A STUDY OF THE APPLICATION OF COMPOSITE BEDS FOR PETROLEUM RESIDUE HYDRODESULFURIZATION

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1983

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the degree of
MASTER OF SCIENCE
December, 1986

A STUDY OF THE APPLICATION OF COMPOSITE BEDS FOR PETROLEUM RESIDUE HYDRODESULFURIZATION

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PREFACE

The purpose of this study was to investigate the possible advantages of using catalyst activity zoning during hydrodesulfurization of a petroleum residue. Three different commercial Ni-Mo catalysts were employed singly or in combination in a two-zone, trickle bed reactor. The operating conditions were 10.3 MPa, 380°C, 1.0 LHSV (based on total bed volume of both zones), and 1,781 std m^3(hydrogen)/m^3(oil).

I am especially grateful to my thesis adviser, Dr. Billy L. Crynes, for his valuable and friendly guidance, patience, and cooperation during this study. I am thankful to Dr. Mayis Seapan and Dr. Gary L. Foutch for their cooperation as committee members. I offer a special note of appreciation and thanks to my friend Hasan Qabazard for his cooperation and companionship throughout the study. I am in appreciation of Harold Wandke, Jung L. Liu, Jirdsack Tscheikuna, Arman Anooshtakin, Larry Crynes, and David Tice for their assistance in operating the equipment. Special thanks are due to Randy Smejkal, Denise Rex, and Patty Inskeep for their attention in samples analyses, and to Melissa Stephenson for her help in editing this thesis.

A special note of thanks is due to Mr. Charles Baker, the laboratory manager and all the office secretaries. The help of Mr. Carlos Ruiz in computer-graphics programming is appreciated.

Financial support from the School of Chemical Engineering and the U.S. Department of Energy is greatly appreciated.

Finally, I wish to dedicate this achievement to my parents Efrain and Mery, my brothers, and my friends who understood, inspired, and supported my work.

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CHAPTER I

INTRODUCTION/LITERATURE REVIEW

The objective of this work was to investigate the possible advantages of using composite beds, compared to single beds, during hydrodesulfurization of a petroleum residue. The effect of metals, nitrogen, and coke depositing compounds present in the residue on the performance of the system is to be evaluated.

Environmental regulations, crude oil availability, and the shift toward heavier crudes are amongst the reasons that have given the oil industry the challenge of finding and optimizing new processing routes to increase bottom-of-the-barrel conversion. In spite of the reduction in oil prices, upgrading of petroleum residues continues to be important in the refining industry.

Catalytic hydrotreating involves the reaction of petroleum feedstocks with hydrogen in the presence of a catalyst under suitable operating conditions. Hydroprocessing effects the conversion to lighter fractions, prepares the feedstocks for downstream conversions, and/or improves the quality of finished products.

The main consideration in the development of new processes for residue upgrading is the presence of impurities such as asphaltenes, metals, sulfur, and nitrogen compounds which affect the catalyst performance and consequently the overall efficiency of the process (Sie, 1980).

The selection of a residue hydrotreating process depends on the kind of feedstock, the market for products, the existing conversion and upgrading units, and financial and environmental considerations (Ebel, 1972; Murphy et al., 1979; Hung et al., 1986).

In this literature review emphasis will be made on the application of composite catalyst beds for petroleum residue upgrading. Following that there will be a general, not comprehensive, review of complementary topics such as residue upgrading, operating conditions, catalyst selection, hydrotreating reactions, and deactivation.

The discussion of the literature review leads to the following conclusions:

1. Catalyst life can be considerably increased using composite catalyst beds. Hydrodemetalation (HDM) catalysts in the upper layers combined with hydrodesulfurization (HDS) catalysts in the lower sections have been found to be effective in residue upgrading.
2. Different approaches for composite catalyst fillings involve the use of variation in catalyst size, pore size, metals capacity, and HDS activity. Besides this, the use of different operating conditions (temperature

zoning) has been suggested.

3. Guard beds containing inexpensive disposable materials have proven to be an effective way of protecting the main reactor from deposition of contaminants.
4. The scheme selection for petroleum residue upgrading strongly depends on the feedstock. For this reason, reliable and complete characterization of the residue is required.
5. The selection of operating conditions needs to be optimized in order to control catalyst deactivation and undesired reactions. On the other hand, catalyst selection depends on feedstock, severity of operation, and product requirements. Nickel-molybdenum catalysts are the best choice when hydrodenitrogenation (HDN) and hydrogen uptake are required in addition to HDS.
6. HDS reactions can be represented as parallel first order reactions; nitrogen removal is determined by the HDS level, and HDM is represented by first order kinetics with respect to metal compound concentration.
7. Metals and coke deposition cause deactivation in hydrotreating catalysts. Coke is associated mainly with initial deactivation and metals with intermediate and final deactivation. Models for deactivation take into account the effect of surface poisoning and pore mouth plugging.

Composite Catalyst Beds

Deactivation in fixed bed catalytic reactors has been found to be more severe in the upper catalyst layers. On the other hand, high metals uptake and/or high coke-resistant catalysts experience relatively low activity, and, conversely, the active catalysts have low contaminants capacity. This suggests that a single catalyst type cannot cope with the wide spectrum of process requirements.

Catalyst life can be extended with the use of graded catalyst beds. High metals capacity (low activity) catalysts are used at the top of the bed followed by high activity (low metals uptake) catalysts further down.

Extensive research has been done in the area of composite catalyst beds. Several approaches include the use of different catalyst types and at various process severity in order to handle heavy and/or high metals stocks. Higashi et al. (1985) upgraded an Arabian Heavy atmospheric residue at 85 wt% desulfurization. They combined a new HDM catalyst (40%) and a conventional HDS catalyst (60%) in a trickle bed reactor. Comparative runs were made using the HDS catalyst alone. Even though the initial reactor temperature of the composite bed was higher, the deactivation was slower than that using the HDS catalyst alone.

Higashi's results indicated that at the upper part of the reactor, the deposition of metals on the HDM catalyst was over 100 wt% of the fresh catalyst and the HDM activity was maintained. These results suggested that HDM reaction takes place autocatalytically by deposited metals. The main differences in properties for the catalysts were surface area (225×10^3 m^2/kg for HDS catalyst and 205×10^3 m^2/kg for HDM catalyst) and pore volume (0.62×10^{-3} m^3/kg for HDS catalyst and 0.71×10^{-3} m^3/kg for HDM catalyst) The quality of the products was also improved by the application of the combination of catalysts.

Sue and Fujita (1986) reported the hydroprocessing of Kuwait and Murban atmospheric residues at 85 wt% HDS. A combination of a new catalyst R-HYC4 (50%) with a conventional HDS catalyst (50%) increased the 650°F+ conversion by 10% and kept the metals content at the same level as compared to the conventional HDS catalyst alone. The new catalyst was reported to have high HDS, HDM, deasphalting, and hydrocracking activity.

Curtis et al. (1985) studied the effect of composite beds on coprocessing petroleum residue and coal. They processed Illinois #6 coal and West Texas and Maya vacuum residues using pyrite, NiMo/alumina, and hydrogen sulfide as catalysts individually and in combination. The combination of pyrite in the first zone and NiMo/alumina in the second showed better performance than thermal processing. However, the best results for oil production and coal conversion were obtained by using the NiMo/alumina catalyst in both zones.

The use of a mixed HDS-HDM catalyst system to process a heavy atmospheric residue (Maya) containing 400+ ppm metals (V plus Ni) and 4.5 wt% sulfur was reported by Christman et al. (1985). A five-month run indicated that deactivation accelerated only slightly near end-of-run (EOR). The product metals level was below 50 ppm and the sulfur content varied between 0.56 and 0.74 wt% but showed no particular trend with time. Christman's results showed no gradual loss in HDS in contrast with a heavy Venezuelan residue run using only a demetallation catalyst. Average metals uptake of 50% based on fresh catalyst weight was reported. Analyses of the results revealed that HDS activity was primarily related to catalytic metals present in the micropore structure (1 to 20 nm), while demetallation was related to the macropore size (20 to 100 nm).

Chevron studied different catalysts for HDS and HDM of petroleum residues (Howell et al., 1985; Hung et al., 1986). The studies indicated that a combination of catalysts or graded catalyst systems give better results for processing high metals feedstocks than any single catalyst. Howell et al. (1985) reported that a three catalyst system provided the longest run life for HDS of Arabian Heavy atmospheric residue. Chevron has reported the use of a two-catalyst graded bed for commercial vacuum residue desulfurization (VRDS) operations at the Richmond and Pascagoula refineries. They concluded that heavier feedstocks will require more HDM capacity while maximum conversion to lighter products will demand higher severity and more active catalysts.

A process for maximum conversion of residual oil using a composite catalyst bed was developed at the OSS Refinery in Japan (Saito et al., 1984). The reactor consisted of three beds with interstage gas quenching to keep a flat temperature profile in the beds. The first bed and upper half of the second bed were loaded with an HDM catalyst having a high tolerance for deactivation by metals and coke deposition. A high activity HDS catalyst was loaded in the remaining reactor volume. The volume ratio of the HDM/HDS catalyst was 33/67. Feedstocks processed included Khafji and Gach Saran vacuum residues and Orinoco atmospheric residue. The average catalyst temperature went from 340°C at start-of-run (SOR) to 410°C at EOR with a rapid initial deactivation period followed by a stable activity level. They reported metal deposition of 40 wt% for the HDM catalyst and 9 wt% for the HDS catalyst. The process proved to be an effective method for maximum conversion of heavy residual oil to middle distillate fractions.

Research at Haldor Topsøe in the area of composite catalyst beds includes design, modelling, and catalyst selection. Nielsen et al. (1981) investigated the application of composite beds and qualitatively described the methods to optimize the metals distribution in each catalyst layer. Tests were performed in a three trickle-bed reactor system equipped with interstage sampling.

Results showed that for a single catalyst bed, metals deposited mainly in the upper layers causing enhanced deactivation. The coke deposition showed a flat profile throughout the reactor system. They postulated that longer life would be obtained if each bed had a uniform rate of deactivation. The use of composite beds of catalysts with high tolerance for metals in the upper layers was suggested.

Several tests were performed to obtain information about the design of a composite catalyst bed. Nielsen et al. (1981) used three different catalysts expecting the same overall deactivation rate for each one. Kuwait atmospheric residue and Iranian Heavy vacuum residue served as feedstocks. Results showed that the optimum catalyst combination depended on the feedstock, the operating conditions, and the catalyst type. The higher metals and heavier residue required a higher amount of the demetalation catalyst and more severe operating conditions.

Hannerup and Jacobsen (1983) in their model for the deactivation of residue HDS catalysts suggested that longer lives can be obtained by using several catalyst types in a composite bed instead of a single catalyst.

Jacobsen et al. (1983) developed a model for prediction of the composite catalyst filling that gives the longest life in a given HDS process. They assumed that the outer part of the pores suffers rapid initial HDS deactivation and the diffusional resistance increases due to accumulation of metal sulfides. The results published by Nielsen et al. (1981) served as a basis for this study.

Different types of catalysts used in the experiments included variation in size, pore size, metals capacity and desulfurization activity. Jacobsen et al. (1983) reported that two-catalyst combinations gave much longer life than a single catalyst when processing Iranian Heavy atmospheric residue at 10.9 MPa (1,575 psi), 1.0 liquid hourly space velocity (LHSV) and 80 wt% HDS. At higher severities (lower pressure) or for heavier feeds the use of a three-catalyst system was suggested. There was an optimum pressure for each particular application. Pressures higher than the optimum resulted in lower metals capacity while at pressures below the optimum the higher penetration of contaminants shortened the catalyst life. They concluded that proper selection of types and amount of catalysts is crucial in the optimization of composite beds.

Bhan (1983) studied the effect of composite catalyst beds in the upgrading of solvent refined coal (SRC) liquids. Two commercial Ni-Mo-alumina catalysts with different pore diameters were used in a two-zone, fixed bed system. Bhan reported no significant advantange of the pore size graded beds over the single catalyst beds for this particular application. Moreover, Bhan evaluated the effect of temperature zoning in the process. The top zone was operated at 260°C (500°F) and the lower zone at 400°C (752°F). He found that almost all of the inorganic and heavy carbonaceous residues were removed in the top (low temperature) zone. Therefore, the overall activity of the temperature zoned bed was reported to be higher than the single temperature bed.

Beazer (1984) studied the hydrotreating of an SRC coal liquid by temperature zoning using the reactor system employed in Bhan's studies. Beazer reported an improvement in hydrodenitrogenation, hydrodemetalation, hydrogenation and conversion when using higher temperatures in the top reactor. The top zone temperature ranged from 425 to 450°C (797 to 842°F). The lower reactor remained isothermal at 400°C (752°F).

The RCD Unibon process licensed by UOP uses a two-catalyst-zone design for HDS of Kuwait reduced crude to the 0.3 wt% level over an 11-month cycle at the Yokohama refinery of the Asia Oil Company (Sikonia, 1980). The catalyst used in the first zone (RCD-5) had excellent metals uptake and good HDS activity. The second zone catalyst (RCD-5A) had high HDS activity and good stability. Results showed more deactivation (metal deposition) in the upper zone. A relatively constant activity in the second stage indicated good tolerance for coke deactivation. No specific operating conditions or catalyst properties were reported.

Another common approach in residues upgrading is the use of guard beds to protect the catalyst in the hydrotreater from deposition of contaminants. The Exxon Residfining process uses guard reactors to protect the main reactor trains against plugging. The guard reactor can be changed without disturbing the system by bypassing the feed around the guard (Shah et al., 1979). Union Oil Company Unicracking/HDS processes employ a guard chamber loaded with a proprietary catalyst. The guard removes particulate matter and residual salt content from the feed (Hydrocarbon Processing, 1984).

Shell's residue HDS process uses guard reactors to reduce the metals (V plus Ni) in the product stream by 60 to 70%, protecting the HDS reactors against metal poisoning (Kwant et al., 1984).

Robinson and Evin (1983) reported the hydrotreating of Shale oils using a guard bed reactor followed by a hydrotreater. The guard bed was filled with alumina extrudates and balls containing no active metals. Unsuccessful results indicated the need to develop stable guard bed catalysts that remove and adsorb iron and arsenic from shale oils without plugging the system.

Residue Upgrading

Commercial Schemes

Several proprietary schemes for residue upgrading have been published in the literature. An Esso-Union scheme includes the fractionation of atmospheric residue to vacuum gas oil (VGO) plus a vacuum residue, desulfurization of the VGO using GO-fining, and then back-blending.

Chevron's proprietary route includes hydrotreating of atmospheric residue by residue desulfurization (RDS) to produce distillates, fluid catalytic cracking (FCC) feedstock or low sulfur fuel oil. Also included is the processing of the vacuum residue by vacuum residue desulfurization (VRDS) followed by coking to produce a low sulfur coke plus distillates. The desulfurization units use specially graded catalyst systems to maintain activity and selectivity in the presence of metals.

An alternative scheme uses solvent deasphalting (SDA) in combination with residue hydrocracking for gasoline production. This route is preferred for feedstocks having most of the contaminants concentrated in the asphaltene portion of the residue (Howell et al., 1985). Flexicoking, an Exxon process, integrates conventional fluid coking with coal gasification. This processing scheme typically converts about 95% of vacuuum residue to gaseous and liquid products (Parkinson, 1985; Allan et al., 1982).

Siewert et al. (1985) presented the evaluation of various processing schemes when switching from light to heavy crude in an hypothetical refinery. They classified the residue process technology as carbon rejection or hydrogen addition processes and categorized them under extraction, thermal conversion and catalytic conversion. Processes involving carbon rejection, i.e. solvent deasphalting or coking, are not attractive for processing heavy oils because of excessive coke production. For these kinds of feedstocks, the hydrogen addition approach seems to be most popular (Parkinson, 1985; Denny et al., 1986).

Hydrocarbon Processing (1984) presented a review of different proprietary commercial processes for hydrotreating residues. Chevron and UOP processes use the concept of graded catalyst beds which have catalysts with high capacity for metals at the top and leave more active catalysts for the rest of the bed. On the other hand, Union Oil and Exxon schemes use guard reactors or chambers to protect the catalyst in the main reactor from metals poisoning.

Characterization of Residues

Process selection for catalytic HDS of the heavy ends of the crude oil requires prior information about a general characterization of the residue structure. According to several investigators, residues are considered as a mixture of heavy oil, waxes, resins, asphaltenes, and other bitumens (Yen, 1972; Murphy et al., 1979). Other compounds present in the residues are porphyrins, polynuclear aromatic hydrocarbons, sulfur and nitrogen compounds. Jewell et al. (1972) gave a classification of components in residues based on solubility relationships as shown here:

	Solvent		
Component	Benzene	n-Pentane	Propane
Asphaltenes	soluble	insoluble	
Maltenes	soluble	soluble	
Resins		soluble	insoluble
Oils		soluble	soluble

In general, low API gravity, high sulfur content, high concentration of very high molecular weight condensed ring hydrocarbons, low H/C atom ratio, and appreciable amounts of metals are common properties of all residues (Schuetze and

Hofmann, 1984).

With respect to carbon-type structure, nuclear magnetic resonance (NMR) data along with chromatography data indicated that bitumen and petroleum residues consist typically of 20 wt% to 40 wt% naphthenic and aromatic carbon (Bunger, 1985). These results are in agreement with those reported by Farcasiu et al. (1985).

With respect to heteroatoms, Richardson and Alley (1975) reported that when asphaltenic sulfur removal is not deep, a large proportion of sterically hindered aromatic sulfur compounds; such as substituted thiophenes, benzothiophenes and dibenzothiophenes; strongly influences the refractoriness of residues.

Generally, the level of nitrogen increases significantly with increasing boiling point; whereas, oxygen and sulfur contents increase to a lesser extent. Nitrogen is characteristically concentrated in coke products and is implicated as a promoter of coke formation (Bunger 1985).

The metals V and Ni are frequently present in complex organic structures called porphyrins as well as in non-porphyrin chelate structures. Apparently porphyrins exist as a low molecular weight homologous series, whereas, the non-porphyrins are associated with even larger-sized structures (Rankel, 1981; Biggs et al., 1985).

The presence of asphaltenes in residues is of considerable significance to hydroprocessing since asphaltenes have been implicated in catalyst deactivation due to deposition of metals and carbon (Elvin, 1983). However, from Bunger et al. (1985), asphaltenes contribute to coke formation only indirectly through their relatively low volatility.

Experimental Techniques for Characterization

The quality and reliability of characterization of petroleum residues always depend on the technique used for determinations. Adequate compositional information will aid in understanding the chemistry of the reactions involved in hydroprocessing. Jewell et al. (1972) developed a useful characterization technique which breaks the residues into saturates, aromatics, resins and asphaltenes. This so-called SARA method is used for qualitative and semi-quantitative analyses. Another technique that gives information about asphaltenes, saturates, aromatics, sulfur compound type distributions and molecular weight distribution is described by Drushel (1972).

