.2 cm (6 in)) was used as a trim heater to maintain the catalyst zone isothermal. The setting of the top section was set above the desired isothermal temperature to diminish heat losses through the reactor head. An aluminum shield was used as a heat sink to moderate temperature fluctuations due to cycling of the furnace heating element and to maintain an isothermal temperature profile in the catalyst bed. A schematic of the reactor is presented in Figure 3.6.
Figure 3.6

Schematic Diagram of Upflow Catalytic Reactor
Gas Product Out

Liquid Product Out

Furnace

Thermocouple

Alumina Ball

Catalyst

Sand

Glass Wool

Holder

Screen

Catalyst Bed
Length = 30.5 cm
Inside Diameter = 2.54 cm
Axial Thermowell = 0.32 cm O.D.

Hydrogen In

Feed In

7.6 cm

5.1 cm

27.9 cm

30.5 cm

27.9 cm
Reactor Pressure Control System

The system pressure was maintained by a back pressure regulating valve (BPRV) and was monitored by an Omega Engineering Model DP-354 pressure indicator. Pressure gauges were located in the feedline from the pump, in the transfer line to the reactor, in the transfer line from the reactor, and at the back pressure regulating valve as indicated in Figure 3.2. A Mity Mite Back Pressure Regulating Valve with a pressure rating of 20.7 MPa (3,000 psig) controlled the total system pressure. The system was pressurized to the desired value by admitting nitrogen to the dome of BPRV.

A schematic of the pressure control system is presented in Figure 3.7. Initially valves a, b and c were opened while valves d was closed. The compressor delivered nitrogen to the dome of the BPRV until the pressure gauge B reading reached the desired value, then all the valves were closed. The system pressure was controlled with a BPRV which functioned by controlling the flow of the vapor product exiting from the vapor-liquid separator. The BPRV functioned as an on-off valve due to the movement of the Teflon diaphragm which deflected to permit vapor product to exit the system through the BPRV orifice. The system pressure at which the BPRV would open to release vapor product was determined by the pressure on the dome side of the diaphragm. When the process pressure was greater than the dome pressure the diaphragm would deflect to permit the vapor to leave the system through the BPRV orifice. The operation of the BPRV permitted steady control of the system pressure (±0.01 MPa).

At the start of each run the dome pressure was loaded with nitrogen to the base case pressure (13.7 MPa). During reactor operation the system pressure was occasionally raised or lowered depending on the desired reactor conditions.
Figure 3.7

Schematic of System Pressure Control System
The dome pressure was changed in the following manner to permit a steady transition from one operating pressure to another:

- The dosing volume was pressurized with gas in manifold 1 to a pressure 0.1-1.2 MPa (15-30 psi) higher than the BPRV. Valve c between the dosing volume and the BPRV was opened. The immediate effect of opening this valve was to increase the BPRV dome pressure 0.05-0.1 MPa (7-14 psi) which in turn increased the system pressure by the same amount. The valve between the BPRV and the dosing volume was only opened when the dosing volume pressure was greater than the BPRV dome pressure to avoid a sudden and uncontrolled drop in the system pressure.

- If the system pressure was to be lowered, then the pressure on the dosing volume/BPRV was slowly vented through the needle valve (valve d) until the dome (and the system) reached the desired pressure. This step was conducted slowly (rate of pressure decreased < 0.07 MPa/min) to permit hydrogen dissolved in elastomeric rubber gaskets and O-rings to diffuse out of the matrix.

- If the system pressure was to be increased, then valves (valves a and b) between manifold #2 and the dosing volume were opened. The dosing volume/BPRV dome pressure was then gradually increased until it was 0.05-0.1 MPa higher than the desired BPRV dome pressure. At that point, the valves between manifold #2 and the dosing volume were shut.

- Because the system pressure responds slower than the dosing volume pressure, the system pressure was permitted to rise until vapor product started to exit the BPRV. Then the additional pressure (0.05-0.1 MPa) in
the connected dosing volume/BPRV dome was slowly vented through the needle valve.

- After adjustments on the BPRV dome pressure were completed the valve between the BPRV and the dosing volume was shut.

**Liquid Product Separation and Sampling System**

A liquid level control system on the high pressure separator was used to withdraw the total liquid product from the system. The system pressure was dropped from 13.8 MPa (2,000 psig) upstream of the control valve to atmospheric pressure downstream at the low pressure separator. A Wee Willie Model 5061 (Annin) control valve manufactured by the Masoneilan Division of the McGraw-Edison Co. was used in concert with a DP liquid level sensor-controller to control the withdrawal of liquid from the system.

The building supply air pressure which was normally 0.5-0.6 MPa (70-80 psig) was regulated to 0.16 MPa (23 psig) for the I/P converter through a 0.04-0.3 MPa (5-40 psig) Masoneilan Dresser regulator and also provided air pressure (0.21 MPa (30 psig)) to the Annin valve. A Pneumotive air compressor fitted with a Solberg air filter and a Speedaire Reducing Regulator was used to provide instrument air in the event that the building air compressor shut down. The compressor starter was set to turn on the compressor when the building air pressure dropped below 0.17 MPa (25 psig) and to shut down the compressor when the instrument air pressure reached 0.31 MPa (45 psig).

A Bailey Type BC Transmitter (BC2/3/4), Bailey Controls Co., measured the differential pressure across the Brooks high pressure vapor-liquid separator. The separator was rated for a maximum pressure of 41.3 MPa (6,000 psig) maximum pressure. The transmitter sent 4-20 mA current output to the Masoneilan Dresser I/P converter through the Honeywell UDC 3000 Universal
Digital Controller which was used to control the liquid level. The I/P converter converted this 4-20 mA signal to 0.02-0.1 MPa (3-15 psig) air signal which controlled the output to the positioner on the Annin valve. The Annin valve had a series A trim which permitted a theoretical \( C_v \) range of 0.001 and 0.01 and had a variable maximum stroke length from 0.025 to 0.38 cm (0.01-0.15 in). A schematic of the Annin control valve system is presented in Figure 3.8.

The \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) in the exit gases were absorbed in a bubbler which contained a 2 molar solution of KOH (potassium hydroxide) before passing through the wet test meter or being vented to the hood.

**Safety System**

A safety alarm was incorporated into the system since it was intended for continuous operation; that is, more than 1,000 hours on stream. If the liquid level reached the maximum permitted level in the vapor-liquid separator, the Sonalert alarm, Mallory Co., was activated and the pump was shut down to prevent flow of bitumen through the BPRV.

Air-flow in the vicinity of the hydrotreater was maintained by continuous operation of the hood. A commercial fan was used to ventilate the hydrotreater during periods of operation to move hydrocarbon vapors and/or hydrogen to the hoods.

**Experimental Procedure**

**Catalyst Loading**

The reactor furnace was divided into three independently controlled regions; the preheater zone, the catalyst bed zone and the exit trim heater zone. The reactor was flanged at both the inlet and outlet. Aluminum and copper
Figure 3.8

Schematic of Annin Valve
4-20 mA

I/P Converter

Regulator

3-15 psi
gaskets were used to seal the flanges to the unit which were set using a torque wrench. The torque wrench force was increased from 10 lbf-in to 60 lbf-in increments of 10 lbf-in.

Alpha alumina balls (0.05 cm (0.13 in)) were placed in the preheater and exit zones of the reactor. The balls in the preheater zone also served to support the catalyst bed. Sand (white SiO₂; -50+70 mesh) from Aldrich Chemical Co. was placed in the interstices of the α-alumina balls to reduce the void volume and to induce higher liquid superficial velocities.

The exit zone was filled with 126.7 cm³ of alundum balls and 34.8 cm³ of fine sand. The reactor was tapped frequently during loading to distribute the sand throughout the alundum balls in the reactor. A pan-shaped holder fitted with a 65-mesh screen (equivalent to 212 mm opening) was used to hold the alundum balls and sand in place. The HDM catalyst bed was not diluted with sand to avoid catalyst bed plugging due to coking of the large molecular weight species in the bitumen. The catalyst charge was 152 cm³ and was placed in the central region of the reactor. The reactor was tapped during catalyst loading to ensure proper packed density. The catalyst bed was held in place by a screen. Finally, 128.3 cm³ of alundum balls and 35.3 cm³ of sand were placed in the preheater zone. The reactor body was connected to the unit.

**Pressure Test**

The reactor system was pressure tested prior to catalyst sulfiding to minimize hydrogen leaks. The pressure test was conducted by increasing the BPRV pressure from atmospheric pressure to 6.9 MPa (1,000 psig) at atmospheric temperature. Nitrogen was used to pressurize the system. After the nitrogen pressure stabilized the system was isolated. The isolated section consisted of the line from the nitrogen regulator to the inlet of the reactor, the
reactor and the line from outlet of the reactor to vapor-liquid separator and the line from vapor-liquid separator to the BPRV inlet line.

The unit pressure was monitored. If there was no loss of pressure over 16 hours the system pressure was increased to 13.8 MPa (2,000 psig). The system pressure was monitored overnight (16 hours). If a significant leak was indicated in any segment of the unit, the line was removed, replaced and the pressure test was performed again. The BPRV section was also pressure tested. Once the system was pressure tight sulfiding could be performed.

**Catalyst Sulfiding**

The hydrotreating catalyst was presulfided in-situ before contact with the liquid feed. The catalyst sulfiding procedure consisted of contacting the catalyst with a sulfiding solution and hydrogen to reduce and sulfide the supported metal oxide component. After sulfiding, the active component of the metal in the catalyst changed from metal oxide to metal sulfide. The sulfiding solution was 2 wt% dimethyldisulfide in kerosene. The kerosene was obtained from the Flying J Refinery in North Salt Lake City, Utah. The dimethyldisulfide used in this study was in a 99 vol% purity obtained from Aldrich Chemical Company, Inc. The solution was prepared in a hood due to the toxicity of dimethyldisulfide. A 4-liter bottle was filled with 2,400 g of kerosene and the desired amount of dimethyldisulfide solution (72 g) was added and stirred for an hour to form a completely mixed solution.

The catalyst sulfiding procedure was recommended by the manufacturer. The conditions were a system pressure of 6.2 MPa (900 psig), 890 m³/(STP)/m³ (5,000 ft³/bbl) hydrogen-to-oil ratio, and 1.0 h⁻¹ liquid hourly space velocity (LHSV). A mass flow controller was used to maintain the feed rate and hydrogen-to-oil ratio. The sulfiding procedure is illustrated in Figure 3.9.
Figure 3.9

Catalyst Sulfiding Sequence
Sulfiding was started at ambient temperature and the catalyst was heated to 505 K (450°F) at a rate of 27.8 °C/h (50 °F/h). The catalyst was held at 505 K for 2 hours. At 478 K (400°F) sulfur uptake by the catalyst increases dramatically; thus, the extended period at 505 K was to ensure complete sulfiding of the catalyst. The initial set points for the three temperature controllers were 550 K (530°F) (bottom), 489 K (420°F) (middle) and 533 K (500°F) (top). The heating rate was checked and adjusted every twenty minutes by monitoring the reactor temperature in the catalyst bed as the reactor heated up to 505 K. After holding the reactor temperature at 505 K for 2 hours, the completion of sulfiding was confirmed by the presence of hydrogen sulfide in the exit gas sampler. The hydrogen sulfide was detected by the color change of copper wool in the sampler from red to black.

The sulfiding solution feed was then stopped and the reactor temperature was lowered to 494-500 K (430-440°F). The bottom and top temperature controllers were set at 494 K (430°F). The middle section controller set point was kept at 489 K (420°F). The hydrogen feed was reversed to force the sulfiding solution out of the reactor and a small amount of hydrogen (mass flow meter reading was 2.0) was fed to the reactor to maintain hydrogen pressure overnight.

The low hydrogen flow was intended to avoid sulfur stripping by hydrogen. Subsequently, hydrogen was introduced to the reactor in the upflow mode at 890 m³/m³ (5,000 scf/bbl) and the sulfiding solution was introduced to the reactor at 1.0 h⁻¹ LHSV. The reactor temperature was increased from 505 K (450°F) to 644 K (700°F) at a rate of 27.8 K/h (50 °F/h). At 644 K the liquid pump was turned off and the hydrogen feed was reversed to flush the sulfiding solution out of the reactor and the reactor temperature was lowered to 617 K (650°F).
Experimental Strategy and Reactor Startup

The effects of operating variables on the extent of denitrogenation, desulfurization, demetallation, residuum conversion and the product distribution and yields were determined.

Initially, the catalyst was deactivated and stabilized for 8 days at the base case conditions; 642 K (696°F), 0.45 h\(^{-1}\) and 13.7 MPa (1980 psig). At this point it was assumed that the catalyst was stabilized because the change in \(^{\circ}\)API gravity with time was negligible. When liquid product started to exit from the reactor system through Annin valve, it was considered to be zero time on stream. The conditions during the initial catalyst deactivation study are presented in Table 3.3. The initial catalyst deactivation, as a function of time on-stream is shown in Figure 3.10.

After the initial catalyst deactivation period, as indicated by the API gravity of the total liquid product, the process variable experiments were conducted in a cyclic mode. A specific operating variable experiment was performed followed by an experiment at the base case condition to determine if the catalyst deactivated during the process variable experiment.

In order to select the optimum operating conditions and to cover as many operating conditions as possible with a limited number of experiments, two variables were fixed while the other variable was varied within a reasonable range. A 3-D representation of the set of operating conditions used in this study is presented in Figure 3.11. The API gravities of the total liquid products produced in the process variable experiments and at the base case conditions with respect to time on-stream are presented in Figure 3.12. The process variable experiments were performed in a random manner to avoid systematic errors; that is, the same operating variable was not studied in sequence. The sequence of experiments performed in this study is presented in Table 3.4.
Table 3.3

Conditions for Initial Catalyst Deactivation

<table>
<thead>
<tr>
<th>Run No.</th>
<th>T K (°F)</th>
<th>WHSV* h⁻¹</th>
<th>LHSV h⁻¹</th>
<th>P MPa (psig)</th>
<th>TOS b h</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1</td>
<td>641 (694)</td>
<td>0.90</td>
<td>0.53</td>
<td>13.7 (1987)</td>
<td>8</td>
</tr>
<tr>
<td>D-2</td>
<td>640 (693)</td>
<td>0.86</td>
<td>0.51</td>
<td>13.6 (1975)</td>
<td>29</td>
</tr>
<tr>
<td>D-3</td>
<td>641 (694)</td>
<td>0.86</td>
<td>0.50</td>
<td>13.7 (1980)</td>
<td>53</td>
</tr>
<tr>
<td>D-4</td>
<td>640 (693)</td>
<td>0.86</td>
<td>0.50</td>
<td>13.6 (1966)</td>
<td>74</td>
</tr>
<tr>
<td>D-5</td>
<td>640 (693)</td>
<td>0.82</td>
<td>0.48</td>
<td>13.5 (1955)</td>
<td>116</td>
</tr>
<tr>
<td>D-6</td>
<td>640 (693)</td>
<td>0.83</td>
<td>0.49</td>
<td>13.6 (1975)</td>
<td>139</td>
</tr>
<tr>
<td>D-7</td>
<td>640 (693)</td>
<td>0.92</td>
<td>0.54</td>
<td>13.6 (1975)</td>
<td>167</td>
</tr>
<tr>
<td>D-8</td>
<td>642 (696)</td>
<td>0.78</td>
<td>0.46</td>
<td>13.7 (1985)</td>
<td>188</td>
</tr>
</tbody>
</table>

* Weight hourly space velocity

b Time elapsed since oil was started over catalyst
Figure 3.10

API Gravity versus Time On-Stream
Figure 3.11

Operating Conditions Used in This Study
Common Point (Run D-11)
Temperature = 664 [K]
WHSV = 0.76 [h⁻¹]
Pressure = 13.7 [MPa]
Figure 3.12

Total Liquid Product API Gravities as a Function of Time On-Stream
Table 3.4

Sequence of Experiments Performed

<table>
<thead>
<tr>
<th>Run No.</th>
<th>T, K (F)</th>
<th>WHSV (LHSV), h⁻¹</th>
<th>P, MPa (psig)</th>
<th>TOS*, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-9</td>
<td>686 (775)</td>
<td>0.75 (0.44)</td>
<td>13.7 (1987)</td>
<td>211</td>
</tr>
<tr>
<td>D-10</td>
<td>642 (697)</td>
<td>0.77 (0.45)</td>
<td>13.7 (1980)</td>
<td>235</td>
</tr>
<tr>
<td>D-11</td>
<td>665 (737)</td>
<td>0.77 (0.45)</td>
<td>13.8 (1995)</td>
<td>259</td>
</tr>
<tr>
<td>D-12</td>
<td>643 (697)</td>
<td>0.78 (0.46)</td>
<td>13.6 (1975)</td>
<td>283</td>
</tr>
<tr>
<td>D-13</td>
<td>664 (736)</td>
<td>0.77 (0.45)</td>
<td>16.7 (2423)</td>
<td>306</td>
</tr>
<tr>
<td>D-14</td>
<td>642 (696)</td>
<td>0.78 (0.46)</td>
<td>13.6 (1975)</td>
<td>334</td>
</tr>
<tr>
<td>D-15</td>
<td>666 (739)</td>
<td>0.24 (0.14)</td>
<td>13.6 (1971)</td>
<td>405</td>
</tr>
<tr>
<td>D-16</td>
<td>642 (696)</td>
<td>0.77 (0.45)</td>
<td>13.7 (1984)</td>
<td>426</td>
</tr>
<tr>
<td>D-17</td>
<td>665 (737)</td>
<td>0.77 (0.45)</td>
<td>11.3 (1634)</td>
<td>450</td>
</tr>
<tr>
<td>D-18</td>
<td>642 (697)</td>
<td>0.77 (0.45)</td>
<td>13.6 (1972)</td>
<td>475</td>
</tr>
<tr>
<td>D-19</td>
<td>665 (738)</td>
<td>0.43 (0.25)</td>
<td>13.7 (1983)</td>
<td>525</td>
</tr>
<tr>
<td>D-20</td>
<td>653 (716)</td>
<td>0.77 (0.45)</td>
<td>13.6 (1974)</td>
<td>561</td>
</tr>
<tr>
<td>D-21</td>
<td>665 (737)</td>
<td>0.76 (0.45)</td>
<td>15.3 (2220)</td>
<td>584</td>
</tr>
<tr>
<td>D-22</td>
<td>642 (696)</td>
<td>0.76 (0.45)</td>
<td>13.7 (1988)</td>
<td>631</td>
</tr>
<tr>
<td>D-23</td>
<td>673 (752)</td>
<td>0.76 (0.44)</td>
<td>13.7 (1989)</td>
<td>656</td>
</tr>
<tr>
<td>D-24</td>
<td>642 (695)</td>
<td>0.78 (0.46)</td>
<td>13.6 (1977)</td>
<td>681</td>
</tr>
<tr>
<td>D-25</td>
<td>662 (732)</td>
<td>1.38 (0.81)</td>
<td>13.6 (1978)</td>
<td>705</td>
</tr>
<tr>
<td>D-26</td>
<td>642 (696)</td>
<td>0.78 (0.46)</td>
<td>13.6 (1972)</td>
<td>727</td>
</tr>
<tr>
<td>D-27</td>
<td>685 (773)</td>
<td>0.76 (0.45)</td>
<td>13.7 (1984)</td>
<td>750</td>
</tr>
<tr>
<td>D-28</td>
<td>641 (694)</td>
<td>0.77 (0.45)</td>
<td>13.7 (1981)</td>
<td>775</td>
</tr>
<tr>
<td>D-29</td>
<td>620 (656)</td>
<td>0.77 (0.45)</td>
<td>13.7 (1980)</td>
<td>799</td>
</tr>
<tr>
<td>D-30</td>
<td>641 (695)</td>
<td>0.79 (0.46)</td>
<td>13.6 (1976)</td>
<td>827</td>
</tr>
</tbody>
</table>

Production Run of 18 °API Total Liquid Product.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>T, K (F)</th>
<th>WHSV (LHSV), h⁻¹</th>
<th>P, MPa (psig)</th>
<th>TOS*, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-31</td>
<td>686 (775)</td>
<td>0.66 (0.39)</td>
<td>13.5 (1965)</td>
<td>849</td>
</tr>
<tr>
<td>D-32</td>
<td>686 (774)</td>
<td>0.70 (0.41)</td>
<td>13.5 (1962)</td>
<td>870</td>
</tr>
<tr>
<td>D-33</td>
<td>685 (773)</td>
<td>0.75 (0.44)</td>
<td>13.5 (1960)</td>
<td>895</td>
</tr>
<tr>
<td>D-34</td>
<td>687 (777)</td>
<td>0.75 (0.44)</td>
<td>13.5 (1957)</td>
<td>919</td>
</tr>
<tr>
<td>D-35</td>
<td>695 (792)</td>
<td>0.76 (0.44)</td>
<td>13.5 (1954)</td>
<td>943</td>
</tr>
<tr>
<td>D-36</td>
<td>698 (797)</td>
<td>0.66 (0.39)</td>
<td>13.6 (1972)</td>
<td>966</td>
</tr>
<tr>
<td>D-37</td>
<td>697 (796)</td>
<td>0.61 (0.36)</td>
<td>13.6 (1972)</td>
<td>992</td>
</tr>
</tbody>
</table>

* Time on-stream.
The API gravities of the hydrotreated products were determined according to the Syncrude Analytical Method [134].