Boduszynsky (1985) discussed recent results and techniques for characterization. A description of the method used at Chevron Company was given. This method combines short-path distillation, high performance liquid chromatography (HPLC), and field ionization mass spectrometry (FIMS) to obtain detailed compositional information not available from other techniques.

The inorganic compounds present in residues are at parts per million levels which make the analytical characterization extremely difficult. Reynolds and Biggs (1985) developed and applied size exclusion chromatography with inductively coupled plasma emission spectroscopy (SEC-HPLC-ICP) to examine V and Ni as a function of process conditions.

Operating Conditions

The selection of the operating conditions relies on the degree of desulfurization desired, the catalyst performance, and the type of feedstock. Typical operating conditions for residue desulfurization are reported in the following paragraphs.

Pressure Effect

Several investigators have studied the effect of operating pressure in residue HDS. Blume et al. (1969) concluded that the economics of residue hydrotreating is favored by lower pressure. The feedstock was a 370°C+ (700°F+) Safaniya atmospheric residue. The range of pressures varied from 5.5 to 20.7 MPa (800 to 3,000 psig). These conclusions are in agreement with the Brunn et al. findings (1975). However, Newson (1972) showed that catalyst deactivation and bed plugging are increased by decreasing hydrogen partial pressure.

The removal of metals is important for low pressure operation. Results from Chang and Silvestry (1976) showed that demetalation of Kuwait atmospheric and vacuum residues decreased with hydrogen partial pressure. Sakabe and Yagi (1979) found that at lower operating pressures cracking can be more extensive, desulfurization lower, removal of vanadium and nickel less, and carbon-forming tendency higher when upgrading Kuwait and Ta-Ching atmospheric residues and Gach Saran vacuum residue.

Pazos et al. (1983) studied the pressure effect on hydrotreating of high metal residues in a fixed bed, down flow, pilot unit. The pressure was changed from 6.9 to 11.7 MPa (1,000 to 1,700 psi) showing increased deactivation by metals after the pressure increase. This agrees with the results from Tamm et al. (1981) which show a decrease in catalyst life with increasing hydrogen pressure when processing Arabian Heavy atmospheric residue.

Temperature Effect

In practice, residue hydroprocessing is not carried out under constant temperature. The temperature is increased to keep a constant weight percent of sulfur or nitrogen in the product. The desired reaction severity and the space velocity employed determine the initial temperature (Nielsen et al., 1981; Tamm et al., 1981).

The upper limit is set by changes in product properties (undesired reactions) at higher temperatures and/or by construction materials. Typical EOR values range from 420 to 440°C (788 to 824°F). Some catalyst manufacturers suggest 400°C (750°F) as un upper limit in order to avoid cracking reactions. Thermal cracking has been shown to accelerate catalyst deactivation rates due to an increase in coke deposition (Jacobsen et al., 1983; Hohnholt and Fausto, 1984).

Space Velocity

Brunn et al. (1975) reported relative weight hourly space time (RWHST) in the range from 1.0 to 3.5 h for HDS of high metal residues (100 to 300 ppm Ni plus V) to produce 0.3 wt% sulfur fuel oil. They observed that when the liquid hourly space velocity (LHSV) increases the level of deactivation decreases. For heavier feeds a decrease in LHSV is recommended to sustain adequate HDS (Hohnholt and Fausto, 1984).

Hydrogen Consumption

The hydrogen consumption in residue hydrotreating depends on the activity and selectivity of the catalyst, the temperature and the hydrogen partial pressure. Consumption increases with increasing severity which is represented by higher temperature, lower space velocity, and higher hydrogen partial pressure. When hydrotreating residues the hydrogen consumption and the corresponding feed rates range from 53.4 to 267 and 890 to 1,780 std m^3/m^3(oil), respectively (Ebel, 1972; Brunn et al., 1975; Billon et al., 1977; Sakabe and Yagi, 1979; Nielsen et al., 1981; van Driesen et al., 1986).

Catalyst Selection

Selection of a catalyst is not a straight-forward proces; optimum choice is a function of feedstock type, operating conditions and product requirements. Experience with actual commercial operations or pilot plants with the same type of feedstock helps in making the proper decision. Often the best choice is not a single catalyst but a combination of several catalysts refered to as graded systems (Moyse et al., 1985; Tsakalis et al., 1984).

Basically, the hydrotreating catalysts consist of an active metal (usually molybdenum or tungsten oxide) promoted with a second active metal (cobalt, nickel, zinc or manganese) on a high surface area alumina and/or silica support. For the reader interested in an extensive study of hydrotreating catalyst characterization, the review by Topsøe (1982) is recommended.

Different catalyst manufacturers and patents (Nalco, 1974; Haldor Topsøe, 1984; Cyanamid, 1979; Alpert et al., 1971) offer varied formulations for residue hydrotreating applications. Table 1 lists typical ranges for properties and composition of HDS catalysts.

With respect to catalyst type, high activity nickel-molybdenum catalysts exhibit not only a substantial HDS activity but also HDN activity and hydrogen uptake. In contrast, cobalt-molybdenum catalysts show good HDS activity, but they exhibit only moderate HDN activity on lighter feedstocks (Kellet et al., 1980; McCulloch, 1983).

TABLE I

TYPICAL PROPERTY RANGES FOR RDS CATALYSTS

NiO or CoO wt%	2 - 6
MoO_3 wt%	5 - 20
Surface Area $m^2/kg \times 10^{-3}$	150 - 300
Pore Volume $m^3/kg \times 10^3$	0.4 - 0.8
Av. Pore Diameter nm	7 - 15

The catalyst selectivity depends mainly on chemical composition, pore size, pore size distribution and surface area. Catalysts having high HDS activity show unimodal, narrow pore size distribution with a small average pore diameter and large surface area. The tolerance for metals deposition in HDM catalysts increases as the pore size increases, as the pore size distribution gets broader, and as the surface area decreases. Thus HDM catalysts in the top of composite beds protect more active HDS, HDN, or hydrocracking catalysts (Howell et al., 1985).

Extensive research has been conducted in order to improve and develop catalysts for particular applications. The research efforts include: pore size distribution effect on asphaltene exclusion, metal deposition, coke deposition and diffusional properties (Moyse et al., 1985; Do, 1984; Ternan, 1983; Hannerup and Jacobsen, 1983; Richardson and Alley, 1975), effect of catalyst composition and the role of promoters on activity, and contaminant tolerance and selectivity of catalysts for hydrotreating applications (Tischer et al., 1985; Thakur et al., 1985; Laine et al., 1985; Lur'e et al., 1984; Kwant et al., 1984; Alekseenko et al., 1984; Wivel et al., 1981).

Several studies have been published covering the support property effects on catalyst performance (Behbahany et al., 1980; Cimino and Angelis, 1975), shape effects on metals tolerance, diffusion restrictions and pressure drop (Pereira et al., 1985; Moyse, 1984; Richardson et al, 1979), presulfiding techniques for activation of catalysts and effect of pretreatment on activity (Arnoldy et al., 1985; Parham and Merrill, 1984; Yang and Satterfield, 1983; Hallie, 1982; Gissy et al., 1980; Jepsen and Rase, 1981).

The research and development program behind catalyst manufacturing has made available families of catalysts for residue hydrotreating ranging from low activity/high contaminants capacity (HDM) to high activity/low contaminants capacity (HDS). These catalysts may be used singly or in combination (Higashi et al., 1985; Saito, 1984; Jacobsen et al., 1983). The application of combinations of catalysts as used in graded catalyst systems was discussed in a separate section.

Hydrotreating Reactions

Trickle Bed Reactor

Hydrotreating is usually carried out in reactors containing fixed beds of catalysts. When the liquid (oil) and the gas (hydrogen) flow cocurrently downwards through the catalyst bed, the reactor is called trickle bed. This type of reactor is relatively easy to operate. However, the complexity of the three phase system creates controversy in the interpretation of the results, and the scale-up of these reactors to commercial size has been made based mainly on experience.

The performance of trickle bed laboratory reactors used for HDM and HDS of heavy oils was described by Garcia and Pazos (1982) using a liquid hold-up model. A model that enables calculation of hydrodynamic properties in trickle bed reactors was published by Topsøe (1982).

Hydrodesulfurization

The principal reactions in catalytic hydrotreating include HDS, HDM, HDN, and to a lesser extent hydrodeoxygenation (HDO), hydrocracking, and hydrogenation of aromatics. All reactions take place simultaneously; thus, the nature of the different compounds present in the residues makes the analyses of particular reaction effects difficult (Sapre and Gates, 1980).

During HDS, hydrogen is necessary not only for reaction of sulfur to hydrogen sulfide but also for saturation (total or partial) of the desulfurized hydrocarbon. A good reference for the catalytic chemistry - reaction kinetics and mechanisms of HDS is Gates et al., (1979).

The complexity of the sulfur containing compounds such as thiophenic molecules present in petroleum residues complicates the HDS operation. Substantial removal of the sulfur atoms which are highly interwined in the complex asphaltenes requires severe conditions (Murphy et al., 1979; Hohnholt and Fausto, 1985).

Drushel (1972) showed that the relative sulfur type content —asphaltenes, polar aromatics, aromatics and saturates— of the feed and desulfurized products is a function of the sulfur conversion. Following the same sulfur-type distribution, Scamangas et al. (1982) observed that saturates and aromatics are the most difficult to hydrodesulfurize while polar aromatics and asphaltenes proceed faster. It appears that thiophenic type sulfur controls the rate of deep HDS. Richardson and Alley (1975) reported that when sulfur conversion levels are pushed above 90%, the unique refractoriness of asphaltenes becomes dominant.

Several researchers have published kinetic data on HDS with rate expressions ranging from first to second order. Sulfur removal following second order kinetics was reported by Scamangas et al. (1982), Nielsen et al. (1981), Hung et al. (1986), and Tamm et al. (1981).

Riley (1978) reported 1.5 order desulfurization kinetics; however, separating the total sulfur into asphaltene and nonasphaltene fractions indicated that the reaction rate was well represented as two first-order reactions whose sum approaches second order kinetics. Van Dongen et al. (1980) found the reaction orders for HDS in constantly stirred tank reactor (CSTR) and plug flow reactor (PFR) to be 1.5 and 2.0 respectively. They explained these findings by showing the wide spread in the reactivities of basically first order HDS reactions.

Frye and Mosby (1976) reported first-order kinetics for catalytic HDS of individual sulfur compounds. Iannibello et al. (1985), in their studies on hydrotreating reactions of residual oils in pilot trickle bed reactors, reported the optimum kinetic order to be dependent on the reactants and the active components of the catalyst.

Hydrodenitrogenation

HDN occurs during HDS of residues, and its level depends on the feedstock, catalyst, and process severity. In residue HDS studies, Riley (1978) showed that the removal reactions of nitrogen and carbon deposition compounds tended to follow the HDS reaction, i.e. the removal was determined once the HDS level was established.

Hydrodemetalation

HDS of petroleum residues is always accompanied by demetalation. As mentioned before, residue feedstocks usually contain high levels of asphaltenes and metals. The removal of sulfur in the presence of metals has been studied extensively. Brunn et al. (1975) suggested an optimum combination of catalysts and operating conditions to maximize HDS over HDM during residue hydrotreatment. Pazos et al. (1983) proposed that the HDM reaction occurred through a series of consecutive and parallel reactions when processing high metal feeds in pilot trickle bed reactors.

Rankel and Rollmann (1983) studied the transformation of metals and metalloporphyrins during HDS of atmospheric residue. The results support the assumption that metals (Ni and V) are deposited onto an HDS catalyst as sulfides with little catalytic activity compared with the cobalt and molybdenum already present.

In the development of a model for catalyst performance in residue HDS, Jacobsen et al. (1983) assumed that at constant HDS, the demetalation rate is also approximately constant and is influenced by catalyst properties and operating conditions. Hohnholt and Fausto (1985) developed correlations between metals and asphaltene removal, with the degree of conversion, depending on the feedstock. They reported that demetalation is independent of severity changes and more dependent on diffusional restrictions. Hung et al. (1986) also found HDM to be more diffusion limited or less sensitive to intrinsic, surface activity than HDS.

With respect to kinetics, several authors reported the kinetics of vanadium removal to be first-order (Hohnholt and Fausto, 1985; Riley, 1978). Agrawal and Wei (1984) proposed a kinetic model for HDM involving the formation of an intermediate, followed by metal deposition on the catalyst. The kinetics was consistent with first order dependency on metal compound concentrations with Langmuir isotherms. More recently, Ware and Wei (1985) investigated the kinetic mechanism of HDM reactions using a model residue oil. A mechanism was developed assuming a sequence of first order reactions and constant hydrogen concentration in the oil.

Van Dongen et al. (1980) showed that vanadium removal follows first-order kinetics in a CSTR and 1.5-order in a PFR when using a simulated moving bed reactor. They explained these differences based on a spread in reactivity of the individual vanadium-bearing species.

Deactivation

Understanding deactivation mechanisms during petroleum residue hydrotreating helps to improve and develop new catalysts and processes. Catalyst deactivation is a function of the catalyst properties, the feedstock and the operating conditions. However, the relationships are complex and may differ greatly from one catalyst to another.

There is experimental evidence which shows that residue hydrotreating catalysts deactivate in a very characteristic or 'S-shaped' manner. This consists of a period of rapid deactivation followed by a more gradual activity decline and finally an accelerated deactivation. Furthermore, catalyst life has been mainly determined by the intermediate deactivation (Sie, 1980).

The initial deactivation is generally associated with coke deposition on the catalyst surface (Nielsen et al., 1981; Brunn et al., 1975). On the other hand, Agrawal and Wei (1984) observed that almost all the coke formed during the total course of the reactor operation deposited itself during the first few hours. Some authors suggested that in addition to coke, metal deposition also has an effect on the initial deactivation period (Ternan and Kriz, 1980; Hannerup and Jacobsen, 1983).

Intermediate deactivation is attributed to metal sulfides deposition on the pore walls causing plugging. In the case of metals deposition from heavy oils, plugging seems to be a consequence of the large volume rather than the high reactivity of the metal-containing molecules (Pazos et al., 1983). Nielsen et al. (1981) showed that at high severity, the deactivation due to coking predominates throughout the run because the equilibrium coke level is not established before the EOR is reached.

The final accelerated deactivation occurs when only a small and rapidly decreasing amount of the available active sites is left. This seems likely to be caused by constriction of the catalyst pore mouth by metal deposits (Tamm et al., 1981; Pazos et al., 1983) or by both metal and coke deposits (Nielsen et al., 1981).

During the HDS of residues in fixed catalyst beds, deactivation is not constant throughout the reactor length. Deactivation acts as a moving front going in the flow direction (Sie, 1980; Beuther et al., 1980; Pazos et al., 1983).

Modelling

Extensive research efforts have been devoted to developing models for catalyst deactivation in hydrotreating. The most popular model includes the effect of active site poisoning and pore mouth plugging. Leung and Haynes (1984) applied this model for deactivation in bidispersed structured catalyst particles used in coal liquefaction .

A model proposed by Yorstos and Tsotsis (1984) includes the effect of diffusion and reaction in the porous catalyst. They postulated that metals and coke deposits build along the pore walls and can rapidly lead to pore mouth closure. Ahn and Smith (1984) developed a model for deactivation that accounts for HDM and also HDS. The model was restricted to isothermal operation and uniform pore size distribution assuming first-order kinetics for HDM and HDS.

Hannerup and Jacobsen (1983) related the catalyst parameters contained in the model to physical and chemical properties of the catalyst. They postulated that diffusional restrictions determine the distribution of metals. This is in agreement with results reported by Tamm et al. (1981).

CHAPTER II

EXPERIMENTAL SYSTEM AND PROCEDURE

Experimental Technique

The two-zone, trickle bed reactor equipped with interstage sampling employed in this study was also used for several SRC coal liquid hydrotreatment studies at Oklahoma State University (Bhan, 1983; Beazer, 1984; Newton, 1985). Figure 1 shows a schematic diagram of the reactor system. This is a typical laboratory, trickle bed reactor for oils hydroprocessing. A Ruska positive displacement pump supplied a constant preset feed rate of oil with negligible variation.

Rupture disks were located on the feed line for pressure build up prevention. The oil and gas lines consisted of 6.35 mm (1/4 in) OD stainless steel tubing. A special feature of this system is the interstage microsampler which allows liquid sampling between the two zones with minimum disturbance of normal operation.

The top and bottom reactors connected in series were 43 cm (17 in) and 46 cm (18 in) long, respectively. They were covered with aluminum blocks and wrapped with heaters for uniform heat distribution (flat temperature profile in the catalyst bed).