**Operating Procedure**

Daily experimental operations consisted of a mass balance followed by changing the reaction conditions for overnight unattended operation. It was assumed that the catalyst activity at each reaction condition was stabilized after overnight operation (16 hours) and that representative samples were taken during the subsequent mass balance.

**Mass/Balances**

A representative sample was collected for subsequent analysis at a specific set of reaction conditions during each mass balance. The mass balance procedure was as follows:

- The gas chromatograph was activated and the sample collection system was prepared to acquire a sample of the gas from vapor-liquid separator. The procedure is described in Product Oil and Gas Analysis Section.
- The empty Erlenmeyer liquid sample collection flask (500 cm³) and the condensable vapor collection tube (60 cm³) were weighed.
- The liquid feed level in the large burette and the time were recorded and the constant overnight feed rate was calculated. It was assumed that the catalyst activity was at steady state since it had been at run conditions for more than 16 hours.
- Deionized water was boiled for the bath in which API gravity of the liquid product collected during mass balance would be measured.
• The hydrogen cylinder pressure was checked. If the hydrogen cylinder pressure was below 5.5 MPa (800 psig), all three cylinders were replaced.

• The small burette was filled with bitumen from the storage drum and the pump feedline was switched from the large to the small burette for the mass balance. The initial volume of feed in the small burette and the starting time of the mass balance were recorded. The liquid sampler was connected to the product line.

• The temperature profile along the catalyst bed was recorded. The detailed procedure is described in the following section (Temperature Measurement). A gas sample from the liquid-vapor separator line was collected and injected into the GC for analysis.

• The gas collector in the liquid nitrogen trap to the product line was connected and a gas sample was collected. The gas sample was collected over 1 hour and the gas flowrate was measured with the wet test meter (Precision Scientific, Inc.). The atmospheric pressure and temperature were recorded and the volumetric hydrogen flowrate exiting the reactor at STP was calculated. A gas sample collected from the liquid nitrogen trap vent line was injected for GC analysis.

• The gas collector and the liquid nitrogen trap were removed from the unit. The amount of gas collected in the liquid nitrogen trap was determined and the rate of gas production was measured.

• A representative liquid sample was collected for 3 to 4 hours. The liquid collection reservoir was disconnected from the system and was replaced by a polypropylene container (19 liter (5 gallon)) for overnight operation. The liquid level in the small burette was recorded and the LHSV during the mass balance was calculated. The mass balance was calculated from
the gas and liquid products collected. All wt% mass balances were in the range 98 to 100 wt% in this study.

- The reaction conditions were changed to those selected for the next experiment. The conditions were checked frequently so that the catalyst system would be equilibrated for the following day’s mass balance.
- The hydrogen and oxygen flow to the GC were discontinued and the GC was turned off. Helium flow was continued for 2 hours until the column temperature returned to ambient.
- The API gravity of the total liquid product was determined to assess the deactivation of the catalyst as a function of the time on-stream.

**Temperature Measurement**

The temperature profile of the catalyst bed was measured along the axis of the reactor with a movable J-type thermocouple. The thermocouple moved inside of the 0.05 cm (1/8 in) O.D. thermowell to measure the temperature in the catalyst region. The three heating elements in the furnace were controlled to give a uniform temperature throughout the reactor length. A typical experimental catalyst bed temperature profile is presented in Figure 3.13. The temperature profile along the length of the catalyst region was almost isothermal. The kinetic average temperature was calculated from the temperature profile.

The kinetic average temperature \( T_{K_a} \) is the temperature of an isothermal reactor required to give the same conversion obtained in a nonisothermal reactor. The following equation was used to calculate the kinetic average temperature:

\[
\int_0^L \exp\left[\frac{-E_a}{RT_{K_a}}\right]dl = \int \exp\left[-\frac{E_a}{RT(l)}\right]dl \tag{3-2}
\]
Figure 3.13

Typical Temperature Profiles in the Catalyst Zone
Kinetic Average Temperature = 664.7 [K]
Arithmetic Average Temperature = 664.7 [K]

Catalyst Region

Direction of Flow

Run D-11
where, $T(l)$ is the measured axial temperature gradient across the reactor; $R$ is the gas constant; $l$ is the length of the reactor at each measurement; $L$ is the total length of the reactor; and $E_a$ is the activation energy.

The kinetic ($T_{ke}$) and arithmetic average temperatures ($T_{ae}$) were calculated as follows:

$$
\frac{1}{T_{ke}} = \left(\frac{R}{E_a}\right) \ln \left[ \frac{1}{L} \int_0^L \exp \left[ \frac{-E_a}{RT(l)} \right] dl \right] \quad (3-3)
$$

$$
T_{ae} = \frac{1}{L} \int_0^L T(l) dl \quad (3-4)
$$

The activation energy for hydrodenitrogenation of bitumen-derived liquid, $E_a=106$ kJ/mol, was determined in a previous study [18] and was used here to calculate the kinetic average temperature. The kinetic average temperature is not strongly dependent upon the value of the activation energy, $E_a$. This assumption should be valid because $T_{Axial} = T_{max} - T_{min}$ is small as can be seen in Figure 3.13. The calculation was based on Trapezoidal Rule using the weighting functions.

The arithmetic average temperature was only slightly higher (0.06 K (0.1°F) at most) than the kinetic average temperature. Thus, the reactor operated essentially isothermally.

**Sample Purging**

The total liquid product samples collected during the mass balances were purged to remove $H_2S$ and $NH_3$ which were dissolved in the hydrotreated liquid.
so as to minimize the uncertainty when elemental analyses of these samples were performed.

About 25 g of the total liquid product was placed in a 60 cm³ test tube fitted with a side arm. The test tube was placed in a 250 ml Erlenmeyer flask containing 175 cm³ of water. The ammonia and hydrogen sulfide were stripped from the sample with helium at a flowrate of 50 cm³/min. The helium was bubbled through the sample for 4 hours while the water in the flask was boiling. The purged liquid and the stripped light ends which were recovered in a cold water trap were mixed to form the final sample. These samples were sent to the Galbraith Lab for elemental analysis.

**Overnight Operating Procedure**

After completion of each mass balance and the collection and preparation of material balance samples, the temperature and pressure were reset for the next experiment. The space velocity was adjusted because the feed rate was affected by the temperature and pressure adjustments. The total liquid product was collected overnight in 19 liter (5 gallon) plastic container and the catalyst attained a steady state at the new reactor conditions. Even though the system was designed to operate unattended overnight, it was periodically checked to minimize the possibility of reactor upsets.

**Shutdown**

After the conclusion of the process variable study a high temperature (775-797 K (685-698°F)) and low LHSV (0.36-0.43 h⁻¹) run was made to produce a high API gravity (18 °API) total liquid product for subsequent hydrocracking and catalytic cracking experiments. After 150 hours on-stream in the production run the compressor failed, hydrogen flow was lost and, severe coking occurred
in the reactor inlet region; thus the bitumen hydrotreating run (Run D) was terminated.

All heat tracing lines were shut off and the system was allowed to return to the ambient temperature. In addition, the reactor pressure was slowly decreased. Kerosene was pumped through the reactor to flush out the bitumen-derived heavy oil. The kerosene flush was discontinued when the color of the liquid exiting from the system changed from black to yellow. Hexane was used as a second flush solution at a reactor temperature of 400 K and a reactor pressure of 1.4 MPa (200 psig). The hexane was pumped through the system until the liquid exiting from the system was colorless. The catalyst was then dried in flowing nitrogen and cooled to ambient temperature.

The reactor was disconnected and removed from the system and the catalyst was removed from the reactor. The catalyst particles were no longer individual pellets but rather were fused due to severe external coking. It was presumed that the coking took place at the time of the compressor failure.

Product Gas and Liquid Analysis

The gas samples produced during mass balances were analyzed by gas chromatography. The liquid samples were analyzed by simulated distillation. Carbon, hydrogen, nitrogen, sulfur, and metals contents were determined along with pour point, Conradson carbon residue, and composition-type analyses.

Gas Product Analysis

The gas from the high pressure vapor-liquid separator was analyzed with a Carle Analytical GC Series SX, Model 211 (FID) (Carle Instruments, Inc.), which was connected to IBM AT computer for integration. The Carle GC was
turned-on each day as part of the mass balance procedure. The helium flow pressure was then started at 0.37 MPa (53 psig) when the column temperature reached 331 K. When the column temperature reached (331 K), the hydrogen flow was started at 0.07 MPa (10 psig) above the run pressure, 32 psig. The FID was ignited after purging the hydrogen line, for 1 to 2 minutes. The air flow was started at 20 psig and the hydrogen flow pressure was reduced to the normal operating pressure (0.22 MPa (32 psig)). Two gas samples from the system were injected, one was taken at a point before the gas collector and the other was taken from after the gas collector in the liquid nitrogen trap. These two samples were necessary because the liquid nitrogen trap did not collect a small amount of the light hydrocarbon gases, methane and ethane. This observation was factored into the calculation of hydrogen consumption.

The FID response factors were used to correct the GC analysis [135]. The FORTRAN program called HYDROGEN.FOR was written to calculate hydrogen consumption for various mass balance and is presented in Appendix A.

**Liquid Product Analysis**

**Simulated Distillation**

The molecular weight distribution of the liquid products was determined by simulated distillation using a Hewlett Packard 5890 Series II Gas Chromatograph with an HP 3396 Series II Integrator and an HP 7673 Controller. The GC was connected to an IBM XT Personal Computer for data logging. A Fused Silica Capillary Column, 5 m long and 0.53 mm ID with a 0.1 mm thick film, by Supelco Inc., was used to separate the sample to carbon number 60 ($C_{60}$). The column was calibrated using an HP boiling point calibration sample No. 1, for the $C_5$ to $C_{60}$ paraffins and Supelco, Inc. boiling point calibration sample for paraffins up to
The column retention time calibrations were performed three times before bitumen and hydrotreated total liquid product analyses were performed. The normal paraffin boiling point distributions corresponding to carbon numbers were obtained from the literature [136]. Then tabulated retention times for the paraffin standard samples were used in the program, SIMDIS.BAS, which is described in Appendix B. The oven temperature program was started at 308 K and held at this temperature for 4.5 minutes. The oven was then heated at the rate of 12 °C/h until the final temperature of 653 K was reached and maintained for 8.75 minutes. The same program was used for both the sample and blank runs. The hydrotreated liquid sample was warmed and dichloromethane (EM Science Co.) was added to obtain a representative sample for GC injection.

The simulated distillation procedures for the hydrotreated total liquid products were repeated in the following manner:

- First conditioning run
- First blank run
- Sample only run
- Second conditioning run
- Second blank run
- Sample and internal standard run

Column conditioning was required after a sample injection to remove all uneluted materials left on the column owing to the heavy nature of the hydrotreated total liquid product.

The initial oven temperature for the conditioning run was 308 K. The oven was then heated at 50 °C/h to 653 K and temperature was maintained at 653 K for 90 minutes to remove the uneluted material from the previous run.
Blank runs were also necessary after conditioning to obtain the stabilized base lines. The Basic program called ZEROBLNK.BAS was written to subtract the baseline from the sample peak. The sample plus internal standard run was conducted to the correct retention times for the high carbon number materials. The C\textsubscript{14} through C\textsubscript{17} paraffin mixture was used as an internal standard. The weight ratios for mixtures of the bitumen, the hydrotreated total liquid product and the internal standard are tabulated in Table 3.5. About 10 hours were required to analyze one sample.

The raw data acquired from the GC, which has ".BNC" extension and was not readable by IBM PC, was integrated using a Basic program called SLICE6.BAS and resulted in files which had ".RPT" extension. The .RPT extension files were readable by an IBM PC, and through the SIMDIS.BAS program in the PC, they were transferred into ASCII text files and tabulated. The basic programs including SIMDIS.BAS and ZEROBLNK.BAS are shown in Appendix A.

**Elemental Analysis**

The bitumen feed and the hydrotreated total liquid products were sent to Galbraith Laboratory, Inc. for elemental analysis. The analyses performed included carbon, hydrogen, nitrogen, sulfur, nickel, vanadium, and arsenic. The hydrotreated samples were nitrogen and sulfur stripped prior to analysis to remove dissolved ammonia and hydrogen sulfide.

The nitrogen analysis was conducted on a LECO FP-428 Nitrogen Analyzer (50-100 mg sample size). The range of the instrument was 0.1 to 100 wt\% nitrogen with a reproducibility of ±0.1 % [137].

The sulfur analysis was done by an Oxygen Bomb/Ion Chromatography method [138,139] due to the low ppm range, 0-3500 ppm of the samples. A
Table 3.5

Mixture Ratios for Internal Standard and Representative Samples

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Amount of Sample [wt%]</th>
<th>Amount of Internal Standard [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed+IS</td>
<td>74.2</td>
<td>25.8</td>
</tr>
<tr>
<td>D-11+IS</td>
<td>69.5</td>
<td>30.5</td>
</tr>
<tr>
<td>D-13+IS</td>
<td>66.4</td>
<td>33.6</td>
</tr>
<tr>
<td>D-15+IS</td>
<td>64.3</td>
<td>35.7</td>
</tr>
<tr>
<td>D-17+IS</td>
<td>68.6</td>
<td>31.4</td>
</tr>
<tr>
<td>D-18+IS</td>
<td>73.7</td>
<td>26.3</td>
</tr>
<tr>
<td>D-19+IS</td>
<td>65.6</td>
<td>34.4</td>
</tr>
<tr>
<td>D-20+IS</td>
<td>67.7</td>
<td>32.3</td>
</tr>
<tr>
<td>D-21+IS</td>
<td>65.5</td>
<td>34.5</td>
</tr>
<tr>
<td>D-23+IS</td>
<td>67.7</td>
<td>32.3</td>
</tr>
<tr>
<td>D-25+IS</td>
<td>75.0</td>
<td>25.0</td>
</tr>
<tr>
<td>D-27+IS</td>
<td>68.7</td>
<td>31.3</td>
</tr>
<tr>
<td>D-29+IS</td>
<td>69.2</td>
<td>30.8</td>
</tr>
</tbody>
</table>
Dionex Model 10/14 Ion Chromatograph was used. Carbon and hydrogen analyses were performed with a Perkin-Elmer 240 Elemental Analyzer [140]. The amount of arsenic of the feed was in the ppm range and was analyzed by Atomic Absorption Spectroscopy using a Perkin Elmer 5000 AA; and a HGA 500 Graphite Furnace [141,142]. The nickel and vanadium analyses were performed by Inductively Coupled Plasma Emission Spectroscopy using a Perkin-Elmer P II instrument [143,144].

**Pour Point and Conradson Carbon Residue Measurement**

Conradson carbon residues were measured according to ASTM D 189-IP 13 [145]. The pour points were measured by the Pycnometer Method described in the Syncrude Analytical Methods Handbook [134].
CHAPTER 4

RESULTS AND DISCUSSION

This chapter describes the extent of heteroatom removal, residuum conversion, product distributions and yield of hydrotreated Whiterocks bitumen over a commercial HDM catalyst as a function of process variables. Also, a comparison of bitumen hydrotreating over a small pore (HDN) catalyst [18,146] and a large pore (HDM) catalyst was generated to determine the effect of metal loading and pore size distribution on hydrotreating. This comparison is based on two experiments in which bitumen was hydrotreated at similar conditions [18, 146]. The kinetics of nitrogen, sulfur and residuum conversion for the hydrotreating of a bitumen-derived heavy oil over the HDN catalyst will also be discussed [18,147]. The Whiterocks bitumen-derived heavy oil was produced in a fluidized-bed pyrolysis reactor [18,147,148].

Properties of Bitumen, Bitumen-Derived Liquid and Hydrotreated Products over HDM and HDN Catalysts

There are significant differences in the properties between commercial HDM and HDN catalysts as indicated in Table 4.1. The HDM catalyst has double the median pore diameter and less than half of the metal loadings as the HDN catalyst.

The large pore diameter of the HDM catalyst diminishes deactivation due to coke formation and metal deposition relative to the HDN catalyst for a fixed
Table 4.1

Properties of UNOCAL Quadralobe HDM and HDN Catalysts

<table>
<thead>
<tr>
<th></th>
<th>HDM Catalyst</th>
<th>HDN Catalyst</th>
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</thead>
<tbody>
<tr>
<td><strong>Pore Volume, cc/g</strong></td>
<td>0.72</td>
<td>0.55</td>
</tr>
<tr>
<td>(by Mercury Porosimetry)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Surface Area, m²/g</strong></td>
<td>155</td>
<td>241</td>
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<tr>
<td><strong>Mean Pore Diameter, Å</strong></td>
<td>180</td>
<td>90</td>
</tr>
<tr>
<td><strong>Average Characteristic Dimension, cm</strong></td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>MoO₃, wt%</strong></td>
<td>6.2</td>
<td>12.8</td>
</tr>
<tr>
<td><strong>NiO, wt%</strong></td>
<td>1.0</td>
<td>3.3</td>
</tr>
<tr>
<td><strong>P₂O₅, wt%</strong></td>
<td>0.0</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Unimodal Pore Structure</strong></td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>
feedstock and set of operating parameters. It also reduces the diffusion barrier to the transport of heteroatoms, metal compounds and residuum molecules to the interior, active surface of the catalyst. Quann et al. [27] reported that metal removal reactions in conventional 0.16 cm (=1/16 inch) hydrotreating catalysts are generally diffusion limited.

The metals in the catalyst serve as sites for catalytic hydrogenation in the hydrotreating process. Therefore, the lower surface area and metals loading of the HDM catalyst was expected to exhibit lower catalytic activity than higher metals content HDN catalyst. An HDM catalyst also has a larger pore volume. The UNOCAL HDM and HDN catalysts were quadralobe shaped extrudates with unimodal pore structures. The quadralobe catalyst was selected for this study since it has been demonstrated that shaped catalysts exhibit improved diffusion characteristics relative to cylindrical extrudates [71].

Selected physical and chemical properties of the feedstocks are presented in Table 4.2. The analyses indicate that the two bitumen samples were quite similar. The bitumen-derived liquid contained significantly less residuum than the bitumen samples as indicated by simulated distillation analysis and it had only about 31% of the residuum content of the bitumen.

The differences in the feedstocks are also reflected in the Conradson carbon residues (CCR) and the asphaltene contents. The asphaltene contents were determined as pentane insolubles in this study. The Conradson carbon residue and the asphaltene content of the bitumen-derived liquid were 79% and 64%; respectively, of the values determined for the bitumen. Elemental analyses indicated that the pyrolysis process in which the bitumen-derived heavy oil was produced resulted primarily in molecular weight and boiling range reduction without selective deposition of heteroatomic species in the carbonaceous residue; however, nickel compounds were deposited in the carbonaceous
Table 4.2

Selected Feedstock Properties

<table>
<thead>
<tr>
<th></th>
<th>Whiterocks Bitumen over HDM Catalyst</th>
<th>Whiterocks Bitumen over HDN Catalyst [18,146,149]</th>
<th>Whiterocks Bitumen-Derived Liquid over HDN Catalyst [18,147,149]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid Gravity, °API</strong></td>
<td>11.7</td>
<td>11.4</td>
<td>18.5</td>
</tr>
<tr>
<td><strong>CCR, wt%</strong></td>
<td>10.2</td>
<td>8.8</td>
<td>8.1</td>
</tr>
<tr>
<td><strong>Pour Point, K(°F)</strong></td>
<td>319(115)</td>
<td>330(135)</td>
<td>250(-10)</td>
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<tr>
<td><em><em>Asphaltenes</em>, wt%</em>*</td>
<td>4.4</td>
<td>5.0</td>
<td>2.8</td>
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</table>

**Simulated Distillation**

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<tr>
<th></th>
<th>Volatility, wt%</th>
<th>C&lt;sub&gt;s&lt;/sub&gt;-478 K(400°F), wt%</th>
<th>478 K(400°F)-616 K(650°F), wt%</th>
<th>616 K(650°F)-811 K(1000°F), wt%</th>
<th>&gt;811 K(1000°F), wt%</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>42.2</td>
<td>1.9</td>
<td>6.0</td>
<td>34.3</td>
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<tr>
<td></td>
<td>43.3</td>
<td>0.0</td>
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<td>37.0</td>
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<td>17.8</td>
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**Elemental Analysis**

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<tr>
<th></th>
<th>C, wt%</th>
<th>H, wt%</th>
<th>N, wt%</th>
<th>S, ppm</th>
<th>Ni, ppm</th>
<th>V, ppm</th>
<th>As, ppm</th>
<th>H/C Atomic Ratio</th>
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<td></td>
<td>85.1</td>
<td>11.6</td>
<td>1.3</td>
<td>3334</td>
<td>72</td>
<td>&lt;10</td>
<td>3</td>
<td>1.6</td>
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<tr>
<td></td>
<td>85.5</td>
<td>11.0</td>
<td>1.1</td>
<td>3700</td>
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<td>3</td>
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<tr>
<td></td>
<td>85.9</td>
<td>11.1</td>
<td>1.0</td>
<td>3200</td>
<td>9</td>
<td>&lt;1</td>
<td>3</td>
<td>1.6</td>
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</table>

* Pentane Insolubles
residue.