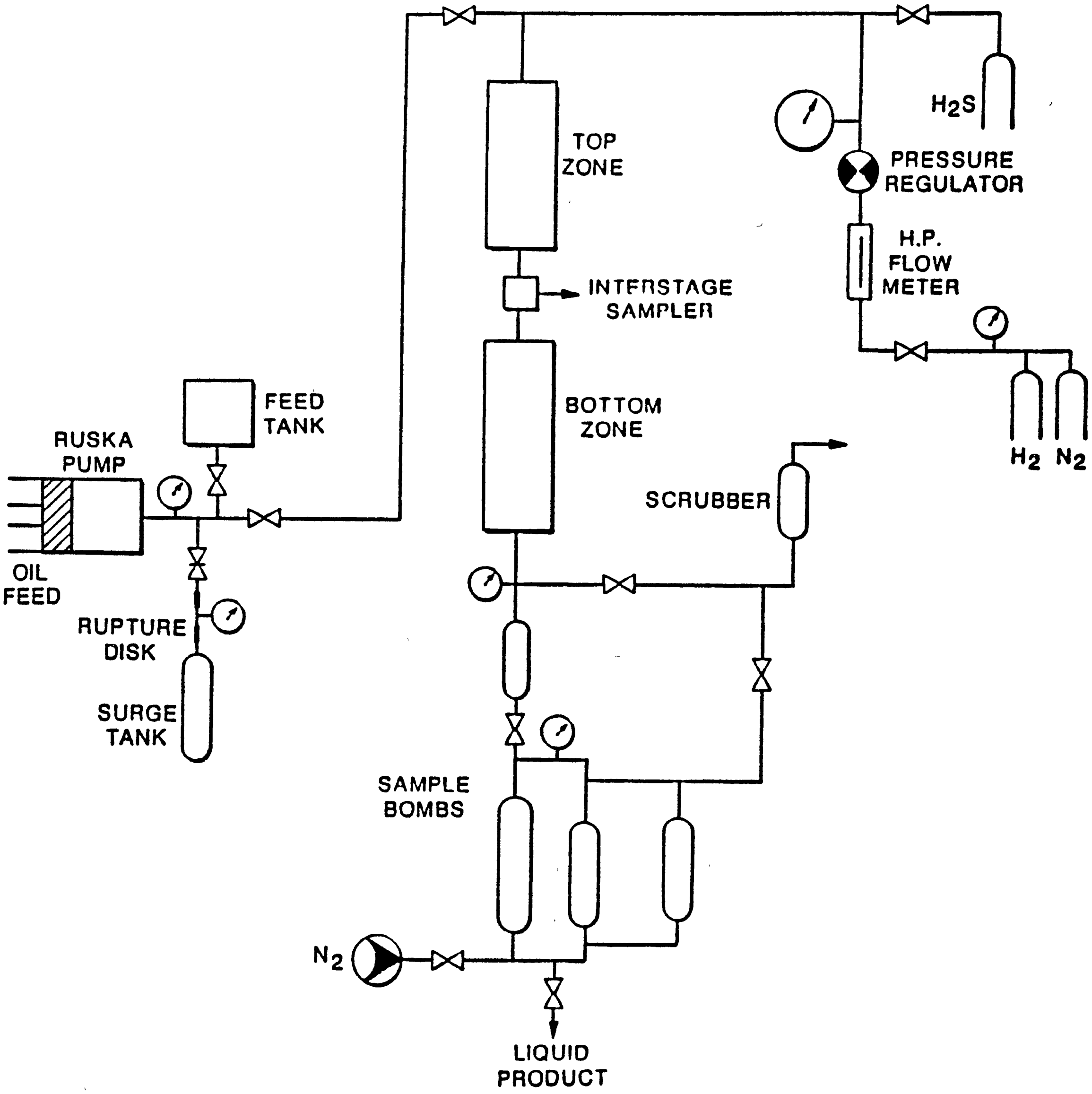

Figure 1. Simplified flow diagram

Sample bombs separated the gas from the liquid. The gases were scrubbed with a 50 vol% ethanolamine solution before leaving the system, and the liquid was collected from the sample bombs every 6 h using the main sampler located at the bottom of the system.

High pressure cylinders supplied the hydrogen, nitrogen, and hydrogen sulfide gases. The system was equipped with pressure regulators, pressure gauges, temperature programmer/controllers, thermocouples, temperature indicators, and flowmeters to control and monitor the operating conditions. For this study the pump, oil lines and sample bombs were wrapped with a heating system which allows the processing of heavy and viscous feedstocks. The heating was provided by electrical tapes connected individually to variacs.

The two reactors consisted of 12.7 mm (1/2 in) OD stainless steel tubing suited with a 3.18 mm (1/8 in) OD, centrally located, stainless steel tubing which served as a thermowell. The two catalyst zones were packed with 7.62 cm (3 in) of glass beads, 20.32 cm (8 in) of catalyst, and 5.08 cm (2 in) of glass beads.

After packing, the reactors were connected to the interstage sampler and to the system; then, the pressure and heating systems were checked. A pressure drop of less than 138 kPa (20 psig) over a one hour period was considered acceptable. Next, the catalyst was activated using 5 vol% hydrogen sulfide in hydrogen at 552 kPa (80 psig), at 800

cm^3/min, and at a heating rate of 50°C (122°F) per hour. The detailed sulfiding procedure is presented in Appendix A. During sulfiding, the preheated feedstock was fed into the Ruska pump set to supply a constant feed rate of 35×10^{-6} m^3/h. Hydrogen was supplied by high pressure bottles at a rate of 6.24×10^{-2} m^3/h giving 1,781 std m^3/m^3 oil (10,000 scf/bbl).

After sulfiding, the petroleum residue and hydrogen flowed downwards through the reactor system. The operating conditions were stabilized at the desired values and this was considered as the starting time for each run. The experimental apparatus and its operation are presented in more detail in appendix A. Also included is a description of the system, reactor preparation, and sampling.

Liquid Sample Analyses

Sulfur Analyses

A Leco automatic sulfur analyzer determined the sulfur content of the feedstock and the samples taken every 6 h. The complete system consisted of a HF-10 model 777-300 induction furnace connected to an automatic titrator model 532-000. A Leco purifying train No. 516-000 removed moisture and acid gases from the oxygen supply and measured the flow rate of the purified oxygen leaving the train. The general operating procedure for this equipment is given in the Leco Bulletin (Leco, 1978).

With the Leco method, the sample is burned in a stream of oxygen by means of the induction furnace. The sulfur is converted mainly to sulfur dioxide which is titrated against a potassium iodate solution in the automatic titrator. A starch solution is used as the indicator.

A furnace factor is determined by the use of an oil sample whose sulfur content is known. The sulfur percentage in the sample is calculated using the furnace factor, the sample weight, and the amount of potassium iodate titrated, following the procedure indicated in the Leco Bulletin.

ASTM Distillation

The ASTM D-1160 (ASTM-a, 1986) vacuum distillation procedure was followed to analyse the feed and the samples taken at 42 h for each one of the experiments. Temperature was recorded against the volume distilled at a pressure of 1.33 kPa (10 mm Hg), and then the data was corrected to atmospheric pressure using ASTM D-2892 charts (ASTM-b, 1986) for hydrocarbons. The distillation was stopped when the operating pressure increased due to the presence of vapors in the system, and this was considered the end point.

Catalyst Samples Analyses

Each of the two catalyst beds for the experiments was divided into four sections. After Soxhlet extraction for 24 h with tetrahydrofuran, the catalyst pellets were ready for coke, metals, surface area, and pore volume analyses.

Coke Content

The coke content was defined as the percentage loss in catalyst weight after combustion at 600°C for 24 h. The catalyst pellets were weighed at ambient temperature before and after combustion. The loss in weight is due not only to combustion of coke, but also to oxidation of the active (Ni, Mo) and deposited (Ni, V, Fe) metal sulfides present in the spent catalysts. The correction for coke content due to the loss in weight for active metal sulfides oxidation was estimated. The estimate of the loss due to oxidation of deposited metal sulfides was not possible because no quantitative data were available on metals deposition.

Surface Area and Pore Volume

The surface area, pore volume, and pore size distribution of the spent and regenerated catalysts were determined on a Quantachrome Autoscan-60 Mercury Penetration Porosimeter.

Metals Deposition

Selected catalyst pellets were analyzed for metal content using a JEOL scanning electron microscope (SEM), model JFM-35 with energy X-ray analyses capabilities (EDAX). The pellets were cut at approximately 1.0 mm and the cross section was radially examined to determine the penetration of metals. From the metals present in the feedstock only vanadium was monitored. The presence of nickel in the fresh catalyst complicated the analyses of nickel deposition onto the catalyst. Iron deposition was not monitored because this element was present as a background element in the SEM.

The electron beam was saturated giving 100 nA at 25 kV. The condenser lens aperture was set at an appropriate value and held constant for all the analyses with the intention of obtaining semi-quantitative information. Selected areas across a diameter of each particle (typically 0.16 mm square areas) were scanned for 120 s. The output was fed into a Tracor Norther Model 2000 computer for identification of the metals present.

Feedstock

Vacuum residue (VR), and vacuum gas oil (VGO) were received from Conoco's Ponca City Refinery. The VR was mixed with the VGO in order to have a feedstock with the desired properties and with viscosity low enough to be processed in the available system without operating problems. A 50 vol% mixture of VR and VGO was prepared by heating the residue and mixing it with the VGO. The mixture was constantly stirred until it was homogeneous.

Table II lists the elemental composition, the API gravity, the metals content, and the ASTM distillation data for the feedstock. The nickel and vanadium contents were determined by atomic absorption. For this study, a feedstock with 1.0 to 2.0 wt% S, 0.3 to 0.5 wt% N, and 100

TABLE II

FEEDSTOCK PROPERTIES

50 vol% vacuum residue in 50 vol% vacuum gas oil

Elemental Analyses (wt%)	
C	84.98
H	13.12
N	0.32
S	0.90
Oxygen + Ash (by difference)	0.68
Metals content (ppm)	
V	58
Ni	43
API Gravity at 15.5°C	10.6

ASTM D1160 Distillation

Volume distilled (%)	Normal boiling point °C (°F)*
IBP	380 (716)
5	413 (775)
10	438 (820)
15	455 (851)
20	468 (874)
25	480 (896)
30	492 (918)
35	504 (939)
40	516 (961)
45	527 (981)
End point	527 (981)
Residue lost (vol%)	4
Residue (vol%)	51

* Data corrected from 1.33 kPa (10 mm Hg) to atmospheric pressure using ASTM D-2892 charts (ASTM-b, 1986)

to 150 ppm metals was felt to be desirable to test the zoned catalyst reactor concept. Even though the sulfur, metals, and nitrogen were in the lower desired level, this combination of properties was considered acceptable to study the effect of composite beds on hydroprocessing of this feedstock.

Fresh Catalyst

Three different commercial Ni-Mo-alumina catalysts were used in this study. Table III lists the properties for the catalysts. Catalyst TK 711 has a high HDM selectivity, very high capacity for metals deposition, and moderate to low HDS activity. Its use is suggested by the vendor as a first stage in composite beds.

Catalyst TK 751 has a moderate HDS activity, good HDM selectivity, and good capacity for metals uptake. It is suggested by the vendor as a second stage in composite beds or singly, for HDS of residues with moderate metals content.

Catalyst TK 771 has a very high HDS activity, low HDM selectivity and low capacity for metals deposition. It is well suited as the final catalyst in composite beds.

The data determined in our laboratory for surface area and pore volume were consistently higher than the vendor's data. This was considered to be an effect of the equipment calibration. The change in catalyst properties for the spent catalysts was analyzed using our data.

TABLE III

CATALYST PROPERTIES

Catalyst*	TK 711	TK 751	TK 771
Chemical Composition wt%			
NiO	2.0	2.3	3.4
MoO_3	6.0	10.0	14.0
Alumina	Balance	Balance	Balance
Physical Properties			
Size (mm)	1.6	1.6	1.6
Shape	extrudate	extrudate	extrudate
Bulk density $x10^{-3}$ kg/m^3	0.64	0.64	0.73
Surface Area $x10^{-3}$ m^2/kg	140(195)#	170(217)#	200(238)#
Pore volume $x10^3$ m^3/kg	0.57(0.79)#	0.58(0.78)#	0.47(0.53)#
Most Frequent pore diameter #,** (nm)	15.3	13.8	9.0

* Haldor Topsøe commercial catalysts.

Data determined in our laboratory.

** The most frequent pore diameter was read from the pore size distribution curve.

Experiments

A set of experiments was designed bearing in mind the characteristics of the selected catalysts. Table IV lists the catalyst combination for each experiment performed. Run number one was performed as a preliminary experiment to choose the operating temperature for the others.

A general description, including the objective, for each experiment is presented in Chapter III. The selected operating parameters were: 10.3 MPa, 1,781 std m^3(hydrogen)/m^3(oil), and 1.0 LHSV. This LHSV was defined as the volumetric rate of oil over the total volume of both catalyst zones. For all the runs, the catalyst volume ratio for the top and bottom zones was 50/50. This ratio was chosen arbitrarily to be used as a base in future hydroprocessing studies using the same kind of feedstock.

TABLE IV

EXPERIMENTS

Reference name	Capacity for metals	HDS activity	Catalyst
A	high	low	HT-TK-711
B	medium	medium	HT-TK-751
C	low	high	HT-TK-771

	Catalyst Type Loaded	
RUN #	Top Zone	Bottom Zone
1	B	B
2	B	C
3	A	C
4	B	B
5	A	B
6	C	C
7	B	B

CHAPTER III

RESULTS AND DISCUSSION

Experimental Conditions

During this study, seven experimental runs were conducted in a two-zone, trickle bed reactor. The operating conditions were 10.3 MPa, 1.0 LHSV (based on total bed volume of both zones), and 1,781 std m^3(hydrogen)/m^3(oil). These conditions were held constant throughout the study. The temperature was chosen after the preliminary run as 380°C. The feedstock and catalyst properties were presented in Chapter II. A general description follows for each experiment including catalyst loading and experimental objective. There was no plugging of the system which allowed all the runs to be shutdown as scheduled after 72 h duration.

Reproducibility and error analysis of this study are discussed in this chapter after the experiments description. Figure 2 summarizes the catalyst configuration and expected performance for each one of the runs. The other 3 possible catalyst combinations (C/A, C/B, and B/A) were not considered because of the restricted time for the study. No significant influence of this restriction is expected in the results.

RUN	1	2	3	4	5	6	7
BED	Single	Composite	Composite	Single	Composite	Single	Single
CATALYST COMBINATION	B B	B C	A C	B B	A B	C C	B B
X*	Good	Good Low	High Low	Good	High Good	Low	Good
Y*	Moderate	Moderate High	Low High	Moderate	Low Moderate	High	Moderate

* X: Expected capacity for contaminants deposition (vendor suggestion)

Y: Expected HDS activity (vendor suggestion)

Figure 2. Summary of the experiments configuration and expectations

Run 1 (Preliminary Experiment)

This experiment served to select the temperature level to be used during the other experimental runs. Both zones in the reactor system were loaded with catalyst B which has large pore size, medium surface area, and medium metals load. A good capacity for contaminants deposition and moderate HDS activity were expected from this catalyst.

The temperature was kept at 350°C during the first 36 h, at 380°C during the following 36 h, and then at 350°C again during the last 36 h for a total of 108 h on stream. Figure 3 shows the trend of relative sulfur content in the product oil as a function of time for this run. The relative sulfur content in the product was defined as the wt% sulfur in the product oil divided by the wt% sulfur in the feed. Error bars in all the HDS curves represent the average standard deviation found during the sulfur analysis. The actual sulfur data for each experiment are given in Appendix C.

At the conditions stated, and for the feedstock used, the HDS level showed relatively low sensitivity to changes in temperature. The HDS level at 380°C was considered appropriate for studying the composite bed concept in the subsequent experiments. The possibility of using a higher temperature was discarded to avoid any chance of excessive coking, thermal cracking, and/or plugging. The time on stream selected for the other experiments was 72 h.

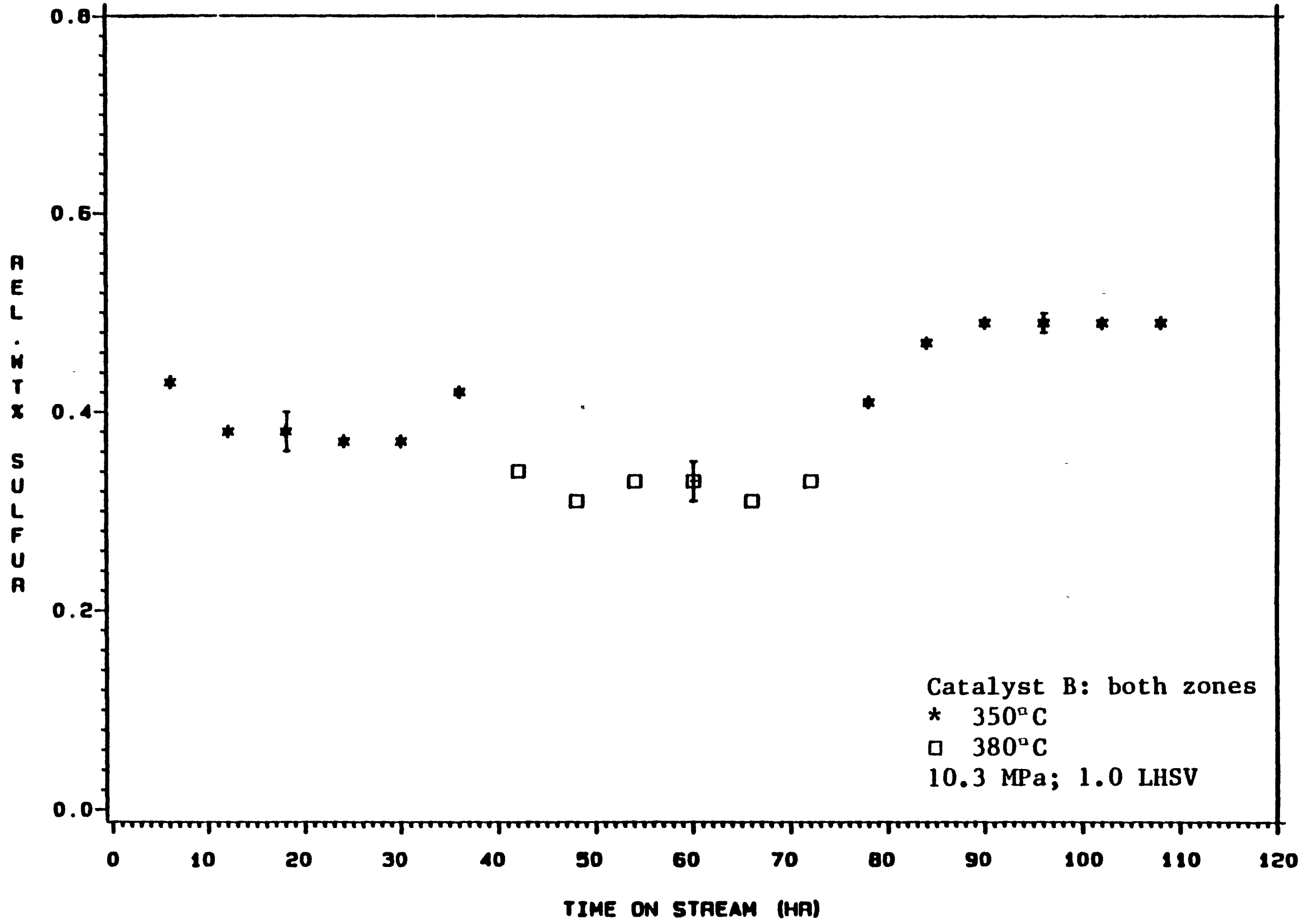

Figure 3. Relative sulfur content in the product as a function of time on stream for run 1

Run 2 (Composite Bed)

During this run, catalyst B was loaded in the top zone and catalyst C in the bottom zone. Catalyst C has smaller pore size, larger surface area and larger promoters load than catalyst B. This produced a composite bed with a first zone of medium capacity for contaminants and moderate HDS activity combined with a zone of high HDS activity and low metals uptake. This experiment was performed to provide comparison with other composite beds and also with single bed experiments.

Run 3 (Composite Bed)

The top zone in this experiment was loaded with catalyst A which has larger pore size but less surface area and lower promoters load than catalysts B and C. Thus, a higher capacity for contaminants deposition is expected from catalyst A. The bottom zone was loaded with the same catalyst C used in run 2. Therefore, the HDS level as well as the catalyst deactivation behavior can be checked when the capacity for contaminants is increased in the top layers of the reactor system.

Run 4 (Single Bed)

This was a single bed experiment loaded with the same catalyst (B) used during the preliminary run. This experiment was intended to serve as a reference to compare the performance of composite bed runs 2, 3, and 5 as well as that of single bed, run 6.

Run 5 (Composite Bed)

Catalyst A was loaded in the top zone and catalyst B in the bottom zone. This produced a composite system with low HDS activity at the top and moderate HDS activity at the bottom zone but with a high overall capacity for contaminants deposition.

Run 6 (Single Bed)

This run was loaded as a single bed with catalyst C (small pore size, high surface area, and high promoters load), and it was intended to check the effect of metals poisoning on catalysts with high HDS activity.

Run 7 (Reproducibility)

This run duplicated run 4 and it was intended to check the reproducibility of the experimental technique. The same catalyst (B) and experimental procedure as used in run 4 was employed.

The performance of the composite and single beds used in this study were compared by determining their activity for removing sulfur, for converting the residue into lighter material, and for showing tolerance to deactivation by metals and coke deposition.

Reproducibility

The results from this study are affected by the performance of the system and the precision of the equipment used to analyze the liquid and catalyst samples. One of the experimental runs was duplicated to check the overall reproducibility of this study.

Overall Reproducibility

The seventh run was intended to check the experimental reproducibility. This run was operated using the same type of catalyst and the same procedure as in run 4. Both runs showed similar HDS activity behavior for the main and interstage samples (Figure 4). Small deviations can be attributed to non-ideal catalyst wetting and mass transfer caused by differences in catalyst packing. These deviations are within the analytical precision range. A linear regression line for run 4 shows the similar performance in HDS activity for both zones. The differences observed in Figure 4 are valuable in distinguishing amongst catalyst performance in the discussion of the HDS results.

Table V lists the liquid product distillations for the two runs. The high correlation of the data indicates that the hydrocracking/hydrogenation activity of the catalyst is reproducible.

The coke content (Table V) showed an average of 3.0 wt% difference between the two runs. Run 2 also having catalyst C in the top zone showed an average of 4.0 wt% difference

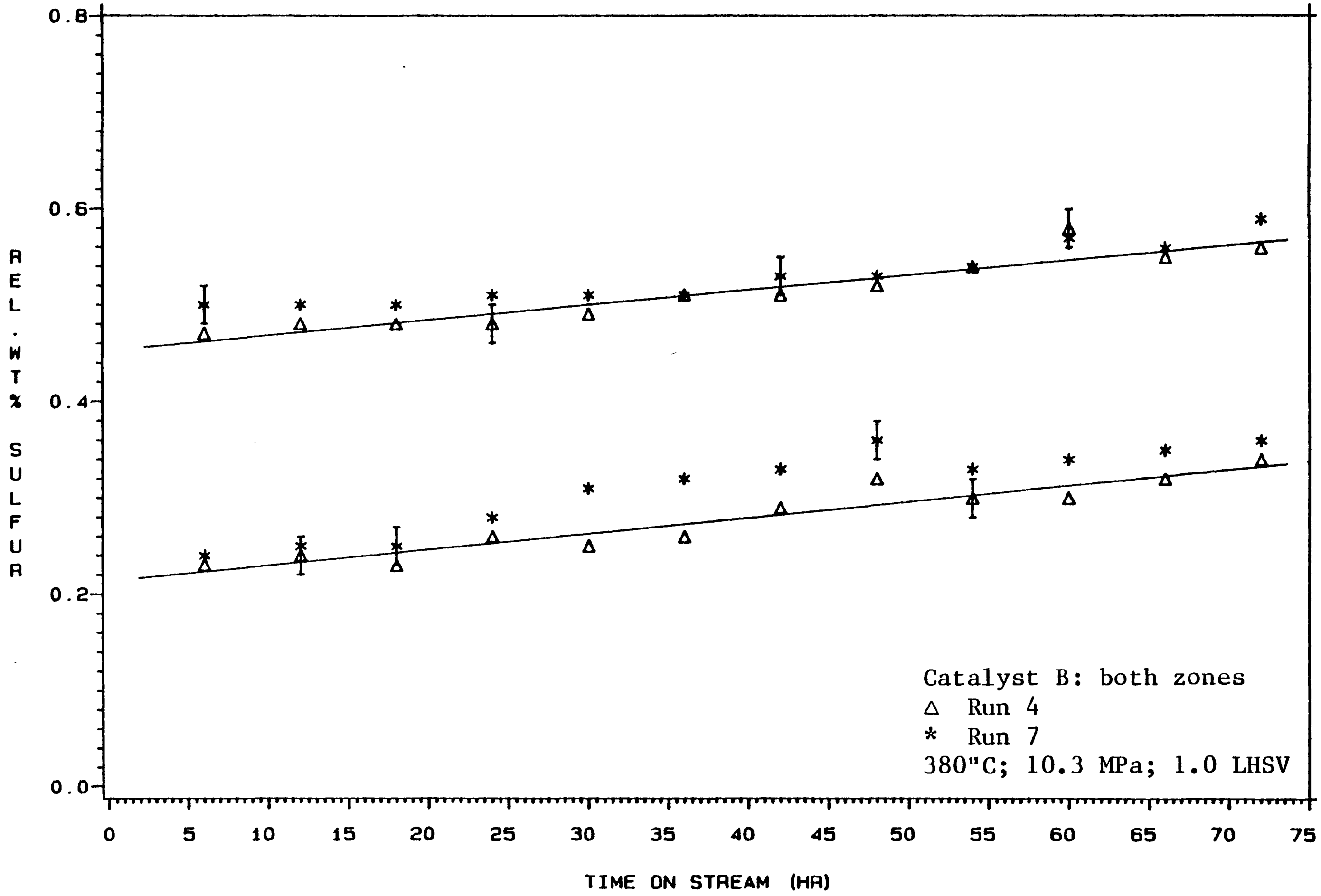

Figure 4. Relative sulfur content in the product as a function of time on stream for runs 4 and 7 (total and interstage)

TABLE V

REPRODUCIBILITY
ASTM DISTILLATION AND COKE CONTENT

ASTM D1160 Distillation of 42 h products (°C)

Volume Distilled (%)	Run 4	Run 7
ibp	286	277
10	402	405
20	445	449
30	473	475
40	499	501
50	528	526
60	550	549

Coke Content of Spent Catalysts (wt%)

Section (Catalyst)	Run 2 (B)	Run 3 (A)	Run 4 (B)	Run 5 (A)	Run 7 (B)
TOP ZONE					
Upper	31	21	25	21	19
Middle 1	29	24	22	18	16
Middle 2	19	19	23	17	17
Lower	23	21	18	18	19
Average	26	21	22	19	18
BOTTOM ZONE					
Upper			25		20
Middle 1			22		18
Middle 2			18		21
Lower			21		17
Average			22		19

with respect to run 4. Comparison between runs 3 and 5 having catalyst A in the top zone shows good agreement (2 wt% average difference). The scattering of the data indicates that this difference can be considered in the range of analytical precision.

Table VI presents the surface area and pore volume for catalyst B (runs 4, 7 and top zone of run 2) and catalyst A (top zone of runs 3 and 5). The results indicate good agreement which shows that the experimental and analytical techniques are fairly reproducible.

Reactor System Operation

The operating parameters influence the reactor performance. The oil feed rate was held at 35 x 10^{-6} m^3/h by a Ruska positive displacement pump, which gave a flow rate with unappreciable fluctuations on an hourly basis. The hydrogen gas flow rate was held at 1,781 std m^3/m^3(oil) by a micrometering valve. Even with occasional fluctuations varying between 215 to 535 m^3/m^3(oil), the hydrogen rate was at least four times the amount required for reaction. Wan (1974) and Sooter (1974) reported wide variation in hydrogen flow rate having negligible effect on hydrotreating. Thus, the gas flow fluctuations experienced during this study should have little or no effect on the results.

A 'Mity-Mite' pressure regulator controller and a 0 - 20.6 MPa (0 - 3,000 psig) Heise gauge monitored the reactor pressure. The inlet hydrogen pressure was maintained at

TABLE VI

REPRODUCIBILITY
SURFACE AREA AND PORE VOLUME

Surface Area of Spent Catalysts x 10^{-3}(m^2/kg)

Section (Catalyst)	Run 2 (B)	Run 3 (A)	Run 4 (B)	Run 5 (A)	Run 7 (B)
TOP ZONE					
Upper	134	144	150	149	155
Middle 1	147	141	156	146	163
Middle 2	166	150	168	156	166
Lower	177	144	166	155	169
Average	156	145	160	152	163
BOTTOM ZONE					
Upper			150		160
Middle 1			160		161
Middle 2			164		163
Lower			174		165
Average			162		162

Pore Volume of Spent Catalysts x$\cdot10^3$(m^3/kg)

Section (Catalyst)	Run 2 (B)	Run 3 (A)	Run 4 (B)	Run 5 (A)	Run 7 (B)
TOP ZONE					
Upper	0.40	0.49	0.45	0.50	0.47
Middle 1	0.44	0.51	0.47	0.51	0.50
Middle 2	0.52	0.54	0.51	0.53	0.52
Lower	0.55	0.50	0.50	0.51	0.52
Average	0.48	0.51	0.48	0.51	0.50
BOTTOM ZONE					
Upper			0.46		0.47
Middle 1			0.49		0.49
Middle 2			0.51		0.50
Lower			0.52		0.51
Average			0.50		0.49

10.3 MPa (1,500 psig) with occasional fluctuations of 0.14 MPa (15 psig). This small variation in operating pressure should have had no effect on the results (Sooter, 1974).

The reactor temperature was maintained constant by temperature controllers. The temperature of the pre- and post-heating sections was maintained at the desired values by variacs. The reactor wall and reactor bed temperatures were measured by Omega J-type (iron-constantan) thermocouples. The variations in temperature observed in the top and bottom zones along the reactor lenght were 10°C and 7°C, respectively. These variations were due to differences in the performance of the heaters. The preliminary run indicated little sensitivity of the HDS activity to a 30°C change in temperature. Thus, the observed deviation from the isothermal operation should have no important effects on the results.

Analytical Precision

Each of the liquid samples was analyzed for sulfur content three times with the average being the reported value. The standard deviation during the sulfur analyses ranged from 0.01 to 0.05 weight percent.

The ASTM-D1160 distillation was performed three times for the feedstock. The normal boiling point showed deviations smaller than 6°C. The product samples (42 h) were analyzed only once due to the large amount of liquid required for each distillation.

The coke content was determined three times for each reactor section. The standard deviation was approximately 2.0 wt% with deviatons as low as 0.4 wt% and as high as 5.5 wt%.

With respect to the surface area and pore volume analyses, the standard deviation varied between 0 and 2 x 10^3 m^2/kg for surface area and between 0.01 and 0.02 x 10^{-3} m^3/kg for pore volume when analyzing the fresh catalysts. The spent catalysts were analyzed only once due to the amount of catalyst required for each analysis.

A discussion of the results for the liquid products and the used catalysts analysis follows.

Liquid Sample Analyses

Sulfur Content

The feed and the liquid samples (main and interstage) taken every 6 h were analyzed for sulfur content. Figures 5 through 9 show the relative sulfur content as a function of time on stream for the main and interstage samples. As can be seen from the figures, the sulfur content of the liquid products generally increased with time on stream giving an indication of decay in HDS activity. The following paragraphs present a discussion of the HDS behavior for the different catalyst combinations. The HDS level ranged from 35 to 50 wt% in the top zone increasing to 60 - 75 wt% in the bottom zone.

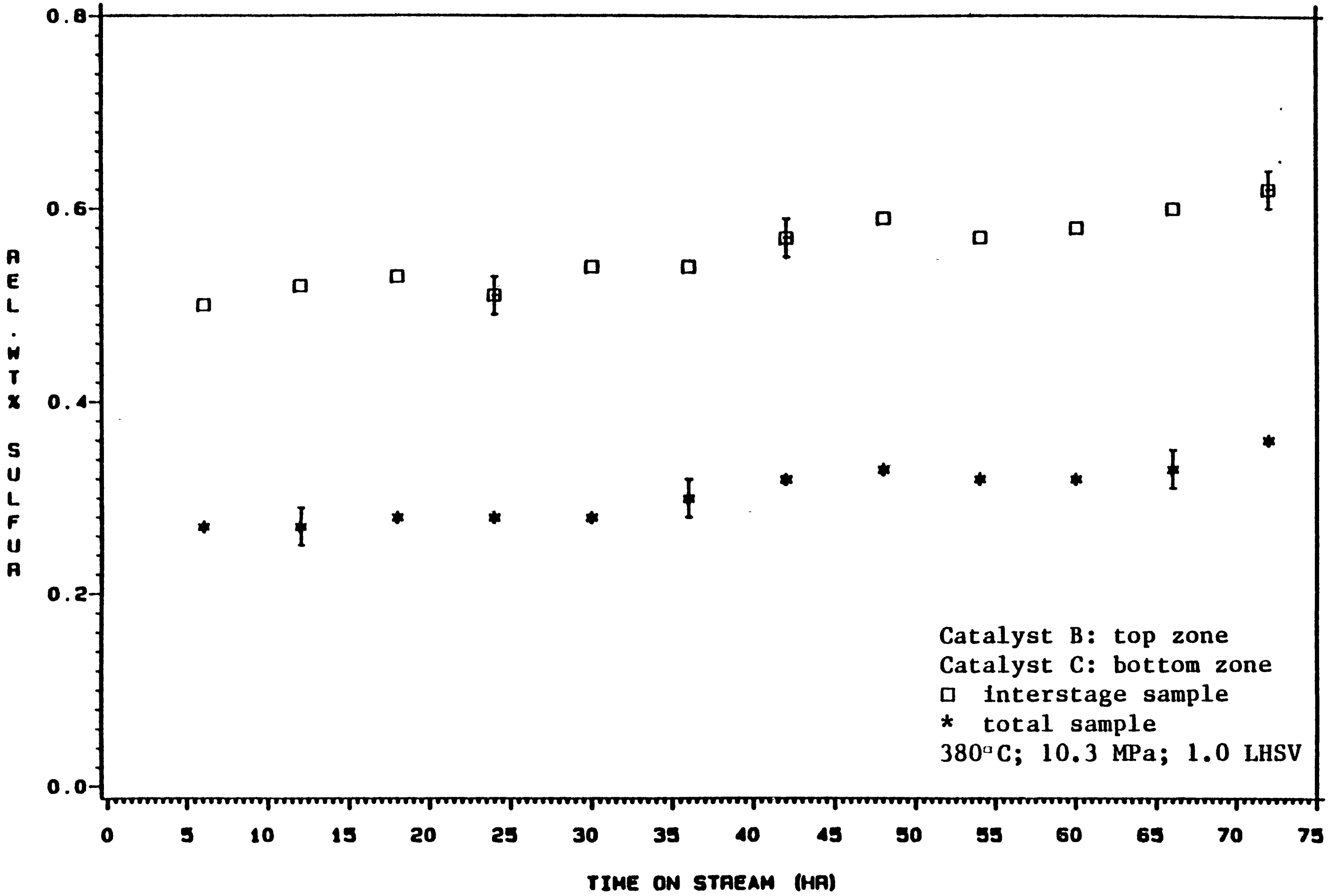

Figure 5. Relative sulfur content in the product as a function of time on stream for run 2

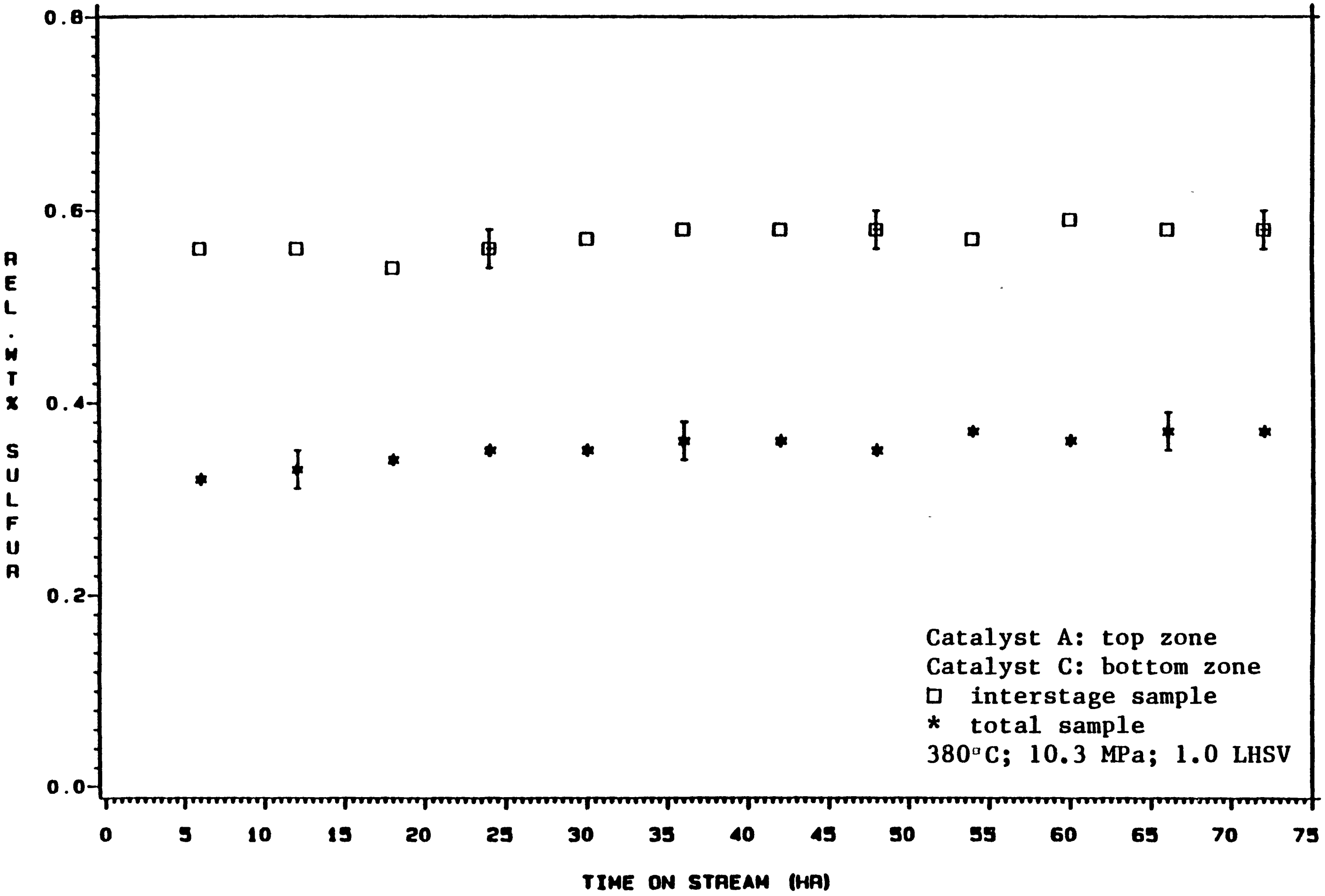

Figure 6. Relative sulfur content in the product as a function of time on stream for run 3