The processing conditions required to hydrotreat the bitumen were more severe than those required for the bitumen-derived liquid. The process operating variable range for bitumen hydrotreating over both the HDM and HDN [18,146,149] catalysts and for bitumen-derived liquid hydrotreating over the HDN catalyst [18,147,149] are summarized in Table 4.3 and in Figure 4.1.

The extent of nitrogen removal was the key reactivity parameter followed during the course of this study; however, the key operating parameter followed on the catalyst testing unit during the run was the specific gravity of the total liquid product. The nitrogen content of the total liquid products produced during hydrotreating the Whiterocks bitumen and bitumen-derived liquid over HDM and HDN catalysts is plotted as a function of API gravity in Figure 4.2. The similarity between the trends indicates that the nitrogen-gravity correlation for the hydrodenitrogenation of bitumen and bitumen-derived liquid could be used with confidence as an online guide to estimate the real time influence of changes in operating variables during the course of the study.

Although the bitumen-derived liquid data [18,147] were obtained under the same sets of conditions as the bitumen data [18,146], the hydrotreated bitumen-derived liquid samples are clustered at lower product nitrogen levels than the hydrotreated bitumen samples. Clearly, the bitumen nitrogen is more refractory than the bitumen-derived liquid nitrogen. The difference is most likely due to the higher molecular weight of the bitumen.
Table 4.3

Process Operating Variable Ranges and Base Case Conditions for Bitumen and Bitumen-Derived Liquid Hydrotreating

<table>
<thead>
<tr>
<th></th>
<th>Bitumen</th>
<th>Bitumen-Derived Liquid</th>
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<tr>
<td></td>
<td>[18,146,149]</td>
<td>[18,147,149]</td>
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<tr>
<td><strong>Base Case Conditions</strong></td>
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<tr>
<td>Temperature, K(°F)</td>
<td>642(696)</td>
<td>618(653)</td>
</tr>
<tr>
<td>Pressure, MPa(psia)</td>
<td>13.7(1980)</td>
<td>13.7(1980)</td>
</tr>
<tr>
<td>WHSV, h⁻¹</td>
<td>0.76</td>
<td>0.78</td>
</tr>
<tr>
<td>LHSV, h⁻¹</td>
<td>0.45</td>
<td>0.48</td>
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<tr>
<td><strong>Process Variable Ranges</strong></td>
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<tr>
<td>Temperature, K(°F)</td>
<td></td>
<td>616-711(650-820)</td>
</tr>
<tr>
<td>Pressure, MPa(psia)</td>
<td></td>
<td>11.0-16.9(1600-2450)</td>
</tr>
<tr>
<td>WHSV, h⁻¹</td>
<td>0.24-1.38</td>
<td></td>
</tr>
<tr>
<td>LHSV, h⁻¹</td>
<td>0.14-0.81</td>
<td></td>
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</table>
Figure 4.1

Operating Conditions for Bitumen and Bitumen-Derived Liquid
Hydrotreating over HDM and HDN Catalysts
Bitumen HT over an HDM Catalyst

Bitumen HT over an HDN Catalyst [18,146]

Bitumen-Derived Liquid HT over an HDN Catalyst [18,147]
Figure 4.2

Nitrogen Concentration versus Total Liquid Product API Gravity
Nitrogen Concentration [wt%]

API Gravity

- Bitumen HT over an HDM Catalyst
- Bitumen HT over an HDN Catalyst [18,146]
+ Bitumen-Derived Liquid HT over an HDN Catalyst [18,147]
Hydrotreated Bitumen over an HDM Catalyst

The chemical and physical properties of the hydrotreated total liquid products produced from bitumen and bitumen-derived liquid at various reaction conditions over an HDN catalyst were reported by Longstaff and co-workers [18,147-149].

The total liquid products produced were upgraded relative to the bitumen (Tables 4.4 through 4.6) as a result of hydrotreating the bitumen over an HDM catalyst. The HDM catalyst selectively removed nickel in the feed under all reaction conditions. The maximum nickel removal was 81.8% at low WHSV, 0.24 h⁻¹ and a temperature of 666 K. Sulfur removal occurred to a greater extent than nitrogen removal which seems to be reasonable considering the need for hydrogenation of the ring prior to nitrogen removal. Sulfur removal ranged from 14.9% to 77.4% whereas nitrogen removal ranged from 2.3% to 29.0%. It is interesting to note that at the least severe conditions there appeared to be an increase in the sulfur content of the hydrotreated total liquid product relative to the bitumen. This may be related to the low sulfur content in the feed. The maximum Conradson carbon residue conversion, 43.4%, was achieved at low WHSV of 0.24 h⁻¹ and a temperature of 666 K.

The pour point of the total liquid product was 279 K at 685 K whereas it was 319 K for the bitumen. This change indicated that the HDM catalyst exhibited little cracking activity under the conditions used in this study. The API gravity was increased from 11.7 to 18.3 °API at low WHSV of 0.24 h⁻¹. Residuum conversion ranged from 10.6% to 61.2%.
Table 4.4

Elemental Analysis of the Bitumen and the Hydrotreated Total Liquid Products
Produced over a Commercial HDM Catalyst

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<tr>
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<td>Whiterocks Bitumen</td>
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<td>11.6</td>
<td>1.29</td>
<td>3334</td>
<td>72</td>
<td>1.6</td>
<td></td>
<td></td>
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<tr>
<td>Temperature:</td>
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<td></td>
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</tr>
<tr>
<td>D-29</td>
<td>620</td>
<td>13.7</td>
<td>0.77</td>
<td>85.3</td>
<td>11.4</td>
<td>1.23</td>
<td>4220</td>
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<td>1.26</td>
<td>2720</td>
<td>55</td>
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<tr>
<td>D-11</td>
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<td>0.77</td>
<td>85.5</td>
<td>11.8</td>
<td>1.15</td>
<td>2030</td>
<td>23</td>
<td>1.7</td>
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<tr>
<td>D-23</td>
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<td>11.7</td>
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<td>1930</td>
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<td>85.8</td>
<td>11.3</td>
<td>1.10</td>
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<td>2030</td>
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<td>1720</td>
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<td>85.5</td>
<td>11.8</td>
<td>1.15</td>
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*Atomic Ratio
Table 4.5

Selected Properties of the Bitumen and the Hydrotreated Total Liquid Products

Produced over a Commercial HDM Catalyst

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**Temperature:**

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**Pressure:**

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<td>287</td>
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<td>0.76</td>
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**WHSV:**

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<td>0.24</td>
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<td>281</td>
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<td>13.7</td>
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<tr>
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<td>13.8</td>
<td>0.77</td>
<td>8.5</td>
<td>287</td>
</tr>
<tr>
<td>D-25</td>
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<td>1.38</td>
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<td>295</td>
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Table 4.6

Yield of Distillate Fractions Produced in Bitumen Hydrotreating over an HDM Catalyst

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<td>40.9</td>
<td>46.5</td>
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<td>D-20</td>
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<td>13.6</td>
<td>0.77</td>
<td>0.8</td>
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<td>665</td>
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<td>0.77</td>
<td>1.3</td>
<td>1.5</td>
<td>10.2</td>
<td>48.2</td>
<td>38.1</td>
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</tr>
<tr>
<td>D-23</td>
<td>673</td>
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<td>0.76</td>
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<tr>
<td>D-27</td>
<td>685</td>
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<td>0.76</td>
<td>3.3</td>
<td>5.3</td>
<td>15.4</td>
<td>49.5</td>
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<td>55</td>
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<tr>
<td><strong>Pressure:</strong></td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>D-17</td>
<td>665</td>
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<td>0.77</td>
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<td>38.1</td>
<td>41</td>
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<tr>
<td>D-21</td>
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<td>15.3</td>
<td>0.76</td>
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<td>4.0</td>
<td>9.7</td>
<td>48.0</td>
<td>36.8</td>
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<tr>
<td>D-13</td>
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<td>0.77</td>
<td>1.3</td>
<td>6.2</td>
<td>10.7</td>
<td>45.6</td>
<td>34.7</td>
<td>66</td>
</tr>
<tr>
<td><strong>WHSV:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>10.7</td>
<td>52.5</td>
<td>32.5</td>
<td>48</td>
</tr>
<tr>
<td>D-11</td>
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<td>0.77</td>
<td>1.3</td>
<td>1.5</td>
<td>10.2</td>
<td>48.2</td>
<td>38.1</td>
<td>41</td>
</tr>
<tr>
<td>D-25</td>
<td>662</td>
<td>13.6</td>
<td>1.38</td>
<td>0.9</td>
<td>1.8</td>
<td>8.4</td>
<td>42.1</td>
<td>46.5</td>
<td>31</td>
</tr>
</tbody>
</table>
Upflow Mode Operation

Laboratory-scale catalytic reactors are frequently used to simulate commercial reactors. However, plug-flow operation is difficult to attain in the trickle-bed mode due to low length-to-diameter ratios of laboratory-scale reactors [89,95,99,150,151]. The reactor diameter used in this study was 2.54 cm and the catalyst was confined to a section of the reactor 30.4 cm long which gave a reactor diameter-to-catalyst particle diameter ratio of 16. It has been reported [89] that hydrodynamic problems associated with liquid distribution and wall flow decrease with an increase in the reactor diameter-to-particle diameter ratio above 10. A reactor diameter-to-particle diameter ratio of 16 would have been expected to have been sufficient to ensure minimal liquid distribution and wall effects for intermediate petroleum feedstocks (°API gravity > 20 °API). However, heavy oils (°API gravity > 10 °API; μ < 10,000 cps) and bitumens (°API gravity < 10 °API; μ > 10,000 cps) may exhibit coning and incomplete wetting of the catalyst even when the reactor diameter-to-particle diameter is 16. The criterion for minimum reactor length which minimizes axial dispersion in shallow, trickle-bed reactors was developed by Mears [108] and is given by Equation (4-1):

\[
\frac{L}{d_e} > \frac{20n}{\ln \frac{C_f}{C_p}} \text{Bo} \quad (4-1)
\]

where \( L \) is the length of reactor bed, \( d_e \) is the equivalent spherical diameter of the catalyst particles, \( n \) is the order of reaction, \( \text{Bo} \) is the Bodenstein number or the liquid particle Peclet number, \( C_f \) is the feed concentration, and \( C_p \) is the product concentration. The Mears criterion [108] was used to assess the feasibility of operating the laboratory reactor used to study the hydrotreating of bitumen and
bitumen-derived liquid in the trickle-bed mode. Even though the criterion was satisfied for downflow or trickle bed operation, the low superficial mass velocities in the reactor may lead to inefficient catalyst utilization, especially for shaped catalysts [110]. Wind et al. [110] proposed that reversing the direction of liquid flow from downflow to upflow in a laboratory-scale reactor would improve catalyst utilization comparable to that attained in commercial units. It also was shown that the utilization of shaped catalysts would vary less in the upflow than in the downflow mode owing to improved wetting, reduced channelling and reduced back-mixing. Thus, the upflow mode which improves catalyst utilization, eliminates channelling and simulates commercial downflow reactor behavior was chosen for these studies.

Plug-Flow Equations

The rate expressions for hydrodenitrogenation, hydrodesulfurization and hydrodemetallation contain a power-law dependence on hydrogen partial pressure. It was, therefore, necessary to estimate the hydrogen partial pressure at the various process operating conditions.

Vapor phase hydrogen fugacities were determined using the Grayson-Streed method [152]. Flash calculations were performed using the Process Simulation Program developed by Simulation Sciences Inc. [153] and parameters calculated by Longstaff [18,146,147] and Hwang [154]. The calculations indicated that vapor phase was predominately hydrogen (Table 4.7) at the reaction conditions employed to hydrotreat the Whiterocks bitumen and bitumen-derived liquid. This is mainly due to the \( \frac{H_2}{oil} \) ratio (\( =890 \text{ m}^3/\text{m}^3 \); 5,000 scf/bbl) used in this study.
Table 4.7

Influence of Operating Variables on Vapor Composition during Bitumen Hydrotreating over an HDM Catalyst

<table>
<thead>
<tr>
<th>Run I.D.</th>
<th>Temperature [K]</th>
<th>Pressure [MPa]</th>
<th>WHSV [h⁻¹]</th>
<th>Vapor [mol%]</th>
<th>Liquid [mol%]</th>
<th>H₂ [mol% in vapor]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-29</td>
<td>620</td>
<td>13.7</td>
<td>0.77</td>
<td>94.6</td>
<td>5.4</td>
<td>98.8</td>
</tr>
<tr>
<td>D-18</td>
<td>642</td>
<td>13.6</td>
<td>0.77</td>
<td>94.6</td>
<td>5.4</td>
<td>97.3</td>
</tr>
<tr>
<td>D-20</td>
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<td>0.77</td>
<td>94.3</td>
<td>5.7</td>
<td>98.2</td>
</tr>
<tr>
<td>D-11</td>
<td>665</td>
<td>13.8</td>
<td>0.77</td>
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<td>5.9</td>
<td>98.2</td>
</tr>
<tr>
<td>D-23</td>
<td>673</td>
<td>13.7</td>
<td>0.76</td>
<td>94.2</td>
<td>5.8</td>
<td>98.0</td>
</tr>
<tr>
<td>D-27</td>
<td>685</td>
<td>13.7</td>
<td>0.76</td>
<td>94.4</td>
<td>5.6</td>
<td>96.3</td>
</tr>
<tr>
<td>Pressure:</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>D-17</td>
<td>665</td>
<td>11.3</td>
<td>0.77</td>
<td>95.0</td>
<td>5.0</td>
<td>96.2</td>
</tr>
<tr>
<td>D-11</td>
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<td>13.8</td>
<td>0.77</td>
<td>94.1</td>
<td>5.9</td>
<td>98.2</td>
</tr>
<tr>
<td>D-21</td>
<td>665</td>
<td>15.3</td>
<td>0.76</td>
<td>93.9</td>
<td>6.1</td>
<td>97.6</td>
</tr>
<tr>
<td>D-13</td>
<td>664</td>
<td>16.7</td>
<td>0.77</td>
<td>93.7</td>
<td>6.3</td>
<td>96.0</td>
</tr>
<tr>
<td>WHSV:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-15</td>
<td>666</td>
<td>13.6</td>
<td>0.24</td>
<td>94.2</td>
<td>5.8</td>
<td>96.4</td>
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<tr>
<td>D-19</td>
<td>665</td>
<td>13.7</td>
<td>0.43</td>
<td>94.0</td>
<td>6.0</td>
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<tr>
<td>D-11</td>
<td>665</td>
<td>13.8</td>
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<td>94.1</td>
<td>5.9</td>
<td>98.2</td>
</tr>
<tr>
<td>D-25</td>
<td>662</td>
<td>13.6</td>
<td>1.38</td>
<td>94.3</td>
<td>5.7</td>
<td>98.6</td>
</tr>
</tbody>
</table>
Evaluation of Plug-Flow Assumption

The plug-flow assumption for the upflow operating mode was evaluated using two models; one assumes plug-flow and a second accounts for possible deviations from plug-flow [95,99].

Plug-Flow \textit{nth Order/Kinetics}

The rate expressions for heteroatom removal contain a power-law dependence on hydrogen partial pressure. The rate expression for \textit{nth order plug-flow} is given by:

$$\frac{dC_i}{dt} = -k C_i^n P_H^\beta$$  \hspace{1cm} (4-2)

where $C_i$ is an appropriate representation of the bitumen or bitumen-derived liquid concentration, $k$ is the apparent rate constant, $n$ is a reaction order, $P_H$ is hydrogen partial pressure and $\beta$ is a power term for hydrogen partial pressure.

The solution of the plug-flow equation for \textit{nth order kinetics} is given by:

$$\ln \frac{C_{i,\text{feed}}}{C_{i,\text{prod}}} = \frac{k P_H^\beta}{\text{WHSV}}$$  \hspace{1cm} (4-3)

$$\frac{1}{C_{i,\text{prod}}} = \frac{1}{C_{i,\text{feed}}} \frac{(n-1)k P_H^\beta}{\text{WHSV}}$$  \hspace{1cm} for $n \neq 1$ (4-4)

where $k = k_0 \exp\left(-\frac{E}{RT}\right)$, $n$ is reaction order, $C_{i,\text{feed}}$ is the feed concentration, $C_{i,\text{prod}}$ is the product concentration, $k_0$ is the pre-exponential factor, $E$ is the apparent activation energy and $R$ is the Universal gas constant.
Yui and Sanford [95,99] recommended that the WHSV should be replaced by WHSV$^\alpha$ to compensate for deviations from plug-flow behavior. These deviation arise because of the lower superficial mass velocities achieved in the laboratory-scale reactors relative to those obtained in the commercial reactor when it was operated in a trickle-bed mode. The integrated equation for nonplug-flow, nth order kinetics is given by

$$
\ln \frac{C_{\text{feed}}}{C_{\text{prod}}} = \frac{k P_H^b}{\text{WHSV}^\alpha}
$$

for $n=1$ \hspace{1cm} (4-5)

$$
\frac{1}{C_{\text{prod}}^{n-1}} - \frac{1}{C_{\text{feed}}^{n-1}} = \frac{(n-1)k P_H^b}{\text{WHSV}^\alpha}
$$

for $n\neq1$ \hspace{1cm} (4-6)

where $k = k_0 \exp \left( -\frac{E}{RT} \right)$.

The kinetic parameters were determined by a nonlinear regression technique which used the Levenberg-Marquardt method [155]. Subroutines from the MINPACK package were used [156]. The results, presented in Table 4.8, indicated that the exponent ($\alpha$) on the WHSV was very close to 1 for the hydrotreating of bitumen and bitumen-derived liquid over both HDM and HDN catalyst when the reactor was operated in the upflow mode. Thus, the plug-flow equation was valid for use in this study. The fact that the value of $\alpha$ was slightly greater than one is attributed to experimental error.

Furthermore, when the terms on the left-hand side in Equations (4-3) through (4-6) are plotted against $(1/$WHSV) or $1/($WHSV$)^\alpha$, the resulting straight lines should pass through the origins if the plug-flow assumption is valid. The plots for heteroatom removal for the bitumen-derived liquid and the bitumen (Figure 4.3) demonstrate that the fixed-bed catalytic reactor used in this study
Table 4.8

Values of the Power $\alpha$ on the Space Velocity to Account for Deviations from Plug-Flow Operation

<table>
<thead>
<tr>
<th>Empirical Power Term for Space Velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bitumen Hydrotreating over an HDM Catalyst</strong></td>
</tr>
<tr>
<td>Hydrodenitrogenation</td>
</tr>
<tr>
<td>Hydrodesulfurization</td>
</tr>
<tr>
<td>Residuum conversion</td>
</tr>
<tr>
<td>Hydrodemetallation (Ni Removal)</td>
</tr>
</tbody>
</table>

| **Bitumen Hydrotreating over an HDN Catalyst** |
| Hydrodenitrogenation | 1.05 |
| Hydrodesulfurization | 1.08 |
| Residuum conversion | 0.97 |

| **Bitumen-Derived Liquid Hydrotreating over an HDN Catalyst** |
| Hydrodenitrogenation | 0.95 |
| Hydrodesulfurization | 1.01 |
| Residuum conversion | 0.98 |
Figure 4.3

Test of Plug-Flow Assumption for HDN and HDS of Bitumen and Bitumen-Derived Liquid over an HDN Catalyst
Hydrodenitrogenation of Bitumen-Derived Liquid over an HDN catalyst

Hydrodesulfurization of Bitumen over an HDN catalyst

Nickel Removal of Bitumen over an HDM catalyst

\[ \frac{1}{(\text{WHSV})^\alpha} \]

\[ \frac{1}{(\text{WHSV})^\alpha} \]

\[ \frac{1}{(\text{WHSV})^\alpha} \]

\[ \Delta \text{ Plug-Flow Approach (nth order)} \]

\[ \square \text{ Nonplug Flow Approach (nth order)} \]
operated under plug-flow conditions when the feed was introduced in upflow mode. Thus, the plug-flow assumption is valid for the upflow operating mode in the laboratory-scale reactor and the plug-flow equation (4-3) was used to analyze the data.

**Alternative Kinetic Representation**

Nickel removal from bitumen over an HDM catalyst and HDS for bitumen and HDN for bitumen-derived liquid over an HDN catalyst exhibited reaction orders greater than one when the data was analyzed by an nth order kinetic approach. Also, residuum conversion for bitumen and bitumen-derived liquid \([18,147]\) over both the HDM and HDN \([18,146]\) catalysts were found to follow higher than first-order kinetics. This indicated that a range of reactivities for heteroatom and residuum compounds was being observed \([157]\). When a significant fraction of the heteroatomic and/or the residuum species are present in unreactive fractions such as asphaltenes, the removal and/or conversion kinetics can be represented by two parallel first-order reactions.

The basis of the alternative model is to assume that the feedstock consists of two reactive lumps or fractions; a facile fraction and a refractory fraction. The rate of removal or conversion of the refractory fraction is presumed to be considerably slower than that of the facile fraction. For the case of HDN of bitumen-derived liquid \([18,147]\), this can be partly attributed to partial dehydrogenation of nitrogen containing compounds during bitumen pyrolysis. Therefore, the conversion or removal of species which gave an apparent order greater than unity was modeled by two parallel first-order reactions \([158]\).