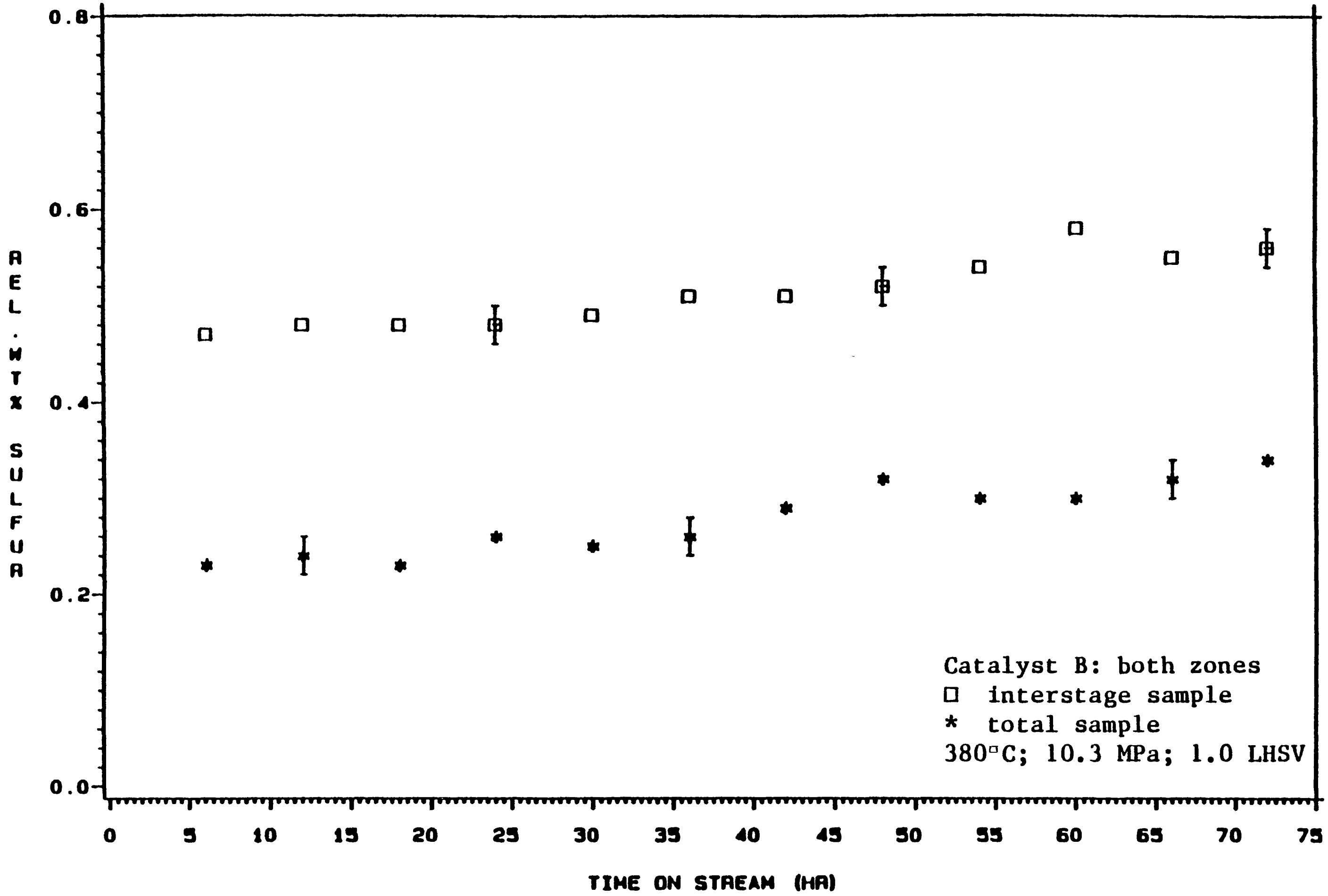

Figure 7. Relative sulfur content in the product as a function of time on stream for run 4

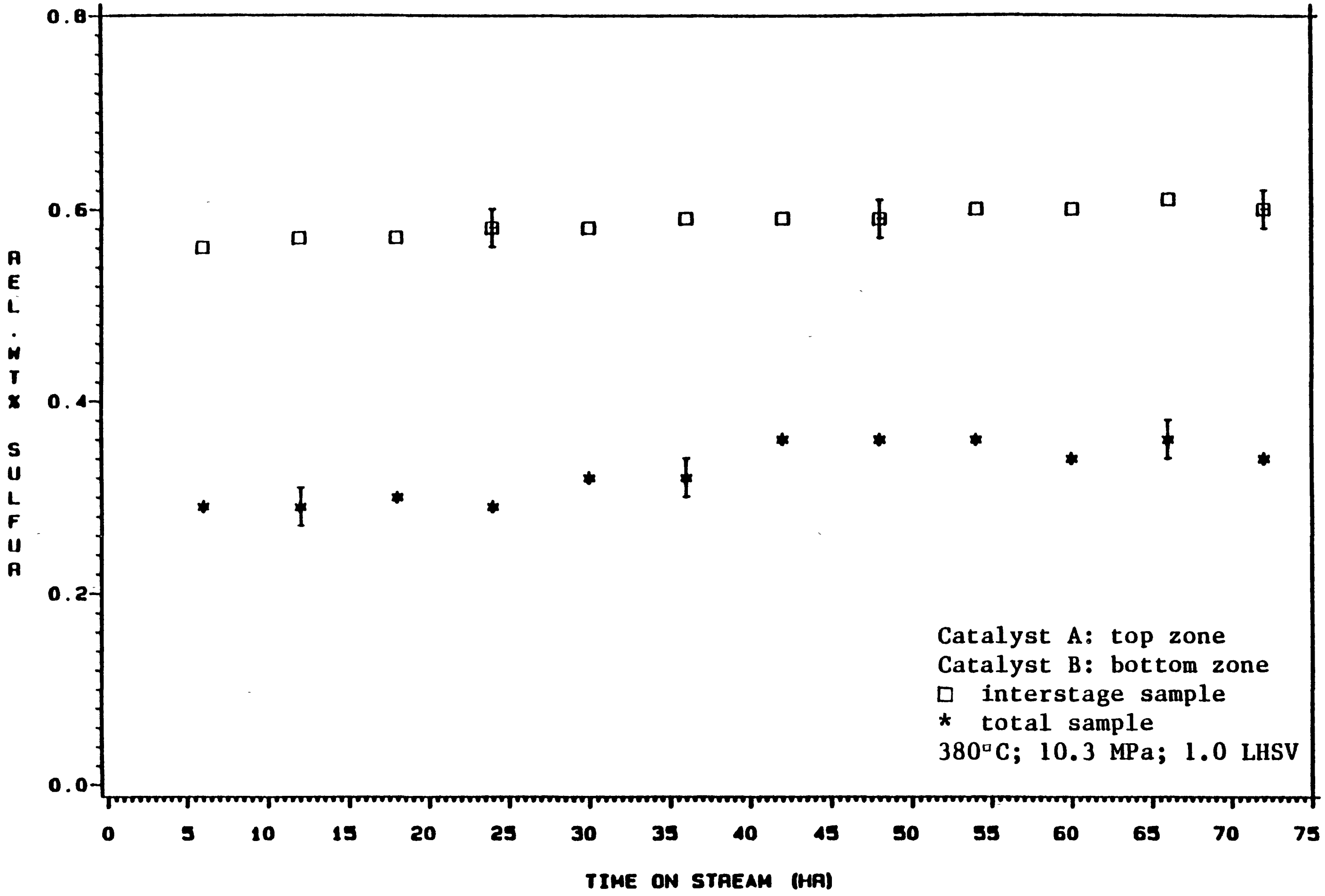

Figure 8. Relative sulfur content of the product as a function of time on stream for run 5

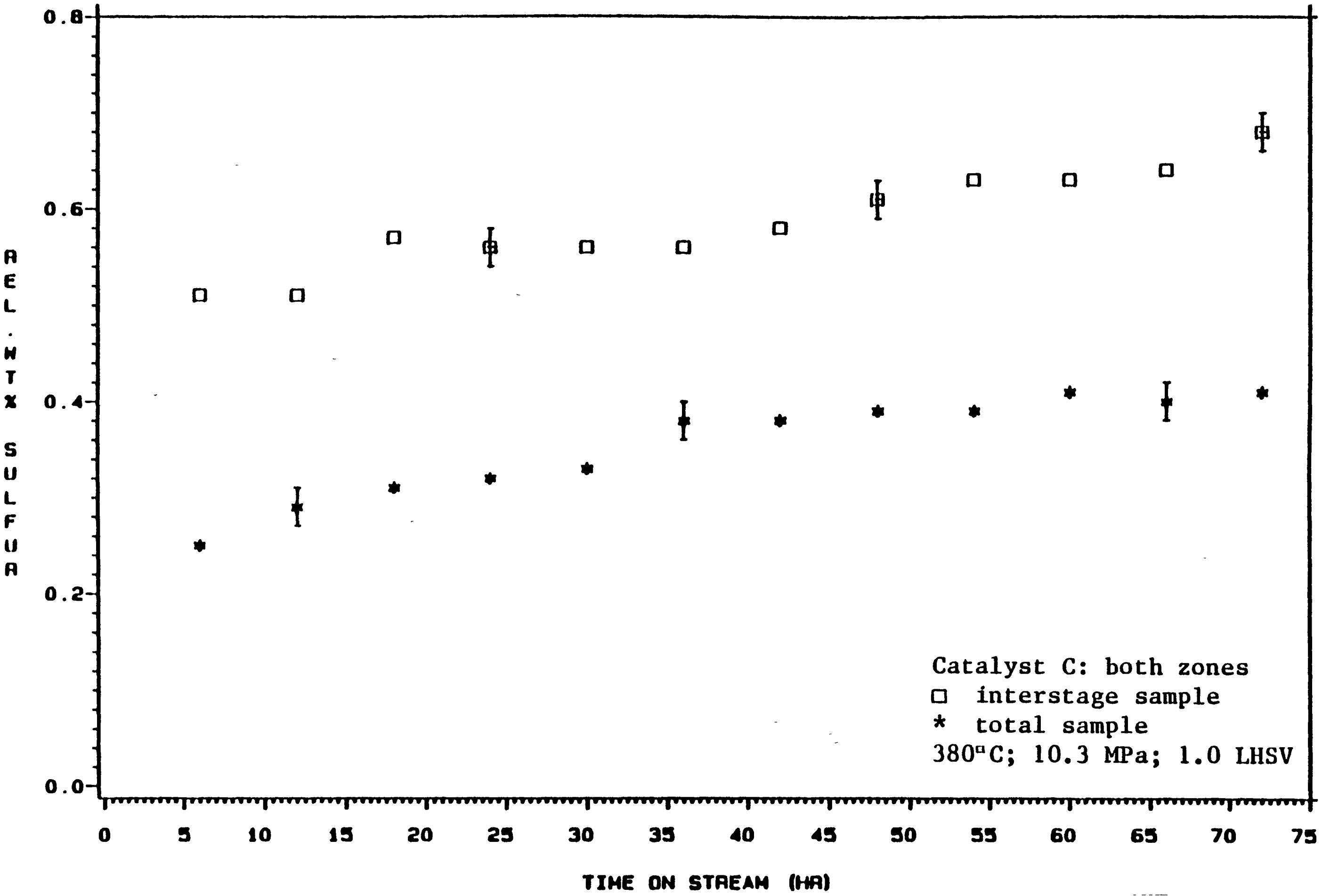

Figure 9. Relative sulfur content in the product as a function of time on stream for run 6

The Top Zone HDS Behavior. Figure 10 represents the behavior of different catalysts used in the top zone. Catalyst C, (run 6) with the highest metals loading and surface area but smallest pore size, showed substantially higher deactivation compared with catalysts B and A. Catalyst B showed better overall HDS activity than catalyst C. Catalyst A, with the largest pore size, showed a fairly constant HDS activity with time on stream. For this particular feedstock and reactor conditions and especially at the short space time there was no great response to changes in catalyst type.

Composite Bed Performance. Figure 11 shows the HDS trend for the three different composite bed runs. Even though there was no substantial difference in the HDS level, run 3 (A and C combination) showed almost no deactivation with respect to time. Run 2 (B and C combination) showed the highest HDS activity but also showed signs of deactivation with time.

Run 5, the composite bed with the highest expected tolerance for contaminants, showed no significant advantage over the other composite beds. Catalyst C (high surface area and metals load) in the bottom zone produced a slightly more active combination with a catalyst (B, run 2) in the top zone having good metal capacity and medium HDS activity than with a catalyst (A, run 3) having higher tolerance for contaminants but lower HDS activity.

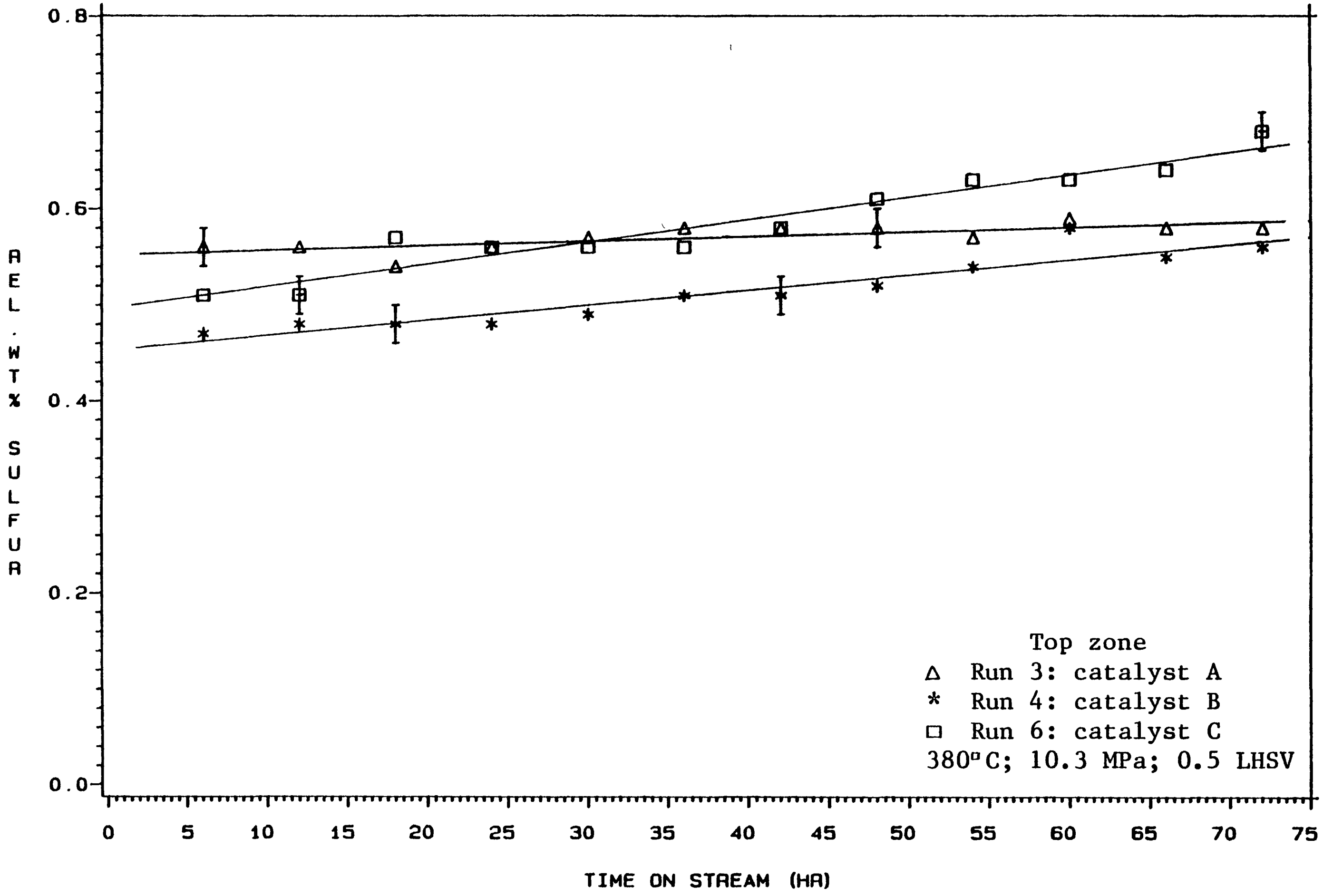

Figure 10. Relative sulfur content in the product as a function of time on stream for different catalysts in the top zone (interstage sample)

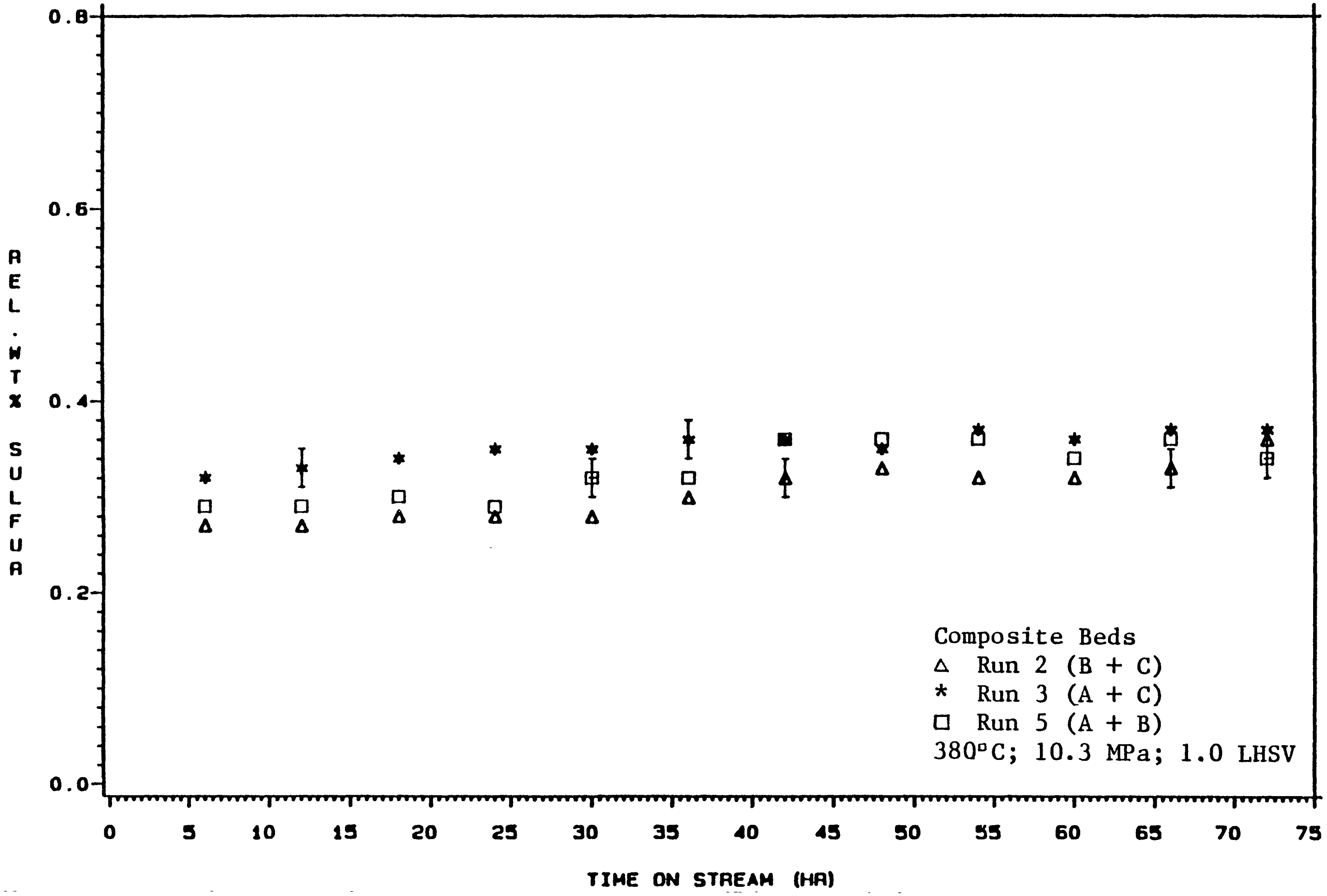

Figure 11. Relative sulfur content in the product as a function of time on stream for the selected composite beds

Single Bed Performance. Figure 12 shows the performance of single catalyst beds (runs 4 and 6). Catalyst B (run 4) with larger pore size and pore volume but less active metals loading showed better overall HDS activity and less deactivation with time than catalyst C (run 6). This is consistent with the behavior of these two catalysts in the top zone. The results indicated that deactivation increased as the activity (promoters load) of the bed increased.

Composite vs. Single Beds. Figures 13 and 14 compare one of the composite beds (run 3) with the single bed runs. Run 4 (catalyst B) showed a better HDS level with signs of deactivation. On the other hand, run 6 (catalyst C) showed high deactivation compared with run 3 which showed fairly constant HDS activity. For single catalysts (top zones and single beds), HDS activity was a function of the catalyst pore size to the extent that catalyst B showed better HDS activity than catalyst C which has higher active metals load but smaller pore size (Figures 10 and 12).

Hohnholt and Fausto (1986) postulated that an increase in nickel content in the catalyst promoted HDN but at the expense of HDS; therefore, this could be the explanation for the performance of catalyst C. Also, it appears that HDS for the small pore size catalyst (C) was severely affected by diffusion restrictions when used as a single bed.

The selected composite beds showed approximately the same HDS level with little sign of deactivation for the more

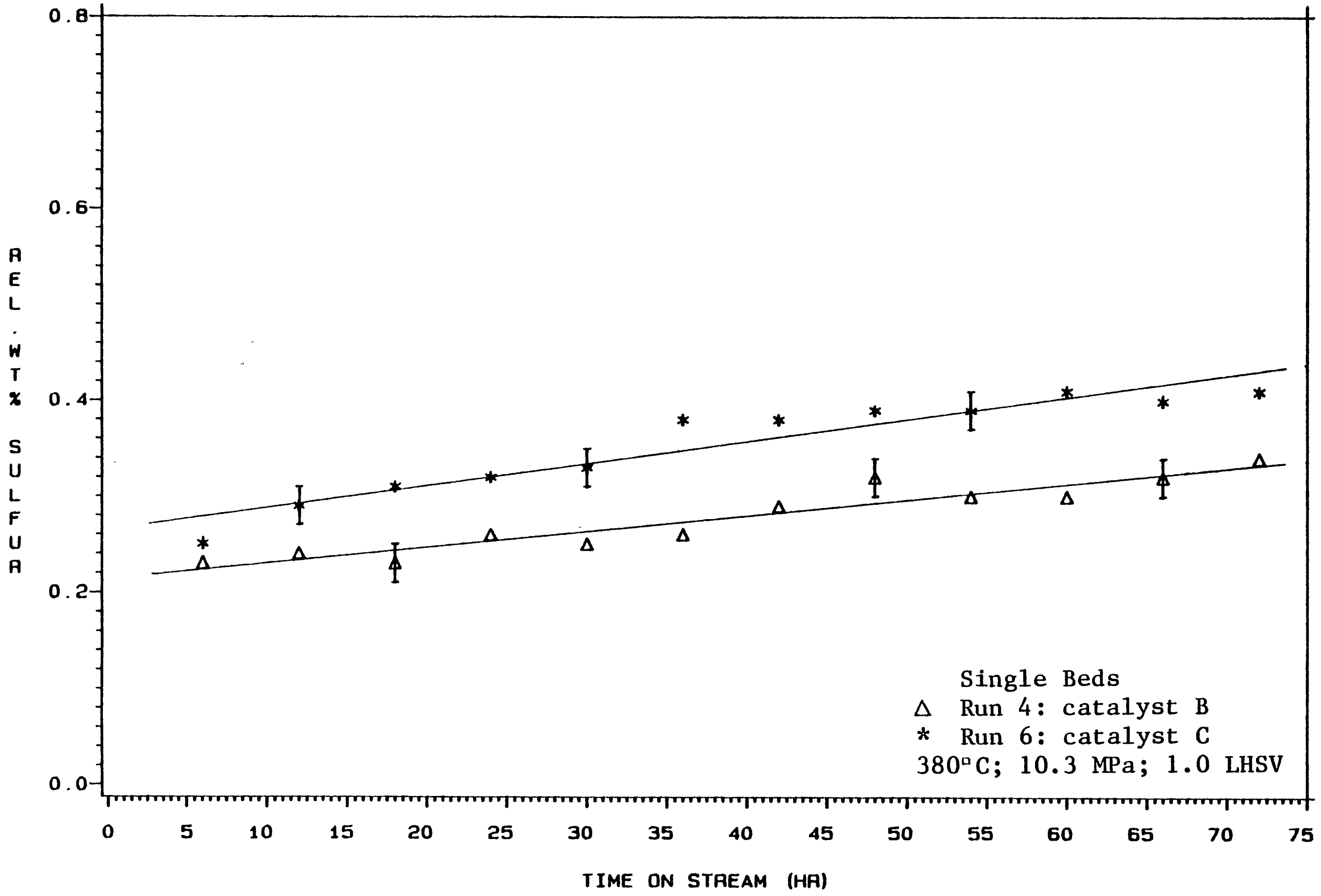

Figure 12. Relative sulfur content in the product as a function of time on stream for the single beds

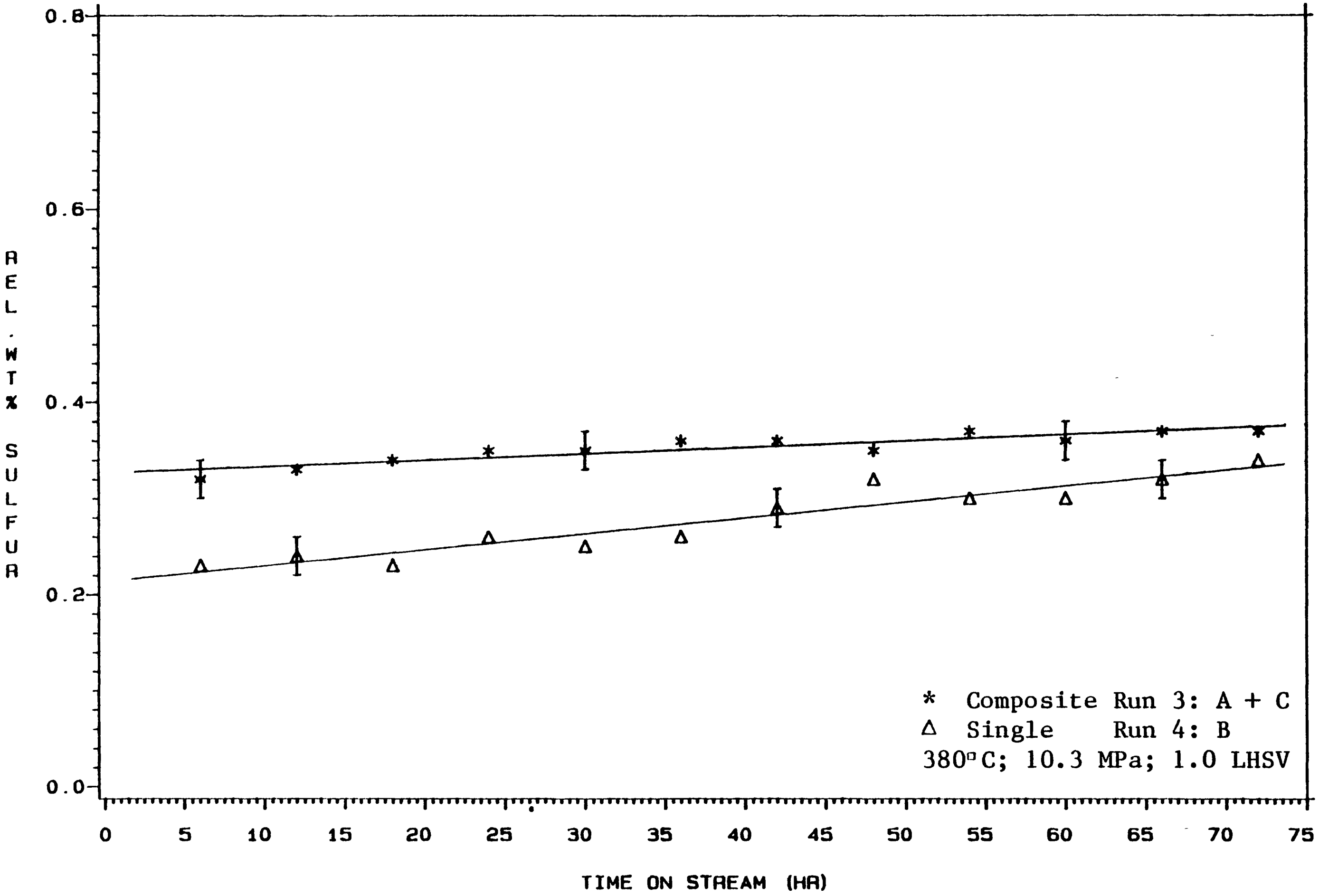

Figure 13. Relative sulfur content in the product as a function of time on stream for runs 3 and 4

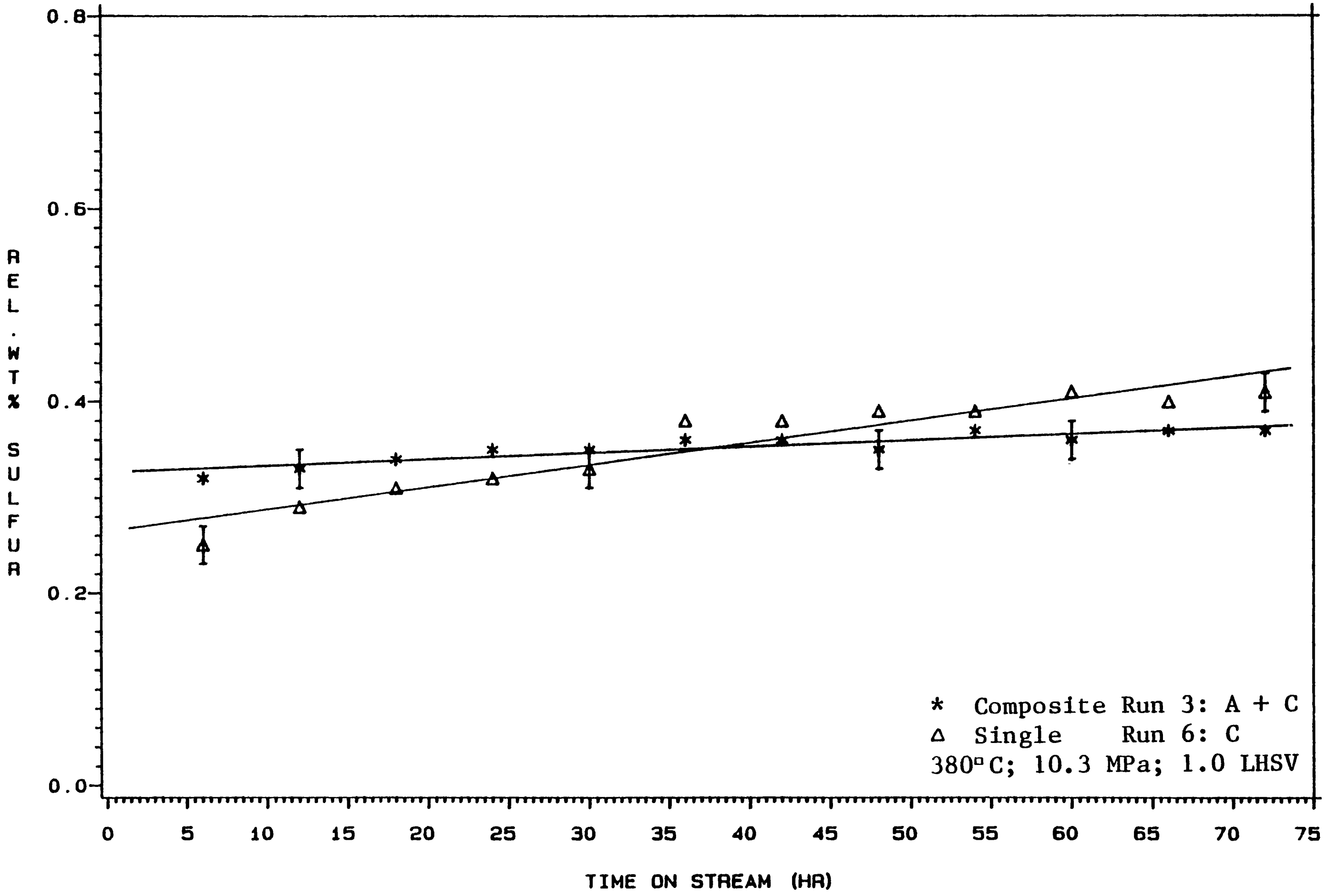

Figure 14. Relative sulfur content in the product as a function of time on stream for runs 3 and 6

active composite bed (Figure 11). Compared to the single beds, the composite beds showed lower rate of deactivation but nearby the same HDS level.

The linear behavior of the HDS curves for all the runs indicated that we were in the period of initial deactivation for the time on stream employed at these specific conditions. This is in agreement with Nielsen et al. (1981) and Higashi et al. (1985) who reported a shift on the HDS curve to intermediate deactivation after 200 h on stream. They processed Kuwait and Arabian Heavy atmospheric residues containing 1.5 and 4.1 wt% sulfur respectively.

No conclusions involving long term catalyst life shall be inferred from these results because the experimental data were obtained during runs of only 72 h.

ASTM Distillation

Liquid samples collected at 42 h on stream were distilled according to the ASTM-D1160 vacuum standard procedure at 1.33 kPa (10 mm Hg). The data were converted to atmospheric pressure. Table VII presents the boiling range distribution for the feed and 42 h products. The single beds (runs 4 and 6) showed slightly higher (5 vol%) conversion to middle distillate (204 to 343°C) than the composite beds. The composite beds having catalyst A at the top zone (runs 3 and 5) showed lower conversion to middle distillate. For the purpose of comparison, the heavy ends were divided in two fractions. The presence of catalyst C,

TABLE VII

ASTM DISTILLATION DATA (°C) AND BOILING RANGE (VOL%) OF THE FEEDSTOCK AND 42 h PRODUCTS

VOLUME PERCENT (Catalysts)	FEED	RUN 2 (B+C)	RUN 3 (A+C)	RUN 4 (B)	RUN 5 (A+B)	RUN 6 (C)
IBP	380	283	280	286	305	266
5	413	363	373	340	395	343
10	438	408	412	402	425	402
20	468	446	447	445	456	443
30	492	470	472	473	481	470
40	516	496	493	499	505	494
45	527	512	503	512	518	506
50	*	519	515	528	530	520
60		*	538	550	553	543
Light Oil Fraction T<204°C	0	0	0	0	0	0
Middle Distillate 204<T<343°C	0	4	3	5	2	5
Heavy Ends 343<T<500°C	33	38	41	35	36	37
500°C+ Fraction (by difference)	67	58	56	60	64	58

* The test ended at this point.

as single bed or in combination, decreased the amount of the 500°C+ fraction. The combination A plus B (run 5) with the lowest active metals loading showed the lowest conversion to lighter fractions and retained the greatest 500°C+ fraction.

The shift of the boiling curve to lighter material is an indication of hydrocracking and hydrogenation. For this study, at the particular conditions used, the conversion to lighter material increased slightly as the active metals (Ni and Mo) load of the catalyst increased. In the composite beds with catalyst C at the bottom, the conversion level was comparable to the conversion of the single beds.

The distillation results were discussed using the trends in boiling range as an indication of performance. No significant difference in the data amongst the runs is noted.

Catalyst Analyses

Each catalyst zone was divided into upper, middle 1, middle 2, and lower sections. After extraction with tetrahydrofuran, the catalyst pellets were analyzed for coke content, surface area and pore volume, and metals deposition as given earlier.

Coke Deposition

The deposition of coke was determined as the relative loss in catalyst weight upon combustion at 600°C during 24 hours. The four sections of catalyst for each reactor zone were analyzed. The reported results were corrected for the loss in weight due to the oxidation of the active metal (Ni, Mo) sulfides but not for the loss due to deposited metals (Ni, V) sulfide oxidation. No method was available for correcting for metals deposition; however, assuming if all feedstock metals were uniformily deposited throughout the bed, only a 1.0 to 1.3 wt% correction would be required.

Table VIII shows the coke results for runs 2 through 6. Run 7 was presented in the reproducibility section. The coke deposition ranged from 11 to 31 wt% (based on fresh catalyst). Coke deposition appears to be a function of the catalyst pore size. The small pore size catalyst (C) showed low coke deposition (14 wt%) when it was used as a single bed. However, the presence of larger pore size catalysts in the top zone (runs 2 and 3) increased the coke deposition in catalyst C at the bottom zone (20 to 25 wt%).