This model has been used to explain hydroprocessing kinetics \([81,82, 159-161]\). Richardson et al. \([81]\) proposed that, although the desulfurization rate of different individual sulfur compounds follow first-order rate expressions, when
these compounds are simultaneously desulfurized the combined results provide an apparent second-order behavior. Oleck and Sherry [159] also reported a similar observation for the desulfurization of an atmospheric reduced Arabian Light crude oil. The desulfurization of nonasphaltenic sulfur compounds is extremely fast and that of asphaltenic sulfur compounds is slow. Both are first-order reactions and the whole may be regarded as a second-order reaction. Frye and Mosby [160] reported that the desulfurization data for three compounds found in a cycle oil feedstock were well organized by a first-order model. Therefore, residuum desulfurization can be considered to be a series of first-order reactions of decreasing rate constants such that the sequence of reactions leads to an apparent second-order dependence [161]. Richardson and Alley [81] suggested that the apparent order with respect to space-time depends on the ratio of the fastest and slowest reactions.

The reaction scheme is presented in equation (4-7).

\[
\begin{align*}
    A_1 & = \gamma A & \xrightarrow{k_1} & B \\
    A_2 & = (1-\gamma) A & \xrightarrow{k_2} & B
\end{align*}
\]

where A₁ represents the facile portion of the heteroatom or residuum fraction in the feedstock and A₂ represents the refractory portion. The reaction scheme is written such that the apparent first-order rate constant k₁ is larger than the apparent first-order rate constant k₂. The parameter \( \gamma \) is the facile fraction of the heteroatom or residuum fraction which is more reactive and \( 1-\gamma \) is the refractory fraction which is less reactive. The integrated rate expression is given by Equation (4-8).
where the rate constants are given by the Arrhenius equation

\[ k_1 = k_{10} \exp \left( -\frac{E_1}{RT} \right) \]

\[ k_2 = k_{20} \exp \left( -\frac{E_2}{RT} \right) \]

and \( k_{10} \) and \( E_1 \) and \( k_{20} \) and \( E_2 \) are the pre-exponential factors and apparent activation energies for facile and refractory heteroatom or residuum fractions, respectively.

The kinetic parameters determined for the two-parallel first-order reactions scheme for HDS, HDN, HDM and residuum conversion are presented in Table 4.9. The objective function \([162,163]\) (OF) which represented the minimization of the function defined in Equation (4-9) was computed.

\[ OF = \sum_{i=1}^{n} \left| C_{P}^{\text{exp}} - C_{P}^{\text{model}} \right|^2 \] (4-9)

The values for objective function indicated that the two-parallel first-order reactions provided a reasonable representation of the data. Experimental and calculated values for Ni removal over an HDM catalyst for both the nth order and two parallel first-order reactions representation are compared in Figure 4.4.
<table>
<thead>
<tr>
<th></th>
<th>HDM</th>
<th>Residuum Conversion</th>
<th>HDS</th>
<th>HDN</th>
</tr>
</thead>
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<tr>
<td>$\gamma$</td>
<td>0.67</td>
<td>0.74</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>$k_{10}$</td>
<td>$9.8 \times 10^4$</td>
<td>$1.3 \times 10^{12}$</td>
<td>$4.3 \times 10^{11}$</td>
<td>$3.8 \times 10^{12}$</td>
</tr>
<tr>
<td>$k_{20}$</td>
<td>$8.5 \times 10^5$</td>
<td>$7.9 \times 10^6$</td>
<td>$6.3 \times 10^{12}$</td>
<td>$1.6 \times 10^{11}$</td>
</tr>
<tr>
<td>$E_1$ [kJ/mol]</td>
<td>94</td>
<td>124</td>
<td>142</td>
<td>160</td>
</tr>
<tr>
<td>$E_2$ [kJ/mol]</td>
<td>81</td>
<td>177</td>
<td>170</td>
<td>158</td>
</tr>
<tr>
<td>OF</td>
<td>$6.0 \times 10^6$</td>
<td>12.8</td>
<td>$1.4 \times 10^4$</td>
<td>$1.2 \times 10^3$</td>
</tr>
</tbody>
</table>
Observed versus Predicted Nickel Content of the Total Liquid Product Produced during Bitumen Hydrotreating over an HDM Catalyst
Computation of Kinetic Parameters

Two methods were used to obtain the kinetic parameters for hydrotreating bitumen and bitumen-derived liquid. The first was a conventional kinetic analysis using a graphical method (Longstaff et al. [18,147]) and the other was a nonlinear regression analysis. The conventional analysis consisted of fixing two operating variables, and changing one variable to obtain data from which the required kinetic parameters were calculated. This method clearly detects the effect of each operating variable; however, many experiments are required since two variables are fixed in each set of experiments. The kinetic parameters for the general plug-flow equations were determined simultaneously by nonlinear regression analysis thus the need to fix two variables at a time was avoided. However, the effect of each variable is not clearly demonstrated. In addition, due to a limited number of data points and the relatively large number of parameters which must be simultaneously determined, the final results may be misleading.

The kinetic parameters for hydrodenitrogenation determined by conventional and nonlinear regression kinetic analyses for HDN of bitumen and bitumen-derived liquid are presented in Table 4.10.

Process Variable Studies

The two most important reactions taking place in bitumen hydrotreating are thermal cracking to lighter products and catalytic hydrogenation related to the removal of heteroatoms [12,164]. Both of these reactions are dependent upon the residence time of the feedstock in the reactor and/or the contact time, the temperature of the reaction and the hydrogen partial pressure in the reactor.
Table 4.10

Comparison of Kinetic Parameters for Hydrodenitrogenation

<table>
<thead>
<tr>
<th></th>
<th>Bitumen HDN over an HDM Catalyst</th>
<th>Bitumen HDN over an HDN Catalyst</th>
<th>Bitumen-Derived Liquid HDN over an HDN Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
<td>Nonlinear</td>
<td>Conventional</td>
</tr>
<tr>
<td>n</td>
<td>1.0</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>α</td>
<td>1.0</td>
<td>0.99</td>
<td>1.0</td>
</tr>
<tr>
<td>β</td>
<td>1.1</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>$k_o$</td>
<td>$2.8 \times 10^4$</td>
<td>$7.3 \times 10^4$</td>
<td>$1.3 \times 10^7$</td>
</tr>
<tr>
<td>$E_a$ [kJ/mol]</td>
<td>71</td>
<td>98</td>
<td>92</td>
</tr>
<tr>
<td>OF</td>
<td>$7.7 \times 10^2$</td>
<td>$5.4 \times 10^3$</td>
<td>$1.5 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
The primary process variables investigated in this study were the liquid hourly space velocity, the reactor temperature and the hydrogen partial pressure.

**Space Velocity**

The space velocity experiments were conducted at a fixed reaction temperature (664 K) and pressure (13.7 MPa) and the effect of space velocity on product distribution and yields is presented in Table 4.11. The effect of space velocity plays an important role in bitumen hydrotreating over an HDM catalyst. In the space velocity ranges studied here, heteroatom removal and residuum conversion increased significantly at lower space velocities. Abdul-Halim et al. [165] reported that LHSV exerted a greater influence on the sulfur removal than temperature at relatively low temperatures. Tables 4.11 and 4.12 represent that the increments of hydrogen consumption from 31 to 75 m$^3$/m$^3$ made 29% of nitrogen removal possible. Also, residence time increments by a factor of six led to 77% of sulfur and 82% nickel removals over a low activity HDM catalyst. Decreasing trends were shown in Conradson carbon residue conversion as WHSV decreased. At 0.24 h$^{-1}$ WHSV, there was about 43% reduction in CCR during hydrotreating.

The product distribution and yields are presented in Figure 4.5. The scatter in the naphtha yields may have been related to the loss of this fraction when the total liquid product samples were stripped of NH$_3$ and H$_2$S prior to elemental analysis. Residuum content is significantly decreased as the residence time of the liquid increased; about 61% residuum conversion was achieved at 0.24 h$^{-1}$ WHSV. The gas, naphtha and distillate fractions monotonically increased with increasing residence time. The gas-oil yield exhibited a maximum at a residence time of 2.3 hours. The maximum in gas-oil
Table 4.11

Effect of WHSV on Product Distribution and Yields
at 664 K (735 °F) and 13.7 MPa (1980 psia)

<table>
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<tr>
<th>Run No.</th>
<th>D-15</th>
<th>D-19</th>
<th>D-11</th>
<th>D-25</th>
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<td>1.3</td>
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<td>662</td>
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<td>13.6</td>
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<td>6.1</td>
<td>7.9</td>
<td>8.5</td>
<td>8.9</td>
</tr>
<tr>
<td>(H_2) consumption, (m^3/m^3)</td>
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<td>48</td>
<td>41</td>
<td>31</td>
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<td>(C_1-C_4), wt%</td>
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</tr>
<tr>
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<td>8.4</td>
</tr>
<tr>
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<td>52.5</td>
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<tr>
<td>&gt; 811 K, wt%</td>
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<td>32.5</td>
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<tr>
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<td>100.4</td>
<td>99.7</td>
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Heteroatom Removal and Residuum and Conradson Carbon Conversions of the Bitumen over a Commercial HDM Catalyst

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<th>Pressure</th>
<th>WHSV</th>
<th>N [%]</th>
<th>S [%]</th>
<th>Ni Residuum [%]</th>
<th>Conradson Carbon Residue [%]</th>
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<td>[K]</td>
<td>[MPa]</td>
<td>[h⁻¹]</td>
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<td>0.77</td>
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<td>23.6</td>
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<td>57.9</td>
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<td>54.4</td>
<td>19.9</td>
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</table>
Figure 4.5

Effect of WHSV on Product Distribution and Yields
at 664 K (735°F) and 13.7 MPa (1980 psia)
yields has been reported by other workers [18,146,164] and implies that gas-oil is formed from residuum and subsequently cracks to produce distillate, naphtha and gas.

The effect of WHSV on the conversion of nitrogen and sulfur at 664 K and 13.7 MPa is shown in Figure 4.6. The plots of the natural logarithm of the fractions of nitrogen and sulfur remaining versus residence time (reciprocal of space velocity) were straight lines and passed through 1 on the log scale y-axis. This indicated that both HDN and HDS removal from bitumen over an HDM catalyst followed first-order kinetics. Also, the differences in the slopes of Figure 4.6 indicates that sulfur removal from the bitumen is easier than nitrogen removal.

First-order nitrogen removal kinetics over an HDN catalyst has been reported previously [15,95,99]. Yui and his coworkers [95,99] showed first-order kinetics for HDN of bitumen-derived coker and hydrocracker heavy gas-oils and Riley [15] reported first-order nitrogen dependence for HDN of heavy oils. The consistent observation of first-order kinetics implies a uniform refractoriness for nitrogen compounds in the bitumens; bitumen-derived liquids, and heavy oils studied.

Hydrotreating studies with different petroleum residua using Co-Mo-alumina catalysts have shown that the hydrodesulfurization reaction may follow apparent first-order [166], pseudo-second order [167] or second-order [168] kinetics with respect to sulfur compounds. Higher than first-order or second-order kinetics for HDS in heavy oil hydrotreating is supported by the majority of experimental results [73]. HDS of Syncrude bitumen-derived coker and hydrocracker heavy gas-oil obeyed an apparent 1.5 order [95,99] over a NiMo catalyst in a trickle-bed reactor. The ranges of the reaction conditions were 623-673 K, 0.7-1.5 h⁻¹ LHSV and 7-11 MPa. Second-order kinetics were reported for
Figure 4.6

First-Order Kinetic Plots for Nitrogen and Sulfur Removal over an HDM Catalyst at 664 K (735°F) and 13.7 MPa (1980 psia)
HDN Reaction Follows First Order Kinetics Over an HDM Catalyst

HDS Reaction Follows First Order Kinetics Over an HDM Catalyst
HDS in coal conversion studies [169] and for HDS in petroleum residuum studies [170-172]. Abdul-Halim [165] used second-order kinetics to organize sulfur removal data for deasphalted oil and Wei et al. [158] used two parallel first-order reactions to obtain apparent overall second-order dependence for HDS.

As indicated earlier, it was found that bitumen HDS over an HDM catalyst followed first-order kinetics. The first-order behavior may be related to the naphthenic nature of the Uinta Basin bitumens compared with conventional heavy oils. George [173] reported that HDS and HDN of feedstocks derived from coprocessing of heavy oil and coal (24 °API; 703 K) followed irreversible first-order kinetics at 673 K, 5 h⁻¹ LHSV, and 13.3 MPa over a commercial NiMo catalyst. Billon et al. [166] also obtained the first-order kinetics for the HDS of petroleum residuum over a CoMo catalyst.

In contrast with nitrogen and sulfur removal, nickel removal and residuum conversion of Whiterocks bitumen over an HDM catalyst did not follow first-order kinetics. Nickel removal and residuum conversion followed higher than first-order kinetics overall. Oleck and Sherry [159] reported that a good fit of the reaction rate data was obtained with second-order kinetics for nickel and vanadium removal from Lagomedio (Venezuelan) atmospheric residuum over CoMo/Al₂O₃ catalysts.

A first-order kinetic plot (Figure 4.7) for nickel removal indicated two distinct regions. This implies that there may be two different classes of nickel species in the feed. One class of nickel reacts considerably faster than the other class of nickel compounds and each compounds follow first-order behavior. Because both classes of compounds react simultaneously apparent overall second-order behavior would be expected. Thus, two parallel first-order reactions involving the two classes of nickel compounds (or lumps) was used as
Figure 4.7

First-Order Kinetic Plot for Nickel Removal over an HDM Catalyst at 664 K (735°F) and 13.7 MPa (1980 psia)
Fraction Nickel Remaining

$\text{Fraction Nickel Remaining}$

$\frac{1}{\text{WHSV}[\text{h}]}$
an alternative scheme to represent nickel removal. This representation has been employed by several researchers for analyzing HDM data [158,174].

The simultaneous occurrence of several first-order metal removal reactions with different rates can lead to an apparent reaction order greater than unity just as in hydrodesulfurization [175]. Metal profiles indicating the presence of "easy" and "hard" to remove metal species have been reported for V [176]. Metalloporphyrins, metal species sometimes referred to as "easy" metals, are readily removed resulting in sharp metal gradients near the exterior surface of the pellets at the reactor entrance. The more refractory, "hard" compounds yield more uniform profiles. The liquid phase in the vicinity of the reactor outlet is depleted of the "easy" Ni species and the relatively uniform metal-deposition profiles reflect deposition from the refractory or "hard" Ni compounds. Galiasso et al. [132] reported that pure metalloporphyrins in clean systems are up to 10 times more reactive than naturally occurring metalloporphyrins in petroleum resins and 100 to 500 times more reactive than nickel and vanadyl compounds in Kuwait atmospheric residuum [131].

The kinetic parameter estimation results indicated that the refractory fractions of residuum and nickel were 0.74 and 0.67, respectively. The rate constants at 664 K indicate that the facile residuum and nickel fractions are 7 and 117 times more reactive than those in refractory fractions, respectively. This large difference in rate constants resulted in the apparent higher than first-order kinetics for nickel removal and residuum conversion over an HDM catalyst, even though the refractory nickel and residuum fractions were more than twice the facile nickel and residuum fractions.
Temperature

The effect of temperature on product distribution and yields at a fixed space velocity (0.76 h\(^{-1}\) WHSV) and pressure (13.7 MPa) is presented in Table 4.13. Increasing temperature favorably affected the heteroatom removal reaction rates and promoted an increase in the thermal conversion of residuum. Sooter [177] observed that the desulfurization of raw anthracene oil, over a CoMo/Al\(_2\)O\(_3\) catalyst at 6.9 MPa (1000 psig), increased from 48% to 84% when temperature was increased from 589 K (600°F) to 644 K (700°F). The low sulfur and nickel contents in the feed in this study account for the scatter in the sulfur and nickel data for the total liquid product. The API gravity increased from 12.7 to 18.0 °API as the temperature increased from 620 to 685 K. The increase in API gravity was accompanied by an increase in hydrogen consumption from 6 to 55 m\(^3\)/m\(^3\). The levels of heteroatom removal and residuum conversion were lower in the temperature range studied than those obtained for the WHSV range studied. This may be due to the relatively low temperature range used in this study (620-685 K) compared to the temperature range used in commercial residuum hydroprocessing (620-713 K) [1,27]. Space velocity appears to exert a greater impact on heteroatom removal at low temperatures than the reactor temperature range itself. The nitrogen content decreased only by 17%, the sulfur content decreased by 44% and the nickel content decreased by 68%. The relatively high nickel removal is related to the selectivity of the HDM catalyst used in this study for demetallation and the low metals loading is reflected in heteroatom conversion. Residuum conversion at 685 K and 0.76 h\(^{-1}\) WHSV (56%) was comparable to that obtained at 665 K and 0.24 h\(^{-1}\) WHSV (61%). This indicated that temperature and residence time exhibit a synergism for residuum conversion whereas heteroatom removal over the HDM catalyst was more dependent on residence time than on temperature. The Conradson carbon
Table 4.13

Effect of Temperature on Product Distribution and Yields
at 0.76 h\(^{-1}\) WHSV and 13.7 MPa (1980 psia)

<table>
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<tr>
<th>Run No.</th>
<th>D-29</th>
<th>D-18</th>
<th>D-20</th>
<th>D-11</th>
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<td>673</td>
<td>685</td>
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<td>44.1</td>
<td>38.1</td>
<td>31.9</td>
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<td>99.4</td>
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residue shows about 28% removal at 685 K and the pour point decreased significantly as the reaction temperature increased.

The product distribution and yields are presented in Figure 4.8. The scatter in the C₁-C₄ gas yields were related to the small amount of gas produced during hydrotreating over the low activity HDM catalyst. The naphtha, distillate, and gas-oil yields increased and the residuum content decreased as the reaction temperature increased. The scatter in the naphtha yields may be related to the NH₃ and H₂S stripping procedure described in the experimental section. A maximum in the gas-oil yield was not observed as the temperature increased; however, it is expected that there would be a temperature above 685 K at which the rate of gas-oil conversion to lighter fractions would exceed the rate of residuum conversion to gas-oil.

The apparent activation energy is a measure of the response of the rate constant to temperature. The effect of temperature on the rate constant for nickel and residuum conversion over an HDM catalyst is presented in Figure 4.9. The apparent activation energies were 98 kJ/mol for HDN and 91 kJ/mol for HDS for bitumen hydrotreating over an HDM catalyst. The activation energies of both HDN and HDS suggest that HDN and HDS for this feedstock over an HDM catalyst were not limited by pore diffusion. The activation energy for CCR removal was 156 kJ/mol which may reflect the significance of thermal conversion on CCR removal. The activation energy for HDN (98 kJ/mol) was comparable to literature values [95,99].

Yui and Sanford [99] reported that the apparent activation energies for HDN of coker HGO and hydrocracker HGO were 96 kJ/mol and 75 kJ/mol, respectively. Diaz-Real [178] reported an apparent activation energy of 104 kJ/mol for HDN of a bitumen-derived heavy gas-oil over a NiMo zeolite based
Figure 4.8

Effect of Temperature on Product Distribution and Yields
at 0.76 h⁻¹ WHSV and 13.7 MPa (1980 psia)
Figure 4.9

Arrhenius Plots for Residuum Conversion and Nickel Removal over an HDM Catalyst at 0.76 h⁻¹ WHSV and 13.7 MPa (1980 psia)
Nickel Conversion

Facile
\[ E_{a,1} = 81 \text{ [kJ/mol]} \]

Refractory
\[ E_{a,2} = 94 \text{ [kJ/mol]} \]

Resid Conversion

Facile
\[ E_{a,1} = 124 \text{ [kJ/mol]} \]

Refractory
\[ E_{a,2} = 177 \text{ [kJ/mol]} \]
catalyst. Yui [95] obtained a similar apparent activation energy, 92 kJ/mol, for HDN of a bitumen-derived coker gas-oil.

The apparent activation energy (91 kJ/mol) for HDS of bitumen over an HDM catalyst in this study was somewhat lower than expected [1,76]. This may be related to the chemical composition of the residuum in the bitumen under investigation as compared to the feedstocks for which data have been reported in the literature [1,73,76,99,179]. Bridge et al. [179] reported an apparent activation energy of 125 kJ/mol for desulfurization of an atmospheric residuum from Arabian heavy crude. Beaton and Bertolacini [1] and Beuther and Schmidt [73] reported that the apparent activation energy for HDS of residuum was 117 kJ/mol and for desulfurization of a Kuwait vacuum residuum was 113 kJ/mol. Yui and Sanford [99] reported that the apparent activation energies for HDS for both bitumen-derived hydrocracker and coker HGO over a commercial NiMo catalyst was 129 kJ/mol.

Residuum conversion of bitumen over an HDM catalyst was found to follow higher than first-order kinetics thus two parallel first-order reactions were used to correlate residuum conversion data. Residuum conversion is primarily a thermal reaction thus the higher value of the apparent activation energy than catalytic conversion would be expected [180]. The activation energies for the facile and refractory fractions of the Whiterocks bitumen residuum in bitumen hydrotreating over an HDM catalyst ranged from 124 kJ/mol to 177 kJ/mol, respectively. The fractions of facile and refractory residuum were 0.26 and 0.74, respectively.