Coke deposition is formed from strong adsorption and eventual degradation to coke of highly polyaromatic, basic molecules (asphaltenes amongst others). These deposits deactivate the active sites and eventually interfere with the reactants/diffusion inside the catalyst pores (Pazos et al., 1983; Brunn et al., 1975).

The more open structure of catalysts A and B allows big molecules to enter the catalyst and react inside the pores. Assuming that the asphaltenes dissociate into smaller units after contact with the active sites of the large pores (top zone), then these lower molecular weight asphaltenes are

TABLE VIII

COKE CONTENT OF SPENT CATALYSTS

	weight percent				
Section	Run 2	Run 3	Run 4	Run 5	Run 6
TOP ZONE (Catalyst)	(B)	(A)	(B)	(A)	(C)
Upper	31	21	25	21	15
Middle 1	29	24	22	18	11
Middle 2	19	19	23	17	11
Lower	23	21	18	18	15
Average	26	21	22	19	13
BOTTOM ZONE (Catalyst)	(C)	(C)	(B)	(B)	(C)
Upper	25	20	25	24	15
Middle 1	22	22	22	24	12
Middle 2	26	20	18	19	16
Lower	26	16	21	16	14
Average	25	20	22	21	14

better able to penetrate the smaller pore size catalyst (C, runs 2 and 3) at the bottom zone. This results in a higher coke laydown than that for the catalyst C alone (run 6).

Usually, the higher the coke deposition, the higher the deactivaion rate. Nevertheless, the higher penetration of the reactants inside the pores results in a better catalyst utilization. In the case of deposition of large molecular weight asphaltenes, the pore will tend to be plugged thereby accelerating the catalyst deactivation.

This theory of coke deposition correlates well with the HDS behavior presented earlier in the chapter. Apparently, for this particular feedstock, catalyst B (large pore size and moderately active metals loading) is the best of the three catalysts employed. That explains why the level of HDS of the single bed (run 4) is higher than that of any of the composite beds.

The performance of catalysts A and B at the top zone is comparable. However, the higher active metals content of catalyst B results in a higher reactivity for asphaltenes dissociation and consequently coke deposition.

The relatively flat profiles for each catalyst zone indicated that the equilibrium level for coke deposition was reached before the 72 h on stream. These results are in agreement with the Agrawal and Wel (1984) studies that reported a period of 15 h sufficient to build up almost all the coke formed during the total course of the reactor operation when processing nickel and vanadyl etioporphyrins.

Surface Area and Pore Volume

Tables IX to XI present the pore volume, surface area and average pore diameter data for the spent catalysts. Run 7 was presented in the reproducibility section. The results in pore volume for the spent catalyst (Table IX) show that the reduction was proportional to the catalyst pore size. The reduction in pore volume was bigger for the smallest pore size (catalyst C) and smaller for the biggest pore size (catalyst A). The loss in pore volume tended to be a function of the reactor length for each zone. The highest reduction was usually present at the entrance of the reactor zone.

The results for surface area and pore volume for run 6 and bottom zone of run 3 are not considered reliable due to unusual performance of the Autoscan Porosimeter. Less weight is given to these results throughout the discussion looking only at general trends.

The relative reduction in surface area (Table X) was at the same level for the catalysts A and B. Catalyst C showed lower reduction than catalysts A and B. The profile for loss in surface area was a slight function of the reactor length which indicates that both metals and coke deposition are responsible for loss in surface area.

Consistent with the pore volume data, the reduction in pore size (Table XI) was proportional to the fresh catalyst pore size. The larger the pore size, the smaller the

TABLE IX

PORE VOLUME OF SPENT CATALYSTS

Section	Pore Volume x 10^3 (m^3/kg) / Percent Reduction Run 2	Run 3	Run 4	Run 5	Run 6
TOP ZONE (Catalyst)	(B)	(A)	(B)	(A)	(C)
Upper	0.40/49	0.49/38	0.45/42	0.50/37	0.28/47
Middle 1	0.44/44	0.51/35	0.47/40	0.51/35	0.33/38
Middle 2	0.52/33	0.54/31	0.51/35	0.53/33	0.33/38
Lower	0.55/30	0.50/36	0.50/36	0.51/35	0.30/43
Average	0.48/39	0.51/35	0.48/39	0.51/35	0.31/42
BOTTOM ZONE (Catalyst)	(C)	(C)	(B)	(B)	(C)
Upper	0.24/55	0.27/49	0.46/41	0.45/42	0.35/34
Middle 1	0.24/55	0.30/43	0.49/37	0.44/44	0.34/36
Middle 2	0.28/47	0.31/42	0.51/35	0.49/37	0.27/49
Lower	0.30/43	0.30/43	0.52/33	0.50/36	0.30/43
Average	0.27/50	0.29/44	0.50/36	0.47/40	0.31/42

TABLE X

SURFACE AREA OF SPENT CATALYSTS

	Surface Area x 10^{-3} (m^2/kg) / Percent Reduction				
Section	Run 2	Run 3	Run 4	Run 5	Run 6
TOP ZONE (Catalyst)	(B)	(A)	(B)	(A)	(C)
Upper	134/38	144/26	150/31	149/23	199/16
Middle 1	147/32	141/27	156/28	146/25	225/6
Middle 2	166/24	150/23	168/23	156/20	237/1
Lower	177/18	144/26	166/24	155/20	190/20
Average	156/28	145/25	160/26	152/22	213/10
BOTTOM ZONE (Catalyst)	(C)	(C)	(B)	(B)	(C)
Upper	145/39	174/27	150/31	148/32	235/1
Middle 1	177/26	215/10	160/27	143/34	234/2
Middle 2	206/13	228/4.0	164/24	158/27	188/21
Lower	205/14	225/6.0	174/20	158/27	197/17
Average	183/23	211/12	162/26	152/30	213/10

TABLE XI

MOST FREQUENT PORE DIAMETER OF SPENT CATALYSTS

Section	Run 2	Run 3	Run 4	Run 5	Run 6
	Av. Pore Diameter (nm) / Percent Reduction				
TOP ZONE (Catalyst)	(B)	(A)	(B)	(A)	(C)
Upper	11.5/17	12.6/18	10.8/22	12.0/22	4.5/50
Middle 1	11.6/16	13.0/15	11.3/18	12.7/17	4.9/46
Middle 2	11.6/16	13.2/14	11.5/17	13.0/15	5.1/43
Lower	12.3/13	13.0/15	11.7/15	13.0/15	5.1/43
Average	11.6/16	13.0/15	11.3/18	12.7/17	4.9/46
BOTTOM ZONE (Catalyst)	(C)	(C)	(B)	(B)	(C)
Upper	5.4/41	5.7/37	11.4/17	11.0/20	4.7/48
Middle 1	5.0/44	6.0/33	11.5/17	11.2/19	5.0/44
Middle 2	5.1/43	6.2/31	11.6/16	11.5/17	5.1/43
Lower	5.4/41	6.2/31	11.8/15	11.4/17	5.4/41
Average	5.2/42	6.0/33	11.6/16	11.3/18	5.0/44

reduction. Besides, the reduction in pore size was a slight function of the reactor zone length having the highest value usually at the entrance of the catalyst bed. Catalyst C showed less reduction when catalyst A was at the top zone than when the others (B and C) were at the top. This shows that composite beds represent an advantage in controlling the deactivation of active catalysts in the bottom zone.

Tables XII and XIII show the pore volume and surface area of the regenerated catalysts. The support properties were recovered to more than 90% with respect to those of the fresh catalyst.

Metal Deposition

EDAX analyses are only semi-quantitative; however, they help in the determination of the elements present in the catalyst and their penetration profile. Focus was placed on the vanadium deposition inside the catalyst pellets. The cross-section of the pellet was scanned from the edge to the center (radially) in five equally spaced areas (Figure 15). Before running the samples, several tests to determine the elements present as a background were performed. These indicated the presence of Cu, Fe, and Zn as the main background elements. Other elements such as Si, K, Al, and S were also present in smaller proportions.

The main metals present in petroleum residues are vanadium, nickel, and iron. The presence of Fe as a background element hides the behavior of Fe deposition

TABLE XII

PORE VOLUME OF REGENERATED CATALYSTS

Section	Pore Volume x $10^3 (m^3/kg)$ Run 2	Run 3	Run 4	Run 5	Run 6
TOP ZONE (Catalyst)	(B)	(A)	(B)	(A)	(C)
Upper	0.80	0.80	0.77	0.78	0.49
Middle 1	0.74	0.83	0.77	0.82	0.52
Middle 2	0.78	0.83	0.77	0.79	0.54
Lower	0.76	0.80	0.79	0.79	0.53
BOTTOM ZONE (Catalyst)	(C)	(C)	(B)	(B)	(C)
Upper	0.52	0.53	0.77	0.79	0.60
Middle 1	0.51	0.52	0.78	0.79	0.53
Middle 2	0.50	0.54	0.79	0.77	0.56
Lower	0.53	0.54	0.76	0.61	0.52

TABLE XIII

SURFACE AREA OF REGENERATED CATALYSTS

Section	Surface Area x 10^{-3} (m^2/kg) Run 2	Run 3	Run 4	Run 5	Run 6
TOP ZONE (Catalyst)	(B)	(A)	(B)	(A)	(C)
Upper	210	187	203	188	233
Middle 1	210	181	205	197	234
Middle 2	210	196	206	187	240
Lower	201	186	213	189	229
BOTTOM ZONE (Catalyst)	(C)	(C)	(B)	(B)	(C)
Upper	244	220	207	201	264
Middle 1	230	225	209	210	242
Middle 2	232	224	207	212	249
Lower	228	236	207	217	233

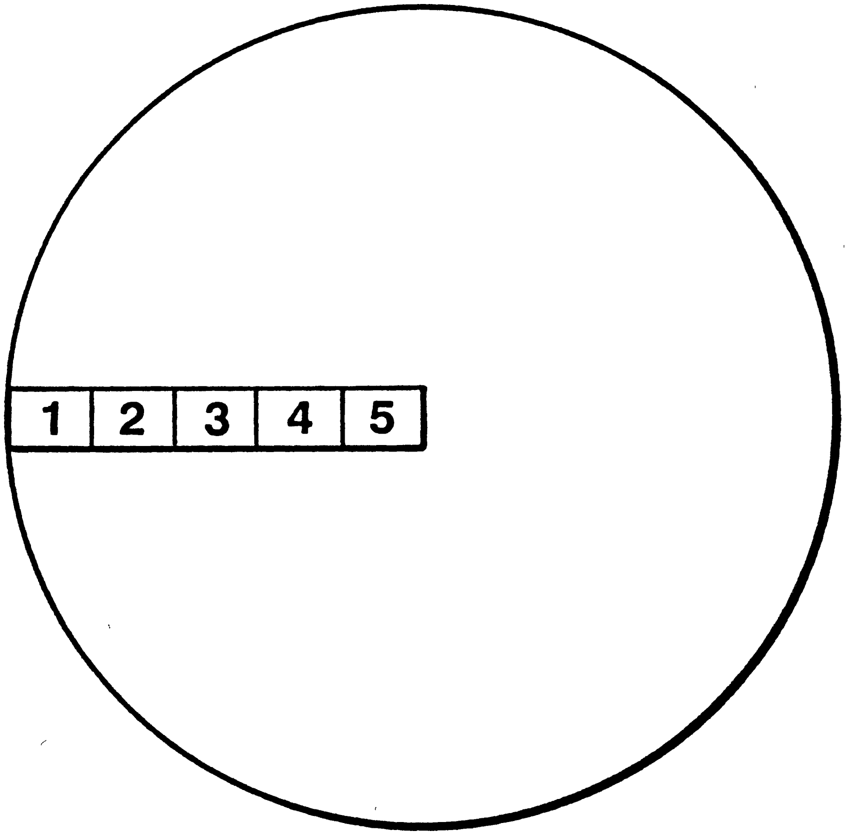

Figure 15. Location of the selected areas scanned across the catalyst pellets

inside the catalyst. The study of the nickel deposition is not an easy task because of the presence of nickel in the catalyst structure. Therefore, neither iron nor nickel deposition was analyzed in this study.

Table XIV presents the total amount of counts of vanadium as a radial profile of its deposition inside the catalyst. Caution must be exercised in comparing different runs. During the EDAX analysis it was observed that the total amount of counts was dependent on the particular microscope conditions at the time of analysis. The performance of the filament with operation time resulted in differences in the total counts for the elements present in a particular selected area - for a new filament the counts were higher; however, the radial profiles were consistent throughout the analysis. The reader should not attempt run-to-run comparisons.

For catalysts A and B (large pore size) the vanadium penetrated the catalyst pellet both in the upper and lower sections of the top zone. The maximum deposition appeared to be at the surface suggesting the typical 'M' profile for the vanadium deposition inside the catalyst pores.

These results correlate well with the coke deposition data. This agrees with Nielsen et al. (1981) who postulated that coke precursors are related to the metal containing compounds in the residue. For this reason, the metal deposition profile reflects the extent of penetration of coke precursors.

TABLE XIV

RADIAL VANADIUM COUNTS OF SPENT CATALYSTS

	Selected Area				
Run (Catalyst)	S1	S2	S3	S4	S5
TOP ZONE					
Upper					
Run 2 (B)	7,643	6,790	1,325	*	*
Run 3 (A)	5,729	3,612	1,032	1,006	*
Run 4 (B)	8,663	5,746	1,752	*	*
Run 5 (A)	2,616	1,731	1,098	*	*
Run 6 (C)	1,481	*	*	*	*
Lower					
Run 2 (B)	3,750	2,348	910	*	*
Run 3 (A)	2,000	2,000	1,092	*	*
Run 4 (B)	6,279	3,931	1,652	*	*
Run 5 (A)	2,045	1,503	830	*	*
Run 6 (C)	3,789	*	*	*	*
BOTTOM ZONE					
Upper					
Run 2 (C)	2,639	*	*	*	*
Run 3 (C)	1,127	*	*	*	*
Run 4 (B)	1,505	*	*	*	*
Run 5 (B)	1,007	1,258	*	*	*
Run 6 (C)	6,164	*	*	*	*
Lower					
Run 2 (C)	934	*	*	*	*
Run 3 (C)	1,074	*	*	*	*
Run 4 (B)	1,790	*	*	*	*
Run 5 (B)	1,342	728	*	*	*
Run 6 (C)	3,600	*	*	*	*

* Counts below instrument detection capacity (400 V counts)

Again, the large pore size catalysts A and B permitted large molecules to react inside the catalyst and, therefore, these catalysts accumulated more metals and coke deposits. Nielsen et al. (1981) postulated that if the metals penetrate completely, the equilibrium level for coke is not established and the poisoning is too fast to consider reasonable catalyst lives. It appears thin for catalysts A and B in the top zone the penetration is not severe, the coke reaches the equilibrium level, and the coke and metals deposition is the main deactivation mechanism.

For the smaller pore size catalyst in the top there is less volume available for large asphaltenes penetration and subsequent metals and coke deposition. As a result, the deactivation by coke and metals deposition is accelerated.

Some authors (Nielsen et al., 1981; Brunn et al., 1975) associate initial deactivation mainly with rapid coke deposition in the catalyst surface. The results from this study showed that both coke and metals deposition play a role in the initial deactivation period as suggested earlier by Ternan and Kriz (1980) and Hannerup and Jacobsen (1983). However, the exposure time (72 h) may not have been enough to cause significant catalyst deactivation due to deposition of metals.

Returning to the topic of HDS behavior, the use of composite beds using catalysts with high capacity for contaminants at the top layers reduced the deactivation of active catalysts at the bottom layers. However, the HDS level was not increased by the use of the selected combinations. This indicates that an optimization of the amount of each type of catalyst and the severity of the operation is required for successful hydroprocessing of a particular feedstock.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The concept of using composite beds to upgrade a petroleum residue was successfully tested. A two-zone, trickle bed reactor loaded with commercial Ni-Mo catalysts having different pore sizes and active metals load was employed.

This study leads to the following conclusions:

1. The use of composite beds with catalysts (catalyst A) having high tolerance for contaminants in the top zone decreased the HDS deactivation rate of more active catalysts (catalyst C) in the bottom zone. However, the composite beds did not show significant advantages with respect to the HDS level. Evidently, there is a tradeoff between tolerance for contaminants and catalyst activity.
2. Single beds with high active metal loading catalysts (catalysts B and C) had slightly higher hydrocracking and hydrogenation activity than the composite beds. Conversion from composite beds with an active catalyst (catalyst C) in the bottom zone was comparable to the conversion from single beds.

3. The coke content was higher for the catalysts A and B with larger pore size. The coke content in the small pore size catalyst C increased when catalysts A and B were in the top zone. This was explained by dissociation of asphaltenes after reaction inside the large pore catalysts. Results indicated that the equilibrium level for coke deposition was reached before 72 h on stream for all the runs.
4. The vanadium penetration was greater for the catalysts with larger pore size (A and B). The relative maximum for vanadium deposition was at the surface of the catalyst pellet, suggesting the classical 'M' shaped profile. The metals penetration decreased from the entrance to the bottom of the reactor. Exposure time may not have been enough to cause significant catalyst deactivation due to metals deposition.
5. The loss in support properties, surface area and pore volume depended on the reactor length for each catalyst zone. The highest reduction was usually present at the top of the zone. More than 90% of these properties were recovered after regeneration by combustion.

In summary, the use of composite beds for hydroprocessing of the petroleum residue has some advantages with respect to catalyst HDS deactivation. Catalysts with high tolerance for contaminants in the top layers protected the more active catalysts further down in the reactor bed. However, optimization of the amount of each catalyst type per zone and optimization of the operating conditions are required for better performance.

Recommendations

1. The composite-bed concept should be tested for other residues containing higher metals (200 to 400 ppm) and sulfur (3 to 4 wt%) content.
2. Further studies should be conducted on the effect of operating conditions in the performance of the composite beds for HDS. The use of several LHSV's and temperatures is suggested to study the kinetics of the HDS process.
3. The effect of the amount of catalyst for the top and bottom zones should be studied. Combination, other than 50 vol% in each zone, of a catalyst with large pore size but low active metals load followed by smaller pore size but higher active metals load is recommended. Possibly 30 vol% and 70 vol% respectively could be used. This will increase HDS activity while maintaining low overall deactivation when using this kind of feedstock.
4. Longer time experiments (> 200 h) should be performed, preferably with higher metal content in the feedstock, to check the effect of metal deposition in catalyst deactivation compared to coke deposition.
5. Studies with the same operating system will require the use of new heating bands to control the reactor

temperature more effectively. The change of valves 6, 3 and 24 is also suggested because they are not working properly.

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APPENDIX A

EXPERIMENTAL PROCEDURE

The steps involved in the experimental procedure are the following: reactor preparation and packing, catalyst presulfiding, start up, normal operation, sampling, shutdown, and clean up. A detailed description of each step follows.