In this study the apparent activation energies for the removal of the facile and refractory nickel species were 81 and 94 kJ/mol, respectively. These values of activation energy seem to be reasonable compared with literature values. Quann et al. [27] reported that apparent activation energies for global metal
removal ranged from 42 to 158 kJ/mol depending on the reaction order. For first-order kinetics the activation energies vary from 42 to 75 kJ/mol. Hung et al. [131] reported activation energies of 115 and 142 kJ/mol for Ni-Etio porphyrin and Ni-TPP porphyrin, respectively, over a CoMo/Al₂O₃ catalyst. The temperature ranged from 553 to 623 K and the hydrogen partial pressure ranged from 4 to 12 MPa. Morales et al. [181] reported that the activation energy for VO-TPP porphyrin was 58-60 kJ/mol with CoMo/Al₂O₃, Co/Al₂O₃, Mo/Al₂O₃ catalysts in the temperature range 423-573 K and the hydrogen partial pressure range 1.4-7.4 MPa.

**Pressure**

The effects of hydrogen partial pressure on product distribution and yields at a fixed space velocity and reaction temperature are presented in Table 4.14. The WHSV and temperature were maintained at 0.76 h⁻¹ and 665 K, respectively, in these experiments. Heteroatom removal was only slightly influenced by increasing the pressure relative to the WHSV and temperature. The API gravity and pour point of the total liquid products changed little with respect to increasing pressure, that is; the API gravity of the liquid product increased from 14.9 to 15.5 °API and the pour point decreased from 288 to 284 K as the pressure increased from 11.3 MPa to 16.7 MPa.

The hydrogen consumption increased from 28 to 66 m³/m³ as the pressure increased from 11.3 to 16.7 MPa (Figure 4.10). Hydrogen consumptions in the same range were observed in the WHSV experiments, that is; an increase from 31 to 75 m³/m³ as the WHSV decreased from 1.38 to 0.24 h⁻¹ at 665 K and 13.7 MPa. However, the extent of residuum conversion at high hydrogen consumption was significantly different (~50% greater) when space
Table 4.14

Effect of Pressure on Product Distribution and Yields
at 0.76 h⁻¹ WHSV and 664 K (735 °F)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>D-17</th>
<th>D-11</th>
<th>D-21</th>
<th>D-13</th>
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<td></td>
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<td>15.3</td>
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<td>WHSV, h⁻¹</td>
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<tr>
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<td>0.964</td>
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<td>287</td>
<td>284</td>
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<tr>
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<td>8.5</td>
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</tr>
<tr>
<td>H₂ consumption, m³/m³</td>
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<td>41</td>
<td>43</td>
<td>66</td>
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<td><strong>Elemental Analysis</strong></td>
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<tr>
<td>C, wt%</td>
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<td>S, wt%</td>
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<td>0.20</td>
<td>0.19</td>
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<tr>
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<tr>
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<tr>
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<td>478-616 K, wt%</td>
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<td>616-811 K, wt%</td>
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<td>&gt; 811 K, wt%</td>
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<td>38.1</td>
<td>36.8</td>
<td>34.7</td>
</tr>
<tr>
<td>Liquid yield, vol %</td>
<td>99.5</td>
<td>99.7</td>
<td>99.4</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Figure 4.10

Reactor Pressure versus Hydrogen Consumption for Bitumen Hydrotreating over an HDM Catalyst
velocity was the independent variable than when pressure was the independent variable.

The high hydrogen consumption and low residuum conversion observed when pressure was varied could be due to aromatic ring hydrogenation in the absence of cracking and/or extensive denitrogenation and desulfurization, 13% and 44%, respectively; and was not the result of saturating cracked products. Beuther and Schmid [73] reported an improvement in desulfurization with increasing hydrogen pressure, however, the response to pressure diminished with increasing pressure at pressure above 6.9 MPa. A similar trend was observed in this study over the pressure range investigated. The residuum and CCR conversions were 41% and 23%, respectively, in this study.

Speight [11] reported that heteroatom removal rates are enhanced by an increase in hydrogen partial pressure in accord with model compound studies. Both feedstock and degree of heteroatom removal may influence the magnitude of the hydrogen response. The heavier feedstocks require substantially more hydrogen addition to achieve a fixed level of upgrading relative to conventional feedstocks. Simultaneous removal of other heteroatoms, aromatics saturation, and nonselective hydrocracking of petroleum are responsible for hydrogen consumption.

Figure 4.11 shows the hydrogen partial pressure dependence for reaction rate for nitrogen, sulfur, and Conradson carbon residue conversion. The hydrogen partial pressure dependence ($\beta$) for bitumen hydrotreating over an HDM catalysts in Equation (4-2) were 1.5 for nitrogen, 0.7 for sulfur, and 1.8 for nickel removal and 0.8 for residuum and CCR conversions.

The high value for the nitrogen removal confirms the presumption [113,114,116] that aromatic ring hydrogenation is required prior to hydrogenolysis of the carbon-nitrogen bond. This step is not necessarily
Figure 4.11

Hydrogen Partial Pressure Dependence for Reaction Rate
for Nitrogen, Sulfur, and CCR Conversion
In PH2 [MPa]

- Nitrogen
- Sulfur
- CCR

\[
\beta \text{ for Sulfur} = 0.7
\]

\[
\beta \text{ for CCR} = 0.8
\]

\[
\beta \text{ for Nitrogen} = 1.5
\]

\[
F = \ln \left( \frac{C_{i,\text{feed}}}{C_{i,\text{prod}}} \right)
\]

\[
\ln (P_{H2}) \text{ [MPa]}
\]
required for the sulfur removal and accordingly sulfur removal results in a lower hydrogen dependence. Residuum conversion is largely dependent on the thermal cracking and hydrogen is consumed in preventing retrograde polymerization.

Yui et al. [95,99] reported that the hydrogen partial pressure power ranged from 1.2 to 1.8 for HDN and from 0.6 to 1.1 for HDS when bitumen-derived coker and hydrocracker gas-oils were hydrotreated. Beaton and Bertolacini [1] reported that desulfurization of residuum responded in a first-order manner to pressure. The low hydrogen partial pressure dependence for HDS of the Whiterocks bitumen compared with literature values (0.7 versus unity) may be related to the naphthenic nature of the Uinta Basin bitumens. This may indicate that hydrogenation becomes more important as the number of aromatic rings increases in the average feed molecule.

Nickel in petroleum exists as soluble organometallic complexes that fall into two categories; metal porphyrins, and nonporphyrin metal complexes. Dean and Whitehead [127] have shown that the majority of the nickel species are present in the 617 K* fraction and are nonporphyrins. The reactivity of the high molecular weight nonporphyrin nickel in an aromatic hydrocarbon structure is therefore sensitive to hydrogen partial pressure. The reported hydrogen partial pressure dependence [131, 181] for HDM varied from 1 to 2.2. The order for nickel removal is likely a function of the rate-limiting metal removal step. The values of hydrogen partial pressure dependence determined in this study are in agreement with these values and seem to be reasonable.
Catalyst Deactivation Rate

The deactivation or aging rate for Whiterocks bitumen hydrotreating over the HDM catalyst was calculated to be 0.18°C/day over approximately 600 hours on-stream which was similar to the deactivation rate obtained over an HDN catalyst (0.20°C/day) [18,147]. The deactivation rate for Whiterocks bitumen-derived liquid hydrotreating over the HDN catalyst [18,147] was also estimated to be the same with those of bitumen hydrotreating over both the HDN [18,146] and HDM catalyst. The similarity in the deactivation rates for the BDL-HDN, BIT-HDN and BIT-HDM systems despite the larger pore size, lower surface area and lower metal loadings of the HDM catalyst relative to the HDN catalyst and the fact that the bitumen-derived liquid contained 1/3 less residuum than the bitumen was puzzling. It is presumed that it may be related to the combinations of thermal and catalytic conversion required to upgrade these heavy oil feedstocks.

Process Variable Effect on Pour Point

The pour point of the hydrotreated total liquid product generally decreased as the temperature and pressure increased, and the space velocity decreased. Temperature and space velocity had the greatest effect on pour point (Figure 4.12). The effect of pressure on pour point was minimal.

Effect of Catalyst and Feed on Conversion

The API gravity was used to correlate the extent of sulfur and nitrogen removal and residuum conversion in the hydrotreated liquid products using two different catalysts (HDM and HDN) and two different feeds (BDL and BIT).

As can be seen in Figures 4.13 through 4.15, heteroatom and residuum conversions correlate with the total liquid product API gravities. Figures 4.13 and 4.14 indicate that the HDM catalyst was less active for heteroatom
Figure 4.12

Pour-Point of Hydrotreated Total Liquid Product
as a Function of Operating Variables
Figure 4.13

Nitrogen Conversion versus API Gravity
Fraction of Nitrogen Converted

API Gravity

- Bitumen HT over an HDM Catalyst
- Bitumen HT over an HDN Catalyst [18,146]
- Bitumen-Derived Liquid HT over an HDN Catalyst [18,147]
Figure 4.14

Sulfur Conversion versus API Gravity
Fraction of Sulfur Converted

- Bitumen HT over an HDM Catalyst
- Bitumen HT over an HDN Catalyst [18,146]
- Bitumen-Derived Liquid HT over an HDN Catalyst [18,147]
Figure 4.15

Residuum Conversion versus API Gravity
Fraction of Residuum Converted

API Gravity

- Bitumen HT over an HDM Catalyst
- Bitumen HT over an HDN Catalyst [18,146]
- Bitumen-Derived Liquid HT over an HDN Catalyst [18,147]
conversion when processing bitumen. Heteroatom removal appeared to represent a continuum for both catalysts (HDN and HDM) and both feedstocks (BDL and BIT) whereas residuum conversion for BDL over the HDN catalyst was distinctly different from residuum conversion for BIT over both the HDN and HDM catalysts. This difference is related to the thermal history of the BDL [148]: pyrolysis of the Whiterocks oil sand to produce the BDL resulted in a significant reduction in boiling range and residuum content; however, it had little influence on heteroatom concentration.

The higher nitrogen and sulfur conversions of bitumen-derived liquid [18,147] compared with those of bitumen over an HDN catalyst [18,146] are likely related to the molecular weight differences between the two feeds which ultimately influenced their reactivities. This explanation seems possible considering that both feedstocks have the same origin and these two experiments were performed at the same operating conditions. The influence of molecular weight on reactivity for heteroatom removal has been discussed previously [182,183]: nitrogen and sulfur conversions are limited by steric hindrance and diffusional constraints. These steric hindrance and diffusional constraints were applied to the results of bitumen hydrotreating over an HDN catalyst [18,146]. These factors seemed to result in the lower conversion of heteroatoms in bitumen than in bitumen-derived liquid over an HDN catalyst. Thus, molecular weight reduction is required prior to heteroatom removal to convert high nitrogen content bitumen to liquid fuels catalytically.

Residuum conversion plots for bitumen and bitumen-derived liquid over an HDN catalyst [18,146,147] in Figure 4.15 exhibit the parallel curves. The displacement of the bitumen-derived liquid curve is related to the molecular weight reduction which occurred during the fluidized bed pyrolysis of the oil sand to produce the bitumen-derived liquid.
The effect that catalyst selection plays on residuum conversion appears to contrast with the work of other researchers [166,184-186] which indicated that residuum conversion is primarily thermal. The residuum conversion in hydrotreating bitumen over an HDN catalyst gives a higher value than that over an HDM catalyst. In addition, the Arrhenius plot for whole residuum conversion shows that the first-order activation energies for bitumen hydrotreating were found to be 132 and 83 kJ/mol for HDM and HDN catalysts, respectively. If residuum conversion is only due to thermal reaction, these two values should be the same. The higher apparent activation energy observed for residuum conversion during the bitumen hydrotreating over an HDM catalyst implies the increasing influence that thermal cracking exhibits when the catalytic activity of the system is reduced. All these results indicate for catalyst/oil systems operating in the ranges of temperature studied that residuum conversion is affected by catalyst selection.

There are two possible explanations for the catalytic effect on residuum conversion. One is related to process operating variables; this study was conducted at lower temperatures (620-685 K) than those reported in the literature (620-713 K) [1,27]. The importance of thermal cracking in the overall residuum conversion would be emphasized if this study had been carried out at higher temperatures. This is basically due to the fact that thermal cracking exhibits a higher activation energy than catalytic cracking.

The second possible explanation is that the catalyst-to-oil ratio used in this study is higher than those used in the literature [1,27]. The system in this study has a very highly concentrated catalyst region which is not diluted. Also, the fixed-bed reactor used in this study had a higher catalyst-to-oil ratio than were used in the dilute catalyst systems such as stirred autoclaves, ebulliated beds or diluted packed beds. In dilute catalyst systems, catalytic cracking is
suppressed whereas thermal cracking remains the same as in the concentrated catalyst systems. Consequently, if thermal and catalytic reactions are approximately equal, it is not possible to compare the results from these two different systems.

**Effect of Catalyst and Feed on Selectivity**

The effect of catalyst and feed selection on the extent of heteroatom removal are shown in Figures 4.16 to 4.18. Sulfur conversions exceed nitrogen conversions as expected since sulfur compounds are known to be more reactive than nitrogen compounds [114]. Heteroatom conversion was lower over the HDM and HDN catalysts when bitumen was used as the feedstock relative to the conversions attained with the bitumen-derived liquid [18,147]. This is due to the steric and diffusional effects which reduce accessibility of heteroatom containing moieties in BIT-HDN system and lower activity of catalyst incorporated in BIT-HDM system.

Residuum conversion in bitumen hydrotreating over an HDM catalyst was reduced relative to an HDN catalyst; however, it was not as significant as the reductions in heteroatom removal. Thermal conversion is not greatly influenced by mass transfer or steric barriers whereas heteroatom removal is more sensitive to catalyst activity, i.e., metal loading, than residuum conversion.

Bitumen hydrotreating over an HDM catalyst indicated that residuum conversion surpassed nitrogen conversion in all cases and was almost the same as sulfur conversion as can be seen in Figure 4.18. In this sense, the results of the bitumen-derived liquid and bitumen hydrotreating over an HDN catalyst demonstrated that heteroatom conversion is more sensitive to catalyst selection than is residuum conversion [18,146,147]. This is because cracking can proceed via a thermal pathway which is unavailable for heteroatom conversion.
Figure 4.16

Nitrogen, Sulfur and Residuum Conversion versus API Gravity for Bitumen-Derived Liquid over an HDN Catalyst System [18,147]
Figure 4.17

Nitrogen, Sulfur and Residuum Conversion versus API Gravity for Bitumen over an HDN Catalyst System [18,146]
Fraction Converted

API Gravity

- Nitrogen
- Sulfur
- Residuum
Figure 4.18

Nitrogen, Sulfur and Residuum Conversion versus API Gravity for Bitumen over an HDM Catalyst System
Molecular Weight Reduction Model for Residuum Conversion

The residuum conversion reaction involves a free-radical mechanism to convert residuum molecules to hydrocarbon gases, naphthas, distillates, and gas-oils. Hydrogen must be present to prevent retrograde polymerization reactions. Mosby et al. [164] showed that the thermal cracking of residuum is not a single first-order reaction and that these cracking reactions are irreversible. The refractory and facile residuum were assumed to crack to form all product fractions (gas-oil, distillate, naphtha, and gases). The rate constants from the model correlate well with intuition in that lower molecular weight reactants have smaller rate constants, and the overall model closely predicts pilot plant results. Mosby et al. [191] reported that the gas-oil yield goes through a maximum at about 30% at 683 K (770°F). This is due to cracking of the gas-oil fraction to lighter products at the higher temperatures. Thermal reaction pathways have been discussed by Savage [187] and Bunger [188], who investigated the reactions of hydrogen during the hydropyrolysis of heavy crudes.

In order to represent the product distributions as a function of process variables, the bitumen and hydrotreated total liquid products were grouped into four lumps; the residuum fraction (R) which boils above 811 K (538°C), the gas-oil fraction (O) with boiling range between 548-811 K (275°C-538°C), the middle distillate fraction (D) which includes C₅ to 548 K (275°C) boiling material, and gases (G) which includes NH₃, H₂S and C₅ to C₄ hydrocarbon gases.

The twelve possible reactions involving these four lumps are shown in the following scheme:
Two assumptions were made to simplify the reaction scheme. First, each reaction was assumed to obey irreversible first-order kinetics, so that reactions 4, 7, 8, 10, 11, and 12 were excluded. The second assumption was that the middle distillate fractions and gases are secondary products. Therefore, reactions 2 and 3 were also disregarded in the final scheme. Accordingly, the simplified reaction scheme for molecular weight reduction can be represented as follows:

\[ R \to O \to D \to G \]

\[ O \to D \to G \]

\[ D \to O \to G \]

\[ G \to D \to G \]

The differential equations describing the system are given by the following equations:

\[
\frac{dC_R}{dt} = -k_{RO}C_R
\]

\[
\frac{dC_O}{dt} = k_{RO}C_R - (k_{OD} + k_{OG})C_O
\]

\[
\frac{dC_D}{dt} = k_{OD}C_O - k_{DG}C_D
\]

\[
\frac{dC_G}{dt} = k_{OG}C_O + k_{DG}C_D
\]
where $C_R$, $C_0$, $C_D$, and $C_G$ represent concentrations of residuum, gas-oils, middle distillates, and gases, respectively. The apparent first-order rate constants; $k_{R0}$, $k_{0D}$, $k_{OG}$, and $k_{DG}$, represent the conversions of residuum to gas-oil, gas-oil to middle distillate, gas-oil to gases and middle distillates to gases, respectively. Reaction rates are usually expressed in terms of molar concentrations for well-defined chemical species and reaction schemes. However, the conversions adopted for lumped kinetic representations of complex reaction schemes are in terms of mass fractions.

The results of the analysis are presented in Table 4.15. The rate of conversion of residuum to gas-oil was about four times greater than that of gas-oil conversion to middle distillates and gases. The production of gases from middle distillates was minimal.

The experimental and calculated values for the residuum, gas-oil, middle distillate, and gas fractions for the molecular weight reduction scheme matched reasonably well (Figures 4.19 and 4.20). The objective function defined in Equation (4-9) was used for computing the differences of the experimental and calculated values [162,163].
Table 4.15

Irreversible First-Order Rate Constants and Objective Functions for the Proposed Molecular Weight Reduction Model at 664 K (735°F) and 13.7 MPa (1980 psia)

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<tr>
<td>( k_{\text{OO}} )</td>
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<td>( k_{\text{OG}} )</td>
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<tr>
<td>Gas-Oil Fraction</td>
<td>2.9 x 10⁻³</td>
</tr>
<tr>
<td>Middle Distillate Fraction</td>
<td>1.1 x 10⁻³</td>
</tr>
<tr>
<td>Gases Fraction</td>
<td>4.8 x 10⁻⁵</td>
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</table>
Figure 4.19

Experimental versus Calculated Yield of Reactant Lumps for Hydrotreating Whiterocks Bitumen over an HDM Catalyst at 664 K (735°F) and 13.7 MPa (1980 psia)
Figure 4.20

Plot of Experimental versus Calculated Values for Residuum Conversion
CHAPTER 5

CONCLUSIONS

1. The plug-flow assumption is appropriate for the hydrotreating of bitumen and bitumen-derived liquid over both HDM and HDN catalysts in the upflow operating mode.

2. The HDM catalyst was effective for nickel and sulfur removal with the Whiterocks bitumen. However, it was ineffective for denitrogenation. Bitumen HDN and HDS followed pseudo first-order kinetics over a commercial HDM catalyst. Nickel removal and residuum conversion gave apparent higher than first-order kinetics. The data were organized by invoking parallel first-order reactions: one involving a facile fraction as reactant and the second involving a refractory fraction as reactant. The activation energies for residuum conversion and metal removal, 124 kJ/mol for facile residuum, 177 kJ/mol for refractory residuum, 81 kJ/mol for facile nickel and 94 kJ/mol for refractory nickel, suggested that residuum conversion and metal removal for bitumen over an HDM catalyst were not limited by pore diffusion.

3. HDM catalyst deactivation was about 0.18°C/day during bitumen hydrotreating over a commercial HDM catalyst.

4. Sulfur conversion appears to be linked to residuum conversion because residuum conversion facilitates conversion of sulfur in higher molecular weight moieties.
5. During hydroprocessing, gas, distillate and naphtha are produced; residuum is converted; and, gas-oil is both converted and produced. The proposed molecular weight reduction model organized the Whiterocks bitumen hydrotreating data reasonably well.

6. Conradson Carbon Residue removal was found to obey first-order kinetics and its activation energy and hydrogen partial pressure dependence indicated that thermal reaction largely influenced its conversion.

7. Pour point reduction during hydroprocessing was most sensitive to temperature and space velocity. The influence of pressure on pour point was minimal.

8. Larger median pore diameters in the HDM catalyst do not result in higher conversion compared with HDN catalyst when hydrotreating bitumen because of the lower activity of the catalyst. Since thermal reactions are emphasized with an HDM catalyst, heteroatom conversion lags behind residuum conversion compared that with an HDN catalyst.

9. Although thermal cracking is important in residuum conversion, some residuum conversion is catalytic. This is in disagreement with the known model that thermal and catalytic reactions can be treated as largely independent and separable. This disagreement can be explained by the fact that the diluted catalyst systems do not have sufficient catalyst concentrations to promote a noticeable increase in activity in residuum removal; this is particularly true at high temperatures when thermal cracking plays a more significant role in residuum conversion.

10. Residuum cracking is less sensitive to catalyst selection than heteroatom conversion because residuum conversion can proceed through a thermal pathway which, for the most part, is not available for heteroatom conversion.
APPENDIX A

BASIC PROGRAMS FOR SIMULATED DISTILLATION OF LIQUID PRODUCTS
(SIMDIS.BAS, ZEROBLNK.BAS)
83 REM
85 REM THIS IS "SIMDIS.BAS" PROGRAM
86 REM
90 REM VERSION TO USE HALF-AND-HALF INTERVALS
94 REM VERSION FOR THE SHORT COLUMN, USING THE
95 REM SHORT RETENTION TIMES
100 REM PROGRAM = SHORTSMD.BAS (SHORT SIMULATED DISTILLATION BASIC)
101 REM
102 REM
103 REM
104 REM
105 REM
110 REM ******** CAUTION ********
120 REM *** THIS PROGRAM USES LONG VARIABLE NAMES, THIS IS NOT
130 REM *** SUPPORTED IN SOME VERSIONS OF BASIC, WHICH READ AS FEW
140 REM *** AS TWO SIGNIFICANT CHARACTERS IN A VARIABLE NAME.
150 REM *** THIS MAY LEAD TO VERY DIFFICULT TO FIND BUGS.
160 REM ******** END OF CAUTION ********
170 REM *** THIS PROGRAM WRITTEN FOR MICROSOFT QBASIC
180 REM
190 REM
200 DIM RETENTIONTIME(99), BOILINGPOINT(99), BLANK(3500)
210 DIM SAMPLE(3500), ISSAMPLE(3500), CARBONNUMBER(99)
220 DIM CUMAREA(99), PEAKAREA(99), E(3500), CUM(99)
230 DIM NORMPEAKAREA(99)
240 REM
250 REM
260 REM READ PARAFFIN PROPERTY DATA
270 GOSUB 1000
280 REM
290 REM
300 REM GET THE VARIOUS FILENAMES
310 GOSUB 3000
320 REM
330 REM
340 REM CALCULATE PEAK LOCATIONS, ETC...
350 GOSUB 4000
360 REM
370 REM
380 REM LOAD DATA FROM SAMPLE (ETC...) FILES, SUBTRACT BLANK
390 GOSUB 5000
400 REM
410 REM
420 REM CALCULATE TOTAL AND PARTIAL SAMPLE AREAS
430 GOSUB 6000
440 REM
450 REM
460 REM CALCULATE UNELUTED FRACTION
470 GOSUB 7000
480 REM
490 REM
500 REM CALCULATE PEAK AND CUMULATIVE AREAS
510 GOSUB 8000
520 REM
530 REM
540 REM PRINT RESULTS
550 GOSUB 9000
560 REM
570 REM
580 STOP
590 REM
600 REM
1000 REM SUBROUTINE FOR PROGRAM INDEX, CARBON NUMBER,
1010 REM RETENTION TIME(MIN), NORMAL BP (F)
1020 DATA 01, 20, 13.27, 651
1030 DATA 02, 21, 13.84, 673
1040 DATA 03, 22, 14.40, 695
1050 DATA 04, 23, 14.94, 716
1060 DATA 05, 24, 15.48, 736
1070 DATA 06, 25, 15.98, 755
1080 DATA 07, 26, 16.48, 774
1090 DATA 08, 27, 16.98, 791
1100 DATA 09, 28, 17.47, 808
1110 DATA 10, 29, 17.95, 824
1120 DATA 11, 30, 18.42, 840
1130 DATA 12, 31, 18.86, 856
1140 DATA 13, 32, 19.30, 871
1150 DATA 14, 33, 19.74, 884
1160 DATA 15, 34, 20.17, 898
1170 DATA 16, 35, 20.66, 912
1180 DATA 17, 36, 21.15, 925
1190 DATA 18, 37, 21.60, 936
1200 DATA 19, 38, 22.05, 948
1210 DATA 20, 39, 22.43, 960
1220 DATA 21, 40, 22.80, 972
1230 DATA 22, 41, 23.18, 982
1240 DATA 23, 42, 23.55, 993
1250 DATA 24, 43, 23.88, 1003
1260 DATA 25, 44, 24.20, 1013
1270 DATA 26, 45, 24.58, 1023
1280 DATA 27, 46, 24.95, 1033
1290 DATA 28, 47, 25.33, 1042
1300 DATA 29, 48, 25.70, 1051
1310 DATA 30, 49, 26.00, 1059
1320 DATA 31, 50, 26.30, 1067
1330 DATA 32, 51, 26.63, 1075
1340 DATA 33, 52, 26.95, 1083
1350 DATA 34, 53, 27.23, 1090
1360 DATA 35, 54, 27.50, 1098
1370 DATA 36, 55, 27.80, 1105
1380 DATA 37, 56, 28.10, 1112
1390 DATA 38, 57, 28.33, 1119
1400 DATA 39, 58, 28.55, 1126
1410 DATA 40, 59, 28.83, 1132
1420 DATA 41, 60, 29.10, 1139
1730 INPUT "MAX C-NUMBER INDEX ELUTED, C60 = 41: ", MAXINDEX
1740 FOR I = 1 TO MAXINDEX
1750 READ TRASH
READ CARBONNUMBER(I)
READ RETENTIONTIME(I)
READ BOILINGPOINT(I)
NEXT I
RETURN
REM
REM
REM
REM GET VARIOUS FILENAMES
INPUT "SUBTRACT A BLANK RUN (1 = YES, 0 = NO) ", FLAG2
PRINT
IF (FLAG2 = 1) THEN INPUT "BLANK RUN FILENAME ", SBLANK$
INPUT "SAMPLE (ONLY) RUN FILENAME ", SSAMPLE$
INPUT "SAMPLE + INTERNAL STANDARD FILENAME ", SISSAMPLE$
INPUT "OUTPUT FILENAME ", OUTPUT$
PRINT
IF (FLAG2 = 1) THEN OPEN SBLANKS FOR INPUT AS #10
OPEN SSAMPLES FOR INPUT AS #11
OPEN SISSAMPLE$ FOR INPUT AS #12
OPEN OUTPUTS FOR OUTPUT AS #13
PRINT #13, "SUBTRACT A BLANK RUN (1 = YES, 0 = NO) ", FLAG2
PRINT #13, "SAMPLE (ONLY) RUN FILENAME ", SSAMPLE$
PRINT #13, "SAMPLE + INTERNAL STANDARD FILENAME ", SISSAMPLE$
PRINT #13, "OUTPUT FILENAME ", OUTPUT$
RETURN
REM
REM
REM CALCULATE SOME PEAK LOCATIONS
INPUT "CHROMATOGRAM TIME IN MINUTES ", CHROMATOGRAMTIME
PRINT #13, "CHROMATOGRAM TIME IN MINUTES ", CHROMATOGRAMTIME
TIMEFACTOR = 30
REM TIMEFACTOR = # OF "SLICES" IN ONE MINUTE
MAXI = CHROMATOGRAMTIME * TIMEFACTOR
INPUT "A TIME BEFORE FIRST I-S PEAK IN MIN. (5 MIN.?) ", FIRSTPEAK
INPUT "A TIME AFTER LAST I-S PEAK IN MIN. (13 MIN.?) ", LASTPEAK
PRINT #13, "A TIME BEFORE FIRST I-S PEAK IN MIN. ", FIRSTPEAK
PRINT #13, "A TIME AFTER LAST I-S PEAK IN MIN. ", LASTPEAK
FIRSTI = FIRSTPEAK * TIMEFACTOR
LASTI = LASTPEAK * TIMEFACTOR
RETURN
REM
REM
REM LOAD DATA FROM SAMPLE (ETC...) FILES, SUBTRACT BLANK
FOR I = 1 TO MAXI
IF (FLAG2 = 1) THEN INPUT #10, TRASH, TRASH, BLANK(I)
INPUT #11, TRASH, TRASH, SAMPLE(I)
INPUT #12, TRASH, TRASH, ISSAMPLE(I)
IF (FLAG2 = 1) THEN SAMPLE(I) = SAMPLE(I) - BLANK(I)
IF (FLAG2 = 1) THEN ISSAMPLE(I) = ISSAMPLE(I) - BLANK(I)
NEXT I
RETURN
REM
REM
REM
REM CALCULATE TOTAL AND PARTIAL SAMPLE AREAS
SAMPAREA = 0
ISSAMPAREA = 0
FOR I = 1 TO MAXI
SAMPAREA = SAMPAREA + SAMPLE(I)
ISSAMPAREA = ISSAMPAREA + ISSAMPLE(I)
NEXT I
PARSAMPAREA = SAMPAREA
PARISSAMPAREA = ISSAMPAREA
FOR I = FIRSTI TO LASTI
PARSAMPAREA = PARSAMPAREA - SAMPLE(I)
PARISSAMPAREA = PARISSAMPAREA - ISSAMPLE(I)
NEXT I
RETURN
REM
REM
REM CALCULATE UNELUTED FRACTION
INPUT "SAMPLE WEIGHT = ", SAMPWT
INPUT "INTERNAL STANDARD WEIGHT = ", ISSAMPWT
PRINT #13, "SAMPLE WEIGHT = ", SAMPWT
PRINT #13, "INTERNAL STANDARD WEIGHT = ", ISSAMPWT
ISFRAC = ISSAMPWT / (ISSAMPWT + SAMPWT)
UNELUTED = (1 / ISFRAC) * (ISSAMPAREA - (SAMPAREA * PARISSAMPAREA / PARSAMPAREA)) - ISSAMPAREA
TEMP = ISSAMPAREA - SAMPAREA * PARISSAMPAREA / PARSAMPAREA
PLUSFRAC = UNELUTED / (UNELUTED + (ISSAMPAREA - TEMP))
PRINT "PLUS FRACTION = PLUSFRAC"
PRINT #13, "PLUS FRACTION = PLUSFRAC"
RETURN
REM
REM
REM CALCULATE PEAK AND CUMULATIVE AREAS
RETENTIONTIME(MAXINDEX + 1) = 2 * RETENTIONTIME(MAXINDEX) - RETENTIONTIME(MAXINDEX - 1)
FOR I = 1 TO MAXINDEX
CUMAREA(I) = 0
FOR J = 1 TO (RETENTIONTIME(I) + RETENTIONTIME(I + 1)) * TIMEFACTOR / 2
CUMAREA(I) = CUMAREA(I) + SAMPLE(J)
NEXT J
PEAKAREA(I) = CUMAREA(I) - CUMAREA(I - 1)
NORMPEAKAREA(I) = PEAKAREA(I) / SAMPAREA
8100 NEXT I
8110 PEAKAREA(1) = CUMAREA(1)
8120 NORMPEAKAREA(I) = PEAKAREA(1) / SAMPAREA
8130 FOR I = 1 TO MAXINDEX
8140 CUMAREA(I) = CUMAREA(I) / SAMPAREA
8150 NEXT I
8160 RETURN
8170 REM
8180 REM
8190 REM
8200 REM
9000 REM PRINT RESULTS
9010 PRINT "CARBON #  NORMAL BP  MASS FRAC  CUMULATIVE FRAC"
9015 PRINT #13, "CARBON #  NORMAL BP  MASS FRAC  CUMULATIVE FRAC"
9020 FOR I = 1 TO MAXINDEX
9030 ACTUALPEAKAREA = NORMPEAKAREA(I) * (1 - PLUSFRAC)
9040 ACTUALCUMAREA = CUMAREA(I) * (1 - PLUSFRAC)
9050 PRINT CARBONNUMBER(I), BOILINGPOINT(I), ACTUALPEAKAREA, ACTUALCUMAREA
9055 PRINT #13, CARBONNUMBER(I), BOILINGPOINT(I), ACTUALPEAKAREA, ACTUALCUMAREA
9060 NEXT I
9070 PRINT "C"; CARBONNUMBER(MAXINDEX); " PLUS FRACTION = "; (1 - ACTUALCUMAREA)
9080 PRINT #13, "C"; CARBONNUMBER(MAXINDEX); "PLUS FRACTION = "; (1 - ACTUALCUMAREA)
9090 RETURN
REM
REM THIS IS "ZEROBLNK.BAS" PROGRAM.
REM
BY SEOKHWAN KWAK

REM

INPUT "SAMPLE FILENAME: ", F1$
INPUT "BLANK FILENAME: ", F2$
INPUT "OUTPUT FILENAME: ", F3$
F1$ = F1$ + ".RPT"
F2$ = F2$ + ".RPT"
INPUT "CHROMATOGRAM TIME (MIN): ", Tyme
OPEN F1$ FOR INPUT AS #10
OPEN F2$ FOR INPUT AS #11
OPEN F3$ FOR OUTPUT AS #12
INPUT "AMOUNT OF START OF RUN TO ZERO OUT (MIN): ", Ztime
FOR I = 1 TO (Ztime * 30)
PRINT #12, USING "########.####"; Trash 1
PRINT #12, USING "########.#####"; 0
NEXT I
FOR I = ((Ztime * 30) +1) TO (Tyme * 30)
INPUT #10, Trash1, Trash2, Sample
INPUT #11, Trash, Trash, Blank
Result = Sample - Blank
PRINT #12, USING "########.####"; Trash1
PRINT #12, USING "########.#####"; Result
NEXT I

STOP
APPENDIX B

FORTRAN PROGRAM FOR CALCULATING HYDROTREATED PRODUCT DISTRIBUTION
The following program is used to calculate heavy oil product distributions for bitumen hydrotreated over Unocal HDM catalyst including NH3, H2S, H2O, C1-C4 Gases, C5+ naphtha, distillate, gas oil and residuum fractions by weight.

By Seokhwan Kwak

implicit double precision (a-h, o-z)
double precision ld, masbal, masbwt, lnorm, liqout
double precision methawt, metha, naphtwt, napht
double precision metha1, napht1, hcgas, methaar

Initialization....

open(22, file='d13c1c6', status='unknown')

Input all feed elemental properties.....
where, fd=wt[in grams] of feed going to hydrotreater.
fdcwt, fdhwt, fdnwt, fdswt, fdowt=wt% of carbon, hydrogen, nitrogen, sulfur and oxygen in the feed respectively.....

write(*,10)
write(22,10)
10 format(2x,'Amount of liquid fed into hydrotreater[grams] ?')
read*, fd
write(*,15) fd
write(22,15) fd
15 format(4x,';',2x1 f9.5,2x,'
grams',/)

fdcwt=85.1
fdhwt=11.6
fdnwt=1.360
fdswt=0.3334
fdowt=100.-fdcwt-fdhwt-fdnwt-fdswt

Calculating actual grams of C, H, O, N, S in the feed.....

fdc=fd*fdcwt/100.
fdh=fd*fdhwt/100.
fdn=fd*fdnwt/100.
fds=fd*fdswt/100.
fd0=fd*fdowt/100.

The following step is used to calculate the mass balance and normalization of the hydrotreated product.....

where,

|d|=wt of liquid coming out of hydrotreater [grams].
out=wt of liquid+gas coming out of hydrotreater [grams]
masbwt=Mass Balance [wt%]
gnorm=wt of gas after normalization [grams]
Inorm=wt of liquid after normalization [grams]

snorm=wt of liquid+gas after normalization [grams],..

```fortran
write(*,20)
write(22,20)
20 format(2x,'Input amount liquid going out [grams']
read*, ld
write(*,25) ld
write(22,25) ld
25 format(4x,';',2x,f9.5,2x,'[grams']/)
write(*,30)
write(22,30)
30 format(2x,'Input amount of liquid+gas going out [grams']
read*, out
write(*,35) out
write(22,35) out
35 format(4x,';',2x,f9.5,2x,'[grams']/)

gas=out-ld
masbal=out/fd
masbwt=masbal*100.
write(*,40) masbwt
write(22,40) masbwt
40 format(2x,'Mass balance;',2x,f9.5/) 

gnorm=gas*1/masbal
Inorm=ld*1/masbal
snorm=gnorm+Inorm
write(*,50)
write(22,50)
50 format(2x,'NORMALIZATION VALUE OF GAS & LIQUID')
write(*,60) gnorm
write(22,60) gnorm
60 format(2x,'Gas;',2x,f9.5)
write(*,70) Inorm
write(22,70) Inorm
70 format(2x,'Liquid;',2x,f9.5)
write(*,80) snorm
write(22,80) snorm
80 format(2x,'gas+liquid after normalization;',2x,f9.5/) 
C Calculating amount of n,s,o converted in grams.... 
write(*,90)
```
WRITE(22,90)
FORMAT(2X,'Input wt% of Carbon in the product')
READ*, PDCWT
WRITE(*,95) PDCWT
WRITE(22,95) PDCWT
FORMAT(4X,';',2X,F9.5,2X,'[wt%]',/) C
WRITE(*,100)
WRITE(22,100)
FORMAT(2X,'Input wt% of Hydrogen in the product')
READ*, PDHWT
WRITE(*,105) PDHWT
WRITE(22,105) PDHWT
FORMAT(4X,';',2X,F9.5,2X,'[wt%]',/) C
WRITE(*,110)
WRITE(22,110)
FORMAT(2X,'Input wt% of Nitrogen in the product')
READ*, PDNWT
WRITE(*,115) PDNWT
WRITE(22,115) PDNWT
FORMAT(4X,';',2X,F9.5,2X,'[wt%]',/) C
WRITE(*,120)
WRITE(22,120)
FORMAT(2X,'Input wt% of Sulfur in the product')
READ*, PDSTW
WRITE(*,125) PDSTW
WRITE(22,125) PDSTW
FORMAT(4X,';',2X,F9.5,2X,'[wt%]',/) C
PDOWT=100.-PDCWT-PDHWT-PDNWT-PDSTW
CONS=FDs-LNORM*PDSTW/100.
CONN=FDN-LNORM*PDNWT/100.
CONO=FDO-LNORM*PDOWT/100.
WATER=CONO*(18./16.)
LIQOUT=LNORM-WATER
AMMONIA=CONN*(17./14.)
HYSULF=CONS*(34./32.)
GASOUT=GNORM-AMMONIA-HYSULF
WRITE(*,130) WATER
WRITE(22,130) WATER
FORMAT(2X,'Water;',2X,F9.5)
WRITE(*,140) HYDROGEN SULFIDE
WRITE(22,140) HYDROGEN SULFIDE
FORMAT(2X,'Hydrogen Sulfide;',2X,F9.5)
WRITE(*,150) AMMONIA
WRITE(22,150) AMMONIA
200 format(2x,'Ammonia;',2x,f9.5)
C write(*,160) liqout
write(22,160) liqout
160 format(2x,'Liquid Product;',2x,f9.5)
C write(*,170) gasout
write(22,170) gasout
170 format(2x,'Gas Product;',2x,f9.5)
C C Input each area of C1 to C6 for hydrotreated gas
C from Carle Gas Chromatograph....
C write(*,180)
write(22,180)
180 format(2x,'Input area of C1 from G.C.')
read*, methaar
write(*,185) methaar
write(22,185) methaar
185 format(4x,';',2x,f9.5)
C write(*,190)
write(22,190)
190 format(2x,'Input area of C2 from G.C.')
read*, ethanar
write(*,195) ethanar
write(22,195) ethanar
195 format(4x,';',2x,f9.5)
C write(*,200)
write(22,200)
200 format(2x,'Input area of C3 from G.C.')
read*, propaar
write(*,205) propaar
write(22,205) propaar
205 format(4x,';',2x,f9.5)
C write(*,210)
write(22,210)
210 format(2x,'Input area of C4 from G.C.')
read*, butanar
write(*,215) butanar
write(22,215) butanar
215 format(4x,';',2x,f9.5)
C write(*,220)
write(22,220)
220 format(2x,'Input area of C5 from G.C.')
read*, pentaar
write(*,225) pentaar
write(22,225) pentaar
225 format(4x,';',2x,f9.5)
C write(*,230)
Consider relative sensitivity data for hydrogen flame detector [FID].....


```
tmethar=methaar/0.97
tethaar=ethanar/0.97
tpropar=propaar/0.98
tbutaar=butanar/1.09
tpentar=pentaar/1.04
thexaar=hexanar/1.03

totalar=tmethar+tethaar+tpropar+
& tbutaar+tpentar+thexaar

methawt=tmethar/totalar*100.
ethanwt=tethaar/totalar*100.
propawt=tpropar/totalar*100.
butanwt=tbutaar/totalar*100.
pentawt=tpentar/totalar*100.
hexanwt=thexaar/totalar*100.

metha=gasout*methawt/100.
ethan=gasout*ethanwt/100.
propa=gasout*propawt/100.
butan=gasout*butanwt/100.
penta=gasout*pentawt/100.
hexan=gasout*hexanwt/100.
```

Input the Simulated Distillation results for hydrotreated product.....

```
write(*,240)
write(22,240)
format(2x,'Input wt% of up to 400 [F] from Simdis')
read*, naphtwt
write(*,245) naphtwt
write(22,245) naphtwt

write(*,250)
write(22,250)
format(2x,'Input wt% of 400 to 650 [F] from Simdis')
read*, distiwt
write(*,255) distiwt
write(22,255) distiwt
```
Based on amount of feed (assumed to be 100 [g]),
calculate all gas and liquid hydrotreated products including
NH3, H2S, H2O, C1-C4 Gases, C5+ naphtha, distillate, gas oil
and residuum fractions by weight.....

ammonia1=(ammonia/fd)*100.
hysulf1=(hysulf/fd)*100.
water1=(water/fd)*100.
metha1=(metha/fd)*100.
ethan1=(ethan/fd)*100.
propa1=(propa/fd)*100.
butan1=(butan/fd)*100.
napht1=((penta+hexan+napht)/fd)*100.
dist1=(dist/fd)*100.
gasoil1=(gasoil/fd)*100.
resid1=(resid/fd)*100.


```
hcgas=metha1+ethan1+propa1+butan1

C
write(*,290)
write(22,290)
290 format(2x,'wt% of ammonia in product')
write(*,295) ammonia1
write(22,295) ammonia1
295 format(4x,:,2x,f9.5)
C
write(*,300)
write(22,300)
300 format(2x,'wt% of hydrogen sulfide in product')
write(*,305) hysulf1
write(22,305) hysulf1
305 format(4x,:,2x,f9.5)
C
write(*,310)
write(22,310)
310 format(2x,'wt% of water in product')
write(*,315) water1
write(22,315) water1
315 format(4x,:,2x,f9.5)
C
write(*,320)
write(22,320)
320 format(2x,'wt% of methane in product')
write(*,325) metha1
write(22,325) metha1
325 format(4x,:,2x,f9.5)
C
write(*,330)
write(22,330)
330 format(2x,'wt% of ethane in product')
write(*,335) ethan1
write(22,335) ethan1
335 format(4x,:,2x,f9.5)
C
write(*,340)
write(22,340)
340 format(2x,'wt% of propane in product')
write(*,345) propa1
write(22,345) propa1
345 format(4x,:,2x,f9.5)
C
write(*,350)
write(22,350)
350 format(2x,'wt% of butane in product')
write(*,355) butan1
write(22,355) butan1
355 format(4x,:,2x,f9.5,/) 
C
write(*,357)
write(22,357)
357 format(2x,'wt% C1 to C4 gases in product')
```
write(*,359) hcgas
write(22,359) hcgas
359 format(4x, ';', 2x, f9.5)

write(*,360)
write(22,360)
360 format(2x, 'wt% of C5 to 400 [F] in product')
write(*,365) napht1
write(22,365) napht1
365 format(4x, ';', 2x, f9.5)

write(*,370)
write(22,370)
370 format(2x, 'wt% of 400 to 650 [F] in product')
write(*,375) disti1
write(22,375) disti1
375 format(4x, ';', 2x, f9.5)

write(*,380)
write(22,380)
380 format(2x, 'wt% of 650 to 1000 [F] in product')
write(*,385) gasoi1
write(22,385) gasoi1
385 format(4x, ';', 2x, f9.5)

write(*,390)
write(22,390)
390 format(2x, 'wt% of >1000 [F] in product')
write(*,395) resid1
write(22,395) resid1
395 format(4x, ';', 2x, f9.5, ' )

total2=ammonia1+hysulf1+water1+hcgas+napht1+disti1+gasoi1+resid1

write(*,400)
write(22,400)
400 format(2x, 'sum of total wt% of products should be 100')
write(*,405) total2
write(22,405) total2
405 format(4x, ';', 2x, f9.5)

stop
end
APPENDIX C

FORTRAN PROGRAM FOR CALCULATING HYDROGEN CONSUMPTION
(HYDROGEN.FOR)
Program "Hydrogen.for"

This program is used to calculate hydrogen consumption for hydrotreating of heavy oil over HDM catalyst.

by Seokhwan Kwak

implicit double precision (a-h,o-z)
double precision metha

Initialization....

c..open(22, file='d13h2cos', status='unknown')
c
Input the amount of hydrogen going into the hydrotreater and the amount of hydrogen+methane+ethane+ethylene coming out of the liquid nitrogen trap.....

c..write(*,10)
write(22,10)
10 format(2x,'Input amount of hydrogen going in [stp]/hr')
read*, hydin
write(*,15) hydin
write(22,15) hydin
15 format(4x,';,,2x,f9.5,2x,'liter[stp]/hr',/)
write(*,20)
write(22,20)
20 format(2x,'Input amount of hydrogen+C1+C2 going out [stp]/hr')
read*, gasout
write(*,25) gasout
write(22,25) gasout
25 format(4x,';,,2x,f9.5,2x,'liter[stp]/hr',/)

Enter gas chromatographic results for hydrogen+C1 to C2 gases from the liquid nitrogen trap.....

write(*,30)
write(22,30)
30 format(2x,'Input area of methane')
read*, metha
write(*,35) metha
write(22,35) metha
35 format(4x,';,,2x,f9.5)
write(*,40)
write(22,40)
40 format(2x,'Input area of ethane')
read*, ethan
write(*,35) ethan
write(22,35) ethan
write(*,50)
write(22,50)
50 format(2x,'Input area of ethylene')
read*, ethyl
write(*,55) ethyl
write(22,55) ethyl
55 format(4x,':1.2x,f9.5,/)

C Calculate volumes of hydrogen, methane, ethane and ethylene
C at std condition based on standard sample areas.....
C
write(*,60)
write(22,60)
60 format(2x,'Input atmospheric temperature [C]')
read*, temp
write(*,65) temp
write(22,65) temp
65 format(4x,';',2x,f5.1,2x, '[C]')
write(*,70)
write(22,70)
70 format(2x,'Input atmospheric pressure [mmHg]')
read*, press
write(*,75) press
write(22,75) press
75 format(4x,';',2x,f5.1,2x, '[mmHg]',/)
C
sareac1=2.6387
sareac2=4.7985
sareac3=8.3760
C
vstd1=(metha*5.e-4/sareac1)*(273.15/(temp+273.15))*(press/760.)
vstd2=(ethan*5.e-4/sareac2)*(273.15/(temp+273.15))*(press/760.)
vstd3=(ethyl*5.e-4/sareac3)*(273.15/(temp+273.15))*(press/760.)
vstd4=5.e-1 - vstd1-vstd2-vstd3
C
Normalization and get the volume % of hydrogen only among
exit gas from liquid nitrogen trap.....
C
vstd=vstd1+vstd2+vstd3+vstd4
C
vstd11=vstd1/vstd
vstd21=vstd2/vstd
vstd31=vstd3/vstd
vstd41=vstd4/vstd
C
hydout=gasout*vstd41
C
Simple check of normalization result.....
C
chtotal=vstd11+vstd21+vstd31+vstd41
C
write(*,80) chtotal
write(22,80) chtotal
After normalization, total volume should be 1.

Finally, calculate hydrogen consumption for heavy oil hydrotreating by HDM catalyst in various units:

\[
hydcons = \frac{(\text{hydin} - \text{hydout}) \times 1000 \times 5.614578}{\text{vel}}
\]
\[
hydcons1 = \frac{(\text{hydin} - \text{hydout}) \times 2}{22.4 \times \text{vel} \times 0.9144}
\]
\[
hydcons2 = hydcons \times \frac{28.31685}{158.98729}
\]

hydrogen consumption in scfH2/bblfeed
hydrogen consumption in gH2/gfeed
hydrogen consumption in liter H2/liter feed
APPENDIX D

FORTRAN PROGRAM FOR KINETICS OF TWO PARALLEL FIRST-ORDER REACTIONS USING NONLINEAR REGRESSION
(MINPACK SUBROUTINE)
This program is used to calculate kinetic parameters for hydrotreating the Whiterocks bitumen over a commercial (UNOCAL) catalyst. This program uses the non-linear regression MINPACK routine and is specially made for two parallel first order nickel removal reactions (facile and refractory fractions).

by Seokhwan Kwak

```c
INTEGER J,M,N,INFO,LWA,NWRITE
INTEGER IWA(5)
DOUBLE PRECISION TOL, FNORM, L2NORM
DOUBLE PRECISION X(5), FVEC(12), WA(99)
DOUBLE PRECISION ENORM, DPMPAR
DOUBLE PRECISION TIME, CAL(12), DIFF, AAD
DOUBLE PRECISION TIME, CALCP, EXPCP, DIFF1
DOUBLE PRECISION T, WHSV, P, EXPT, ALPHA, BETA, CP
COMMON /KWAKDAT/ T(12), WHSV(12), P(12), EXPT(12), ALPHA, BETA, CP(12)
EXTERNAL FCN

LOGICAL OUTPUT UNIT IS ASSUMED TO BE NUMBER 11.

DATA NWRITE /11/

M = 12
N = 5

THE FOLLOWING STARTING VALUES PROVIDE A ROUGH FIT.

Here, X(1) = gamma
        X(2) = K10
        X(3) = K20
        X(4) = E1 [J mol^-1]
        X(5) = E2 [J mol^-1] ....

X(1) = .1d0
X(2) = 0.6d5
X(3) = 0.6d6
X(4) = 0.78d5
X(5) = 0.89d5

LWA = 150

SET TOL TO THE SQUARE ROOT OF THE MACHINE PRECISION.
UNLESS HIGH PRECISION SOLUTIONS ARE REQUIRED,
THIS IS THE RECOMMENDED SETTING.

TOL = DSQRT(DPMPAR(1))*1.d4

CALL LMDIF1(FCN,M,N,X,FVEC,TOL,INFO,IWA,WA,LWA)
FNORM = ENORM(M,FVEC)

OPEN(NWRITE,FILE='hdnialtr.out',STATUS='UNKNOWN')

WRITE (NWRITE,1000) FNORM, INFO, (X(J),J=1,N)
```
```
WRITE (*,1000) FNORM,INFO,(X(J),J=1,N)

1000 FORMAT (5X,31H FINAL L2 NORM OF THE RESIDUALS,D15.7 //
      * 5X,15H EXIT PARAMETER,16X,110 //
      * 5X,27H FINAL APPROXIMATE SOLUTION // 3X,5D15.7)

WRITE(6,9994)
WRITE(NWRITE,9994)
9994 FORMAT(/5X, 'Time(hr)', 6X, 'Exptl.', 9X, 'Cald.',
1  9X, 'Diff', 10X, 'AAD %',
2 /5X, '========', 6X, '======', 9X, '====',
3 9X, '====', 10X, '====')
C
S=0.0D0
DO 5 I=1,M
CALL CALCUL(I, N, X, CAL)
TIME=1.0D0/WHSV(I)
DIFF=CAL(I)-EXPT(I)
AAD=100.0D0*ABS(DIFF)/EXPT(I)
S=S+AAD
WRITE(6,9993) TIME, EXPT(I), CAL(I), DIFF, AAD
WRITE(NWRITE,9993) TIME, EXPT(I), CAL(I), DIFF, AAD
9993 FORMAT(7X, F5.3, 4X, 4(1 X, F12.8))
5 CONTINUE
C
S=S/M
WRITE(6,9992) S
WRITE(NWRITE,9992) S
9992 FORMAT(/5X, 'AAD:', F14.8, '%//')
C
WRITE(6,1112)
WRITE(NWRITE,1112)
1112 FORMAT(/5X, 'Time(hr)', 6X, 'Cp(exp)', 9X, 'Cp(cal)',
1  9X, 'Diff', 10X, 'L2 norm',
2 /5X, '========', 6X, '======', 9X, '====',
3 9X, '====', 10X, '====')
C
DO 6 I=1,M
CALL CALCUL(I, N, X, CAL)
TIME=1.0D0/WHSV(I)
EXPCP=CP(I)
CALCP=(CAL(I))
DIFF1=EXPCP-CALCP
L2NORM=DIFF1**2.0D0
S1=S1+L2NORM
WRITE(6,9993) TIME, EXPCP, CALCP, DIFF1, S1
WRITE(NWRITE,9993) TIME, EXPCP, CALCP, DIFF1, S1
6 CONTINUE
C
WRITE(6,*') S1
WRITE(NWRITE,*') S1
C
STOP
END
```
SUBROUTINE FCN(M,N,X,FVEC,IFLAG)
  INTEGER M,N,IFLAG,I
  DOUBLE PRECISION X(N),FVEC(M),CAL(12),EXPT
  DOUBLE PRECISION CONCPROD,CONCFEED,CP(12)
  COMMON /KWAKDAT/T(12),WHSV(12),P(12),EXPT(12),ALPHA,BETA,CP

  DATA CONCFEED/0.0072D0/
  DATA (CP(I),I=1,12)/0.0039d0,0.0040d0,0.0055d0,0.0023d0,
  & 0.0025d0,0.0030d0,0.0033d0,0.0019d0,
  & 0.00137d0,0.0031d0,0.0025d0,0.0022d0/

  DO 50 1=1,12
  CONCPROD=CP(I)
  EXPT(I)=CONCPROD
  CALL CALCUL(I,N,X,CAL)
  FVEC(I)=CAL(I) - EXPT(I)
  CONTINUE

  RETURN
END

SUBROUTINE CALCUL(I,N,X,CAL)
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION X(N)
  DOUBLE PRECISION WHSVE,PRESS,TEMP,CAL(12),K1,K2
  DOUBLE PRECISION T,WHSV,P,EXPT,ALPHA,BETA,CP
  COMMON /KWAKDAT/T(12),WHSV(12),P(12),EXPT(12),ALPHA,BETA,CP

  DATA (P(I),I=1,12)/13.4892d0,13.2361d0,13.3706d0,13.5050d0,
  & 13.4268d0,13.1797d0,13.4434d0,13.3926d0,
  & 13.1069d0,1.9383d0,16.0327d0/
  DATA (T(I),I=1,12)/619.8550d0,642.3613d0,652.9521d0,664.7213d0,
  & 673.3173d0,684.6519d0,662.2412d0,665.1570d0,
  & 665.7481d0,664.6790d0,664.7027d0,664.4580d0/
  DATA (WHSV(I),I=1,12)/0.76978d0,0.76578d0,0.76945d0,0.76676d0,
  & 0.75710d0,0.76250d0,0.76578d0,0.76578d0,0.76250d0,
  & 0.76578d0,0.76578d0,0.76578d0,0.76578d0/

  DATA CONCFEED/0.0072D0/
  DATA ALPHA,BETA/0.9164538d0,1.759649d0/

  TEMP=T(I)
  WHSVE=WHSV(I)
  PRESS=P(I)

  K1=X(2)*EXP(-(X(4)/8.314D0)*(1.0/TEMP))
  K2=X(3)*EXP(-(X(5)/8.314D0)*(1.0/TEMP))
CAL(I)=((X(1)*EXP(-K1*PRESS**BETA/(WHSVE**ALPHA)))+(1.0D0-X(1)))*
* EXP(-K2*PRESS**BETA/(WHSVE**ALPHA)))*CONC_FEED
RETURN
END
APPENDIX E

INPUT FILE FOR PROCESS SIMULATION
TITLE PROBLEM=HTTEMP, PROJECT=HDMBIT, USER=KWAKRJDS, DATE=JUN/10/93
DIMENSION ENGLISH, TEMP=F
PRINT INPUT=NONE, STREAM=NONE
COMPONENT DATA
LIBID 1, HYDROGEN / 2, WATER / 3, HYSULFID / 4, AMMONIA / 5, METHANE / 6, ETHANE / 7, PROPANE / 8, BUTANE / 9, PENTANE / 10, HEXANE
TBPCUTS 100, 1488, 15
THERMODYNAMICS DATA
METHODS SYSTEM=GS, TRANSPORT=PETRO
STREAM
OUTPUT FORMAT=1, NSTREAMS=4, STREAMS= F13, F14, F15, F16
FORMAT IDNO=1, PAGE, NAME, PHASE, LINE, CPCT(M), LINE, ARATE(M, HR), * ARATE(W, LB, HR), TEMP, PRES, LFRAC, LINE, ENTHALPY(T), * ENTROPY(T), DENSITY, TC, PC, VC, ZC, ACENTRIC, LINE, * SSPGR(WATER), SAPI, MW, NBP, CP(W), PAGE, NAME, PHASE, LINE, * CRATE(W), LINE, CPCT(W)
$ INPUT STREAMS
PROPERTY STRM=F13, TEMP=350, PRES=1983, RATE(W)=256.586, ASSAY=WT
TBP STRM=F13,
DATA 0.4822, 304 / 1.6495, 421 / 6.2566, 520 / 9.7234, 601 / * 18.8604, 716 / 26.8391, 808 / 44.2711, 911.5 / * 61.5871, 1003 / 76.2614, 1105 / 100, 1285.14
API AVG=15, 183, STRM=F13
PROPERTY STRM=F14, TEMP=350, PRES=1983, RATE(W)=27.668, * COMP(W)=1, 0.78868 / 2, 0.03044 / 3, 0.01353 / 4, 0.02671 / * 5.0, 0.02773 / 6, 0.02625 / 7, 0.04473 / 8, 0.02185 / * 9, 0.01169 / 10, 0.00837
UNIT OPERATIONS
FEED F13, F14
PROD V=F15, L=F16
ISO TEMP=736.8, PRES=1995
END
APPENDIX F

OUTPUT FILE FOR PROCESS SIMULATION
VIII.A UNIT - STREAM CORRELATION MATRIX

UNIT ID: HD11

NUMBER: 1

NAME: FLASH

FEEDS:
- F13
- F14

PRODUCTS:
- F15 (V)
- F16 (L)

TEMP, DEG F: 736.8000
PRESSURE, PSIA: 1995.0000
FRACTION LIQUID: 0.06414
DUTY, MM BTU /HR: 0.10339
### USER-DEFINED STREAM SUMMARY OUTPUT

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<th>F13</th>
<th>F14</th>
<th>F15</th>
<th>F16</th>
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<td>14.8166</td>
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<tr>
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<td>8.0139</td>
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<tr>
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<tr>
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<td>10.9240</td>
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<td>350.0000</td>
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<tr>
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<td>0.0411</td>
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<td>0.0800</td>
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<tr>
<td>ACT.DENS, LB /FT3</td>
<td>56.0270</td>
<td>0.5386</td>
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<td>CRIT. TEMP, F</td>
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<td>-376.0008</td>
<td>747.6270</td>
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<tr>
<td>CRIT. PRES, PSIA</td>
<td>212.5301</td>
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<tr>
<td>CRIT. VOLUME, FT3/LB MOLE</td>
<td>1.0580</td>
<td>1.1642</td>
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<td>0.3041</td>
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<td>ACENTRIC FACTOR</td>
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<td>STD. API GRAVITY</td>
<td>1521.3000</td>
<td>858.0804</td>
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<td>NML. BOIL PT., (MOLE) F</td>
<td>839.9493</td>
<td>-415.3532</td>
<td>520.2131</td>
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<tr>
<td>CP, BTU /LB F</td>
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<td>2.8503</td>
<td>1.8979</td>
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</table>
APPENDIX G

NONLINEAR NUMERICAL INTEGRATION FORTRAN PROGRAM FOR
MOLECULAR WEIGHT REDUCTION MODEL
This is the main program for solving ODE equations and performing nonlinear regressions using the SIMPLEX method simultaneously. This program was developed to obtain the best reaction constants at 735 [F] for the series of irreversible first-order reactions in a plug-flow reactor. All data were obtained for hydrotreating of Whiterocks bitumen over a commercial UNOCAL hydrodemetallation catalyst.....

By Seokhwan Kwak

The molecular weight reduction reaction scheme was examined by lumping HT products into four representative groups, which are
- Resid (b.p. > 538 C)
- Total Gas Oil (275 C < b.p. < 538 C)
- Middle Distillates (C5 < b.p. < 275 C)
- Gases (including NH3, H2S, C1 to C4 Hydrocarbon gases).....

The proposed irreversible first order reaction scheme is as follows.....
Resid--(kro)-- Total Gas Oil --(kod)-- Middle Distillates
<p>| |</p>
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
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</table>

where,
- kro = rate constant from resid to total gas oil [1/hr] (=X(1))
- kod = rate constant from total gas oil to middle distillates [1/hr] (=X(2))
- kog = rate constant from total gas oil to gases [1/hr] (=X(3))
- kdg = rate constant from middle distillates to gases [1/hr] (=X(4)).....

IMPLICIT REAL*8 (A-H, O-Z)
CHARACTER *1 CC, CC1, CC2, CNAME*11
DIMENSION X(6), XX(7,6), FX(7), C(6), Y(6), Z(6), V(6)
EXTERNAL F
WRITE(6,200)
200 FORMAT(2X, 'The name of output file: ', $)
READ (5,210) CNAME
210 FORMAT(A11)
OPEN (1, FILE=CNAME, STATUS='NEW')

Input all the initial informations including initial guesses.....
WRITE(6,150)
150 FORMAT(2X, 'The dimension of parameter: ', $)
READ(5,*') N
WRITE(6,170)
READ(5,*') ITMAX
WRITE(6,190)
READ(5,*) EPS
5 CONTINUE
WRITE(1,220) N, ITMAX, EPS
220 FORMAT('1 ', 'Dimension of parameter: ', I9,
*     2X, 'Maximum iteration time: ', I9,
*     2X, 'Convergence criterion: ', E9.2)
WRITE(6,100)
100 FORMAT(2X, 'The initial guesses: ')
DO 10 I=1,N
WRITE(6,110) I
110 FORMAT(5X, 'X(', 12, ')= ? ', $)
READ(5,*) X(I)
10 CONTINUE
WRITE(6,120) (X(I), I=1,N)
WRITE(1,120)(X(I), I=1,N)
120 FORMAT (2X, The initial value: ', 6D12.4)

Now call subroutine SIMPLEX for solving nonlinear regression, which calls
FX in RK4 for solving ODEs simultaneously.....

CALL SIMPLEX(N, ITMAX, EPS, X, XX, FX, C, Y, Z, V, FY, 0, IP1, F)

The subroutine STTEST is used to evaluate the overall performance of the
results obtained from this program. This will include the relative
errors like AAD, etc......

CALL STTEST(N,X,IP1)

If the desired AAD was not obtained in the previous run
the following subroutine will rerun the program.....

WRITE(6,130)
130 FORMAT (2X, 'Going on with another initial values? (Y/N) ', $)
READ(5,140) CC
140 FORMAT(A1)
IF(CC .EQ. 'Y' .OR. CC .EQ. 'y') THEN
WRITE(6,160)
160 FORMAT(2X, 'to change the max. iteration time? (Y/N) ', $)
READ(5,140) CC1
IF (CC1 .EQ. 'Y' .OR. CC1 .EQ. 'y') THEN
WRITE(6,170)
170 FORMAT(2X, 'The max. number of iterations: ', $)
READ (5,*) ITMAX
ENDIF
WRITE(6,180)
180 FORMAT(2X, 'to change the convergence criterion? (Y/N) ', $)
READ(5,140) CC2
IF (CC2 .EQ. 'Y' .OR. CC2 .EQ. 'y') THEN
WRITE(6,190)
190 FORMAT(2X, 'The convergence criterion: ', $)
READ (5,*) EPS
The following subroutine is a general SIMPLEX method.....

SUBROUTINE SIMPLEX(N, ITMAX, EPS, X, XX, FX, C, Y, Z, V, FY,}
   IP, IP1, IP2)

IMPLICIT REAL *8 (A-H, O-Z)
CHARACTER ACTIONS 2, FLIP*5, ACTP*17
DIMENSION X(N), XX(N+1,N), FX(N+1), C(N), Y(N), Z(N), V(N)
EXTERNAL F
DATA R, T, S/1.0D0, 2.0D0, 0.5D0/
DATA FLIP/'Flip'/

Initialization.....

ITER=0
LINE=0
IFLIP=0
ACTION=''
ACTP = '',
L=N/7+1

Calculate the coordinate of other N vertices.....

SQ1 = SQRT(FLOAT(N+1))-1
SQ = N*SQRT(2.0D0)
P = (SQ1+N)/SQ
Q = SQ1/SQ
DO 200 I=1,N
   XX(1,I)=X(I)

200 CONTINUE
DO 210 I=2,N+1
   I1=I-1
   DO 210 J=1,N
      IF (I1.EQ. J) THEN
         XX(I,J)=X(J)+P
      ELSE
         XX(I,J)=X(J)+Q
      ENDIF
   210 CONTINUE

Calculate the function values at every vertex.....
DO 10 I=1,N+1
DO 8 J=1,N
X(J)=XX(I,J)
8 CONTINUE
CALL F(X,N,FX(I))
10 CONTINUE
C
C Search for the max. and the min. points.....
C
15 CONTINUE
FMAX=-1.0D38
FMIN=1.0D38
DO 17 I=1,N+1
IF (FX(I) .GT. FMAX) THEN
FMAX=FX(I)
IMAX=I
ENDIF
IF (FX(I) .LT. FMIN) THEN
FMIN=FX(I)
IMIN=I
ENDIF
17 CONTINUE
C
C Print the title for the intermediate results.....
C
IF (MOD(LINE,53) .EQ. 0) THEN
C WRITE(1,1000)
IF (IP1 .EQ. 1) WRITE(6,1000)
C
1000 FORMAT('1'No of IT', 2X, 'Action1 , 16X, ^m in)',
* 11X, 'X(min)',
* /1X, '=======', 2X, '=======', 16X, '=======',
* 11X, '=======',/)
ENDIF
C
C Check to see if the action is combined with flip.....
C
IF (IFLIP .EQ. 1) THEN
ACTP=FLIP//ACTION
IFLIP=0
ELSE
ACTP=ACTION
ENDIF
C
C Print the intermediate results: iteration time, action taken,
C coordinate and function value at the minimum point.....
C
C WRITE(1,11010) ITER, ACTP, FX(IMIN), (XX(IMIN,J),J=1,N)
IF (IP1 .EQ. 1) "WRITE(6,11010) ITER, ACTP, FX(IMIN), (XX(IMIN,J),J=1,N)
C
11010 FORMAT(2X, I4, 5X, A17, D15.6, 2X, /5X, D11.3)
ACTP=' ' 
LINE=LINE+1

C
C Check to see if the criterion is satisfied, if so, return.....

C
SS=0.0D0 
DO 170 I=1,N+1
SS=SS+(FX(I)-FX(IMIN))**2 
170 CONTINUE
SS=SQRT(SS/N)
IF (SS .LT. EPS) THEN
FY=FX(IMIN)
DO 175 I=1,N
X(I)=XX(IMIN,I)
175 CONTINUE
WRITE(6,1020) ITER, FY, (X(I),I=1,N)
WRITE(1,1020) ITER, FY, (X(I),I=1,N)
1020 FORMAT(5X, 'No. of iterations:', 110, 
      * /5X, 'Function value(min):', D20.10/
      * 5X, 'The coordinate:', 5X, (4X, 7D18.10, ::))
RETURN
ENDIF

C
C Check to see if the max. iteration times have been reached, if
C so, print a message and return.....

C
IF (ITER .GT. ITMAX) THEN
DO 180 I=1,N
X(I)=XX(IMIN,I)
180 CONTINUE
FY=FX(IMIN)
WRITE(1,1030) ITMAX, ITER, FY, (X(I),I=1,N)
WRITE(6,1030) ITMAX, ITER, FY, (X(I),I=1,N)
1030 FORMAT(//2X,' ** The max. iteration time,', 15,' has been ',
      * 'reached, but the convergence is not satisfied.',
      * /5X, 'No. of iterations:', I10,
      * /5X, 'Function value(min):', D20.10,
      * /5X, 'The coordinate:',/5X, (4X, 7D18.10, ::))
RETURN
ENDIF

C
C Search the second max. point.....

C
SS=-1.0D38 
DO 18 I=1,N+1
IF (I .NE. IMAX) THEN
IF (FX(I) .GT. SS) THEN
SS=FX(I)
IMAXS=I
ENDIF
ENDIF
CONTINUE

Calculate the coordinate of the centroid.....

DO 20 I=1,N
C(I)=0.0D0
20 CONTINUE

DO 22 I=1,N
DO 22 J=1,N+1
IF (J .NE. IMAX) C(I)=C(I)+XX(J,I)
22 CONTINUE

DO 25 I= 1 ,N
C(I)=C(I)/N
25 CONTINUE

Print the coordinate and function values at every vertex,
and the coordinate of centroid if IP=1.....

IF (IP .EQ. 1) THEN
WRITE(2,1040) ITER, (C(I),I=1,N)
1040 FORMAT(/2X,'ITERATION TIME:', 110, 5X,'CC:',/5X, F10.3)
DO 270 I=1,N+1
JJ=0
DO 265 J=1,N
IF (ABS(FX(J)) .LT. 1E-3) THEN
JJ=1
GOTO 267
ENDIF
265 CONTINUE
267 CONTINUE
IF (JJ .EQ. 0) THEN
WRITE(2,1050) I, FX(I), (XX(I,J),J=1,N)
ELSE
WRITE(2,1060) I, FX(I), (XX(I,J),J=1,N)
ENDIF
1050 FORMAT(2X, 'FX(', 11,'):', E10.3, 5X, 'XX:', /5X, F10.3)
1060 FORMAT(2X, *FX(', 1 1 , F 1 0 .3 , 5X, 'XX:', /5X, F10.3)
270 CONTINUE
ENDIF
ITER=ITER+1

Reflection.....

DO 30 I=1,N
Y(I)=C(I)+R*(C(I)-XX(IMAX,I))
30 CONTINUE

The function value at the new point.....

CALL F(Y,N,FY)
IF (FY .LT. FX(IMIN)) THEN

Expansion.....

DO 40 I=1,N
   Z(I)=C(I)+T*(C(I)-XX(IMAX,I))
40 CONTINUE
CALL F(Z,N,FZ)
IF (FZ .LT. FY) THEN

The expansion has succeeded.....

DO 45 I=1,N
   XX(IMAX,I)=Z(I)
45 CONTINUE
FX(IMAX)=FZ
ACTION='Expansion'
GOTO 15
ELSE
DO 50 I=1,N
   XX(IMAX,I)=Y(I)
50 CONTINUE
FX(IMAX)=FY
ACTION='Reflection'
GOTO 15
ENDIF
ELSEIF (FY .LT. FX(IMAXS)) THEN

Exchange .....

DO 60 I=1,N
   XX(IMAX,I)=Y(I)
60 CONTINUE
FX(IMAX)=FY
ACTION='Exchange'
GOTO 15
ELSE
IF (FY .LT. FX(IMAX)) THEN

Flip.....

DO 70 I=1,N
   XX(IMAX,I)=Y(I)
70 CONTINUE
FX(IMAX)=FY
IFLIP=1
ENDIF

Contraction.....
DO 80 I=1,N
V(I)=C(I)+S*(XX(IMAX,I)-C(I))
CONTINUE
CALL F(V,N,FV)
IF (FV .LT. FX(IMAX)) THEN
DO 90 I=1,N
XX(IMAX,I)=V(I)
90 CONTINUE
FX(IMAX)=FV
ACTION='Contraction'
GOTO 15
ELSE
ACTION='Contraction'
GOTO 5
ENDIF
ENDIF
RETURN
END

C
C
C The following subroutine is for solving ODEs by Runge-Kutta
C fourth method.....
C
SUBROUTINE F(X,N,FX)
IMPLICIT REAL *8 (A-H,O-Z)
DIMENSION X(N), CONST(2)
INCLUDE 'MOLREDTN.DAT'
DO 5 I=1,N
XX(I)=X(I)
IF (XX(I) .LT. 0.0D0) THEN
FX=1.0D10
GOTO 20
ENDIF
5 CONTINUE
FX=0.0D0
DO 20 JCOL=1,NT
TK=TEMP(JCOL)
Y(1)=Y10
Y(2)=Y20
Y(3)=Y30
Y(4)=Y40
Y(5)=Y50
CALL DERIVS (NN,Y,DY)
JEXP=1
TIME1=TIME(JEXP,JCOL)
20 CONTINUE

C
C
C Shrink....
C
DO 100 I=1,N+1
DO 100 J=1,N
XX(I,J)=0.5D0*(XX(I,J)+XX(IMIN,J))
100 CONTINUE
ACTION='Shrink'
GOTO 5
ENDIF
ENDIF
RETURN
END
Here is the ODE solver....

SUBROUTINE RK4(N,H,Y,DY,YC,Y1)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION Y(N), DY(N), YC(N), Y1(N), A(4)
A(1)=0.5D0*H
A(2)=A(1)
A(3)=H
A(4)=H
DO 1 I=1,N
  Y1(I)=Y(I)
1 CONTINUE
DO 3 K=1,3
  DO 2 I=1,N
    YC(I)=Y1(I)+A(K)*DY(I)
2 CONTINUE
  CALL DERIVS(N,YC,DY)
3 CONTINUE
  DO 4 I=1,N
    Y(I)=Y(I)+A(1)*DY(I)/3.0D0
4 CONTINUE
  CALL DERIVS(N,Y,DY)
RETURN
END

C
C This subroutine is for derivatives of the differential equations for
the reaction scheme.
where,

\[
Y(1) = \text{time}
\]

\[
Y(2) = \text{Fraction of the Resid in the total HT product}
\]

\[
Y(3) = \text{Fraction of the Total Gas Oil in the total HT product}
\]

\[
Y(4) = \text{Fraction of the Middle Distillates in the total HT product}
\]

\[
Y(5) = \text{Fraction of the Gases in the total HT product}
\]

Also,

\[
X(1) = kro
\]

\[
X(2) = kod
\]

\[
X(3) = kog
\]

\[
X(4) = kdg
\]

\[
DY(1) = \frac{dY(1)}{dt}, \quad DY(2) = \frac{dY(2)}{dt}, \quad DY(3) = \frac{dY(3)}{dt},
\]

\[
DY(4) = \frac{dY(4)}{dt}, \quad DY(5) = \frac{dY(5)}{dt}.
\]

SUBROUTINE DERIVS(N,Y,DY)
IMPLICIT REAL*8 (A-H,O-Z)
DOUBLE PRECISION Y(5), DY(5)
COMMON /DKWAK/TEMP, X(10)
DO 10 I=2,N
IF(Y(I) .LT. 0.0D0) Y(I)=0.0D0
IF(Y(I) .GT. 1.0D0) Y(I)=1.0D0
10 CONTINUE
DY(1)=1.0D0
Y2=Y(2)
Y3=Y(3)
DY(2)=-X(1)*Y2
DY(3)=X(1)*Y2-Y3*(X(2)+X(3))
DY(4)=X(2)*Y2-X(4)*Y(4)
DY(5)=X(3)*Y3+X(4)*Y(4)
RETURN
END

The following subroutine checks the performance of this program.
It compares the experimental and calculated value of the estimated
kinetic constants and gives the performance ranges.

SUBROUTINE STTEST(N,X,IP1)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION X(N)
INCLUDE 'MOLREDTN.DAT'
DIMENSION DIFFA(NP),DIFFB(NP),DIFFC(NP),DIFFD(NP),DIFE(NP),
1 YAA(NP),YBB(NP),YCC(NP),YDD(NP),YEE(NP),
2 PERCTA(NP),PERCTB(NP),PERCTC(NP),PERCTD(NP)
DIMENSION DIFA(NT*NP),DIFB(NT*NP),DIFC(NT*NP),DIFD(NT*NP)
1 ,DIFE(NT*NP)
2 DIMENSION DIFFA(5),DIFFB(5),DIFFC(5),DIFFD(5),DIFE(5),
1 YAA(5),YBB(5),YCC(5),YDD(5),YEE(5),
2 PERCTA(5),PERCTB(5),PERCTC(5),PERCTD(5)
DIMENSION DIFA(5),DIFB(5),DIFC(5),DIFD(5),DIFE(5)

INCLUDE 'MOLREDTN.DAT'

DO 5 I=1,N
XX(I)=X(I)
5 CONTINUE

ICOUNT=0
AADA=0.0D0
AADB=0.0D0
AADC=0.0D0
AADD=0.0D0
DO 200 JCOL=1,NT
TK=TEMP(JCOL)
Y(1)=Y10
Y(2)=Y20
Y(3)=Y30
Y(4)=Y40
Y(5)=Y50
NUM=NUMBER(JCOL)
JEXP=1
TIME1=TIME(JEXP,JCOL)
CALL DERIVS(NN,Y,DY)
DO 10 I=1,1000
CALL RK4(NN,H,Y,DY,YC,Y1)
IF(ABS(Y(1)-TIME1).LE.1.0D-8) THEN
DIFFA(JEXP) = A(JEXP,JCOL)-Y(2)
DIFFB(JEXP) = B(JEXP,JCOL)-Y(3)
DIFFC(JEXP) = C(JEXP,JCOL)-Y(4)
DIFFD(JEXP) = D(JEXP,JCOL)-Y(5)
ICOUNT=ICOUNT+1
DIFA(ICOUNT)=DIFFA(JEXP)
DIFB(ICOUNT)=DIFFB(JEXP)
DIFC(ICOUNT)=DIFFC(JEXP)
DIFD(ICOUNT)=DIFFD(JEXP)
YAA(JEXP)=Y(2)
YBB(JEXP)=Y(3)
YCC(JEXP)=Y(4)
YDD(JEXP)=Y(5)
PERCTA(JEXP)=DIFFA(JEXP)/A(JEXP,JCOL)*100.0D0
PERCTB(JEXP)=DIFFB(JEXP)/B(JEXP,JCOL)*100.0D0
PERCTC(JEXP)=DIFFC(JEXP)/C(JEXP,JCOL)*100.0D0
PERCTD(JEXP)=DIFFD(JEXP)/D(JEXP,JCOL)*100.0D0
AADA=AADA+ABS(PERCTA(JEXP))
AADB=AADB+ABS(PERCTB(JEXP))
AADC=AADC+ABS(PERCTC(JEXP))
AADD=AADD+ABS(PERCTD(JEXP))
JEXP=JEXP+1
TIME1=TIME(JEXP,JCOL)
IF(JEXP.GT.NUM) GOTO 20
ENDIF
10 CONTINUE
20 CONTINUE
C WRITE(*,100) TK
WRITE(1,100) TK
100 FORMAT(/5X,'TEMPERATURE=',F7.2,' K',
     1 /5X, 'RESID FRACTION:')
WRITE(*,110)
WRITE(1,110)
110 FORMAT(7X,'TIME',4X,'EXPERIMENTAL',10X,'CALCULATED',7X,
     1 'DIFFERENCE',5X,'PERCENTAGE'/
     2 7X,'-—',5X,'---------',13X,'--------',8X,
     3 '---------',5X,'----------')
DO 30 I=1,NUM
WRITE(6,120) TIME(I,JCOL),A(I,JCOL),YAA(I),DIFFA(I),PERCTA(I)
WRITE(1,120) TIME(I,JCOL),A(I,JCOL),YAA(I),DIFFA(I),PERCTA(I)
30 CONTINUE
120 FORMAT(3X,F8.1,2X,G13.5,G22.7,G18.7,G13.5)
WRITE(*,130)
WRITE(1,130)
130 FORMAT(/5X, 'TOTAL GAS OIL FRACTION:')
WRITE(*,110)
WRITE(1,110)
DO 40 I=1,NUM
WRITE(*,120) TIME(I,JCOL),B(I,JCOL),YBB(I),DIFFB(I),PERCTB(I)
WRITE(1,120) TIME(I,JCOL),B(I,JCOL),YBB(I),DIFFB(I),PERCTB(I)
40 CONTINUE
140 FORMAT(/5X, 'MIDDLE DISTILLATE FRACTION:')
WRITE(*,110)
WRITE(1,110)
DO 50 I=1,NUM
WRITE(*,120) TIME(I,JCOL),C(I,JCOL),YCC(I),DIFFC(I),PERCTC(I)
WRITE(1,120) TIME(I,JCOL),C(I,JCOL),YCC(I),DIFFC(I),PERCTC(I)
50 CONTINUE
150 FORMAT(/5X, 'GASES (NH3, H2S, C1 TO C4):')
WRITE(*,110)
WRITE(1,110)
DO 60 I=1,NUM
WRITE(*,120) TIME(I,JCOL),D(I,JCOL),YDD(I),DIFFD(I),PERCTD(I)
WRITE(1,120) TIME(I,JCOL),D(I,JCOL),YDD(I),DIFFD(I),PERCTD(I)
60 CONTINUE
200 CONTINUE
C
C Now calculating each fraction's AADs.....
C
S1=0.0D0
DO 70 J=1,NT
NUM=NUMBER(J)
DO 70 I=1,NUM
S1=S1+A(I,J)
S1=S1+B(I,J)
S1=S1+C(I,J)
S1=S1+D(I,J)
CONTINUE
S1=0.25D0*S1/ICOUNT
RGS=0.0D0
DO 80 J=1,NT
NUM=NUMBER(J)
DO 80 I=1,NUM
RGS=RGS+(A(I,J)-S1)**2
RGS=RGS+(B(I,J)-S1)**2
RGS=RGS+(C(I,J)-S1)**2
RGS=RGS+(D(I,J)-S1)**2
80 CONTINUE
RSDA=0.0D0
RSDB=0.0D0
RSDC=0.0D0
RSDD=0.0D0
DO 90 I=1,ICOUNT
RSDA=RSDA+DIFA(I)*DIFA(I)
RSDB=RSDB+DIFB(I)*DIFB(I)
RSDC=RSDC+DIFC(I)*DIFC(I)
RSDD=RSDD+DIFD(I)*DIFD(I)
90 CONTINUE
RSD=RSDA+RSDB+RSDC+RSDD
R2=1.0D0-RDS/RGS
AADA=AADA/ICOUNT
AADB=AADB/ICOUNT
AADC=AADC/ICOUNT
AADD=AADD/ICOUNT
WRITE(1,170) RSDA,AADA,RSDB,AADB,RSDC,AADC,RSDD,AADD
WRITE(*,170) RSDA,AADA,RSDB,AADB,RSDC,AADC,
1     RSDD,AADD
170 FORMAT(/5X,'COMP.',16X,'SSE',12X,'AAD',
1     /5X,'------',16X,'---',12X,'---',
2     /8X,'RESID',8X,2G16.5,/8X,'GAS OIL',6X,2G16.5,
3     /8X,'MID.DIT.',5X,2G16.5,/8X,'GASES',8X,2G16.5)
RETURN
END
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