Reactor Preparation and Packing

The catalysts used throughout this study are commercial 1.6 mm (1/16 in) extrudates TK 711, TK 751, and TK 771 nickel-molybdenum on alumina support from Haldor Topsoe. The properties of these catalysts were given in Chapter II. Glass beads (over and under the catalyst bed) served as pre- and post-heating sections and catalyst support. Figure 16 shows the experimental apparatus.

The reactors are packed using the following steps:

Top Reactor

1. Fit the top of the reactor with a 1.27 cm (1/2 in) union cross. Secure the thermowell using a 0.318 cm (1/8 in) fitting. Next, wedge a 50 mesh screen at the top of the reactor.
2. Hold the thermowell in the center of the reactor and

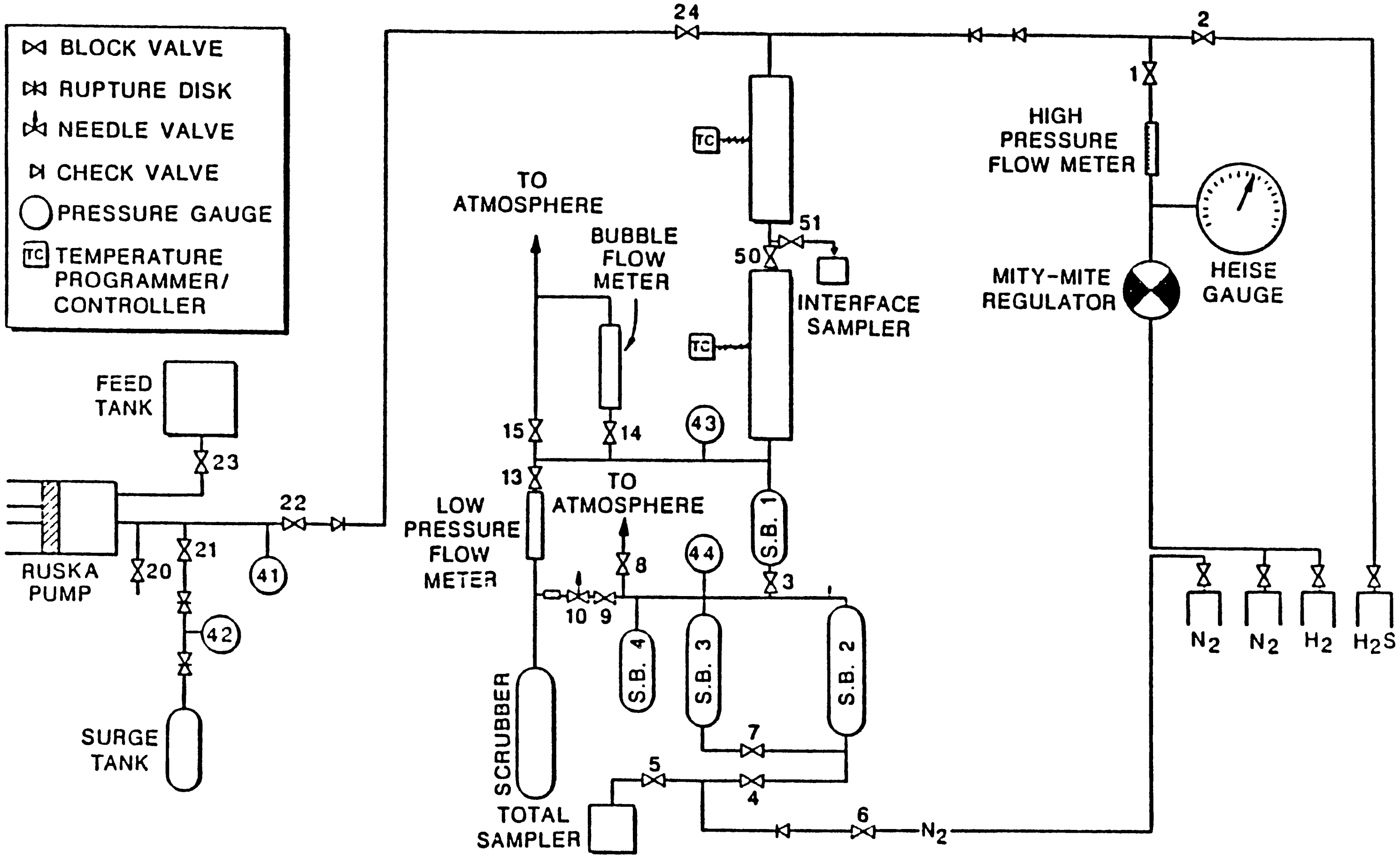

Figure 16. Diagram of the experimental apparatus

pour glass beads (3 mm diameter) into the reactor to a height of 7.62 cm (3 in). Gentle tapping is required while pouring the beads and catalyst to achieve uniform packing around the thermowell.

3. Weigh the required amount of catalyst. (For this study, the catalyst volume for each bed was 17.5 x 10^{-6} m^3 to give 1.0 LHSV at 35 x 10^{-6} m^3oil/h. The catalyst weight was calculated using the density (vendor's data) for each catalyst). Pour half of the catalyst particles into the reactor. Place a liquid redistributor (stainless steel disk) over the catalyst bed to improve the efficiency of the solid-liquid contact. After this, pour the remaining catalyst particles into the reactor.
4. Pour glass beads to a height of 5.08 cm (2 in) and then, slide a 50 mesh screen with a 0.318 cm (1/8 in) diameter hole in the center down until it touches the glass beads.
5. Place a 0.953 cm (3/8 in) outer diameter piece of tubing over the screen to fill the empty reactor space and support the catalyst bed. Place a 50 mesh screen over the 0.953 cm tubing.
6. Fit the bottom of the reactor with a 1.27 cm (1/2 in) to 0.635 cm (1/4 in) reducing union to connect it to the three-way interstage sampler.
7. Connect the hydrogen and oil feed lines to the legs of the cross, and connect the interstage sampler to the bottom of the reactor.

Bottom Reactor

1. Bend the thermowell 90 degrees and fit the top of the reactor with a 1.27 cm (1/2 in) union tee. Secure the thermowell using a 0.318 cm (1/8 in) fitting. Wedge a 50 mesh screen at the top of the reactor. Follow steps 2 to 5 from the top reactor packing procedure, being certain to tap the reactor during packing to assure uniform distribution of the catalyst particles.
2. Fit the bottom of the reactor with a 1.27 cm (1/2 in) to 0.635 cm (1/4 in) reducing union to connect it to the first sample bomb.
3. Connect the top of the union tee to the three way valve, and connect the bottom of the reactor to the first sample bomb by means of a 6.35 mm (1/4 in) stainless steel tube.

Check each fitting in the reactor system for leaks by gradually pressurizing the system with nitrogen gas at 11.09 MPa (1,600 psig) which is 693 kPa (100 psig) higher than the reactor operating pressure. A pressure drop of 138 kPa (20 psig) over one hour period is the maximum acceptable value for reliable reactor operation.

After successful pressure testing, tighten the heating blocks to each one of the reactors. Then, wrap three 12.7 cm (5 in) heating bands around each heating block, and insulate the system. Finally, connect the electrical wires of the heating bands to the corresponding temperature programmer/controller, and put the thermocouples at the designated position in the heating blocks and inside the thermowells.

Catalyst Sulfiding

The following is a step by step procedure for catalyst sulfiding using a mixture of 5 vol% hydrogen sulfide in hydrogen. This procedure was suggested by the catalyst manufacturer.

1. Close valves 1, 4, 7, 8, 14, 51, (Figure 19).
   Open valves 2, 3, 9, 13, 15, 50.
   Note that valve 1 is closed to protect the Heise gauge from hydrogen sulfide corrosion.
2. Turn on the hydrogen sulfide detector and start the gas flow through the reactor at a pressure of 552 kPa (80 psig) and a flow rate of 800 cm^3/min.
3. Turn the temperature programmer/controllers on and control the heating rate at 50°C (122°F) per hour.
4 When the reactor temperature reaches 200°C (392°F) raise the pressure in the unit to 1,380 kPa (200 psig). Keep the heating rate at 50°C (122°F) per hour.
5. When the reactor temperature reaches 350°C (662°F) set the temperature controllers to the isothermal mode for three hours.
6. Cut off the hydrogen sulfide gas by closing the main valve in the hydrogen sulfide cylinder and wait for the gas to completely exit the system. This is indicated by a pressure reading of zero on the bottle regulator

and the pressure gauge 43.

7. Close valve 2 and flush the system with nitrogen gas for 0.33 h by opening valve 1 and the main nitrogen bottle valve. Set the nitrogen flow rate at 400 cm^3/min at a pressure of 1,725 kPa (250 psig).

Start-Up Procedure

1. Preheat the feed tank (100°C),the pump (150°C), the oil lines (120°C), the sample bombs and interconnecting lines (110°C), and heat the feed until a freely flowing liquid is obtained (100°C).
2. Set the temperature controllers 10°C (18°F) lower than the desired operating temperature.
3. Charge the feedstock into the feed tank. Set the pump to the desired feed rate. Throughout this study the feed rate used is 35 x 10^{-6} m^3/h. Then, charge the feed into the pump by opening valve 23 (Figure 19) and traversing the pump to draw in the feed.
4. Close valve 23 and open valve 22 making sure that valve 24 is closed. Then, traverse the pump until the pump pressure is 10.34 MPa (1,500 psig). After that, close valves 11 and 3.
5. Pressurize the reactor with hydrogen to 10.34 MPa (1,500 psig).
6. Open valves 4 and 9 and make sure that valves 5, 7, 8, and 13 are closed.
7. Pressurize the sample bombs with nitrogen to 10 MPa (1,450 psig) and then close valves 4 and 6, and open

valves 1, 3, 9, and 13.

8. Adjust the hydrogen flow rate to 1,040 cm^3/min, using the needle valve 10 and the bubble flowmeter.
9. Start the Ruska pump and open valve 24. After the feed moistens the catalyst beds, adjust the temperature controllers to the desired operating temperature.

Normal Operation

Record the temperature profile of the reactor, the temperature of the heating blocks, pressure gauge readings, the pump scale reading, inlet and outlet gas flow rates, and the hydrogen bottle pressure every hour. Also, record the temperature profiles of the oil lines and sample bombs. In the case of plugging, depressurize the sample bombs slowly until the hydrogen starts flowing again into the system. Check the position of the valves right after start-up and after every sampling and refilling of the feedstock.

Sampling Procedure

1. Place a container under the spout in the sampling compartment and close valves 3, 9, and 50.
2. Very slowly open valve 8 to drop the pressure in sample bomb 2 to atmospheric pressure. If the pressure in sample bomb 1 drops, tighten valve 3.
3. Make sure the valve in the interstage sampler is shut. Place a small container (special size) in the sampler, and place a gasket under the cover before tightening it gently. Connect the sampler to the reactor and to a

pressure gauge. Check the time and go to step 8.

4. After 0.083 h, very slowly open valve 51 and allow the sample to flow into the sampler. A rise in the pressure gauge reading indicates that hydrogen gas is flowing into the sampler.
5. Close valve 51 and depressurize the sampling system carefully to avoid oil spilling out of the system.
6. Disconnect the interstage sampler. Take the sample container out, clean it and label it.
7. Open valve 50. Go back to step 9.
8. Raise the pressure of the nitrogen purge cylinder to 2,070 kPa (300 psig). Open valve 4 and then slowly open valve 6 to pressurize sample bomb 2 to 1,380 kPa (200 psig). Check the time and go back to step 4.
9. Purge for five minutes. Then close valves 8 and 6 in that order.
10. To take the sample, open valve 5 extremely slowly to avoid foaming.
11. Open valve 7 and allow the liquid from sample bomb 3 (if there is any liquid) flow out.
12. Close valves 5 and 7, and make sure valve 8 is closed. Take the sample out, label it, and keep it for analysis.
13. Raise the nitrogen purge cylinder pressure to 10.3 MPa (1,500 psig). Open valve 6 slowly to pressurize sample bomb 2 to 10 MPa (1,450 psig). Close valves 4 and 6 and check that valves 5 and 7 are closed.
14. Open valves 3 and 9. Then close the nitrogen purge

cylinder.

Shut-Down Procedure

1. Turn off the feed pump switch and close valve 24.
2. Turn off the temperature controllers and the variacs.
3. Depressurize the pump by traversing until the pump pressure is zero. Drain the remaining liquid from the pump by opening valve 20 and traversing the liquid out.
4. Cut the hydrogen flow when the catalyst bed temperature reaches 250°C (482°F).
5. Depressurize the reactor to 1,730 kPa (250 psig) and start the nitrogen flow in order to purge and cool the reactor.
6. Collect the last sample using the normal liquid sampling procedure after the reactor reaches room temperature.
7. Depressurize the system and the remove the reator insulation. Pull off the heating bands and aluminum blocks, and disconnect the reactor from the feed and hydrogen lines, the interstage sampler, and the sample bombs.
8. Cut each reactor bed into six sections as illustrated in Figure 17. Remove the catalyst particles from the reactor pieces, label each section and keep them for analysis

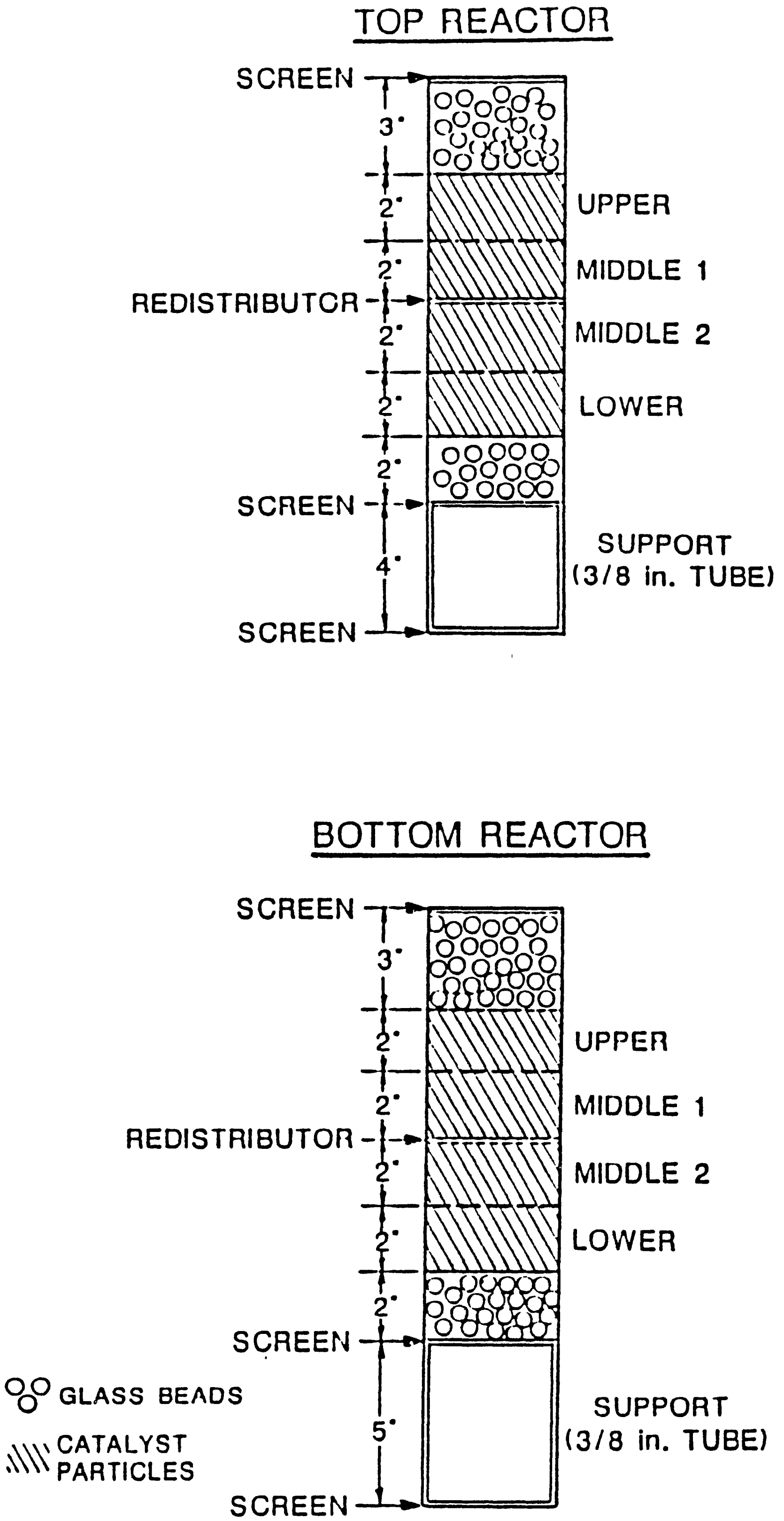

Figure 17. Reactor packing and sectioning

Clean-Up Procedure

Always clean-up the system after each experiment. Drain the remaining feed from the feed tank and wash the pump, feed lines and sample bomb system with toluene until the toluene is clean.

APPENDIX B

LIST OF MAJOR EQUIPMENT AND CHEMICALS

The equipment and chemicals employed were mainly the same as those used by Bhan (1983). The principal materials and reactants will be listed in this appendix. The vendor data is also included.

Equipment

1. Reactors: 316 stainless steel tubing, 1.27 cm (1/2 in) OD, 0.089 cm (0.035 in) wall thickness. Top zone 43.2 cm (17 in) long, bottom zone 45.7 cm (18 in) long.
   Vendor: Precision Fitting & Gauge Co., Tulsa, Ok.
2. Thermowells: 316 stainless steel tubing, 0.318 cm (1/8 in) OD, 76.2 cm (30 in) long with one end welded.
   Vendor: Precision Fitting & Gauge Co., Tulsa, Ok.
3. Reactor Fittings: Parker union crosses, 1.27 cm (1/2 in). Parker reducing unions, 1.27 to 0.635 cm (1/2 to 1/4 in). Parker reducing unions, 0.635 to 0.318 cm (1/4 to 1/8 in). Parker tube end reducers, 1.27 to 0.635 cm (1/2 to 1/4 in). Parker union tees, 1.27 cm (1/2 in).
   Vendor: Precision Fitting & Gauge Co., Tulsa, Ok.
4. Heating Blocks: Two aluminum blocks, each 10.2 cm (4 in) diameter. Top 38.1 cm (15 in) long and bottom 40.6

cm (16 in) long.

5. Band Heaters: 11.4 cm (4.5 in) diameter, 0.48 cm (3/16 in) gap, 120 volts, 400 watts.
   Vendor: Thermal Corporation, Huntsville, AL.
6. Bed Thermocouples: Iron-constantan, 0.025 and 0.05 cm (0.01 and 0.02 in) OD, 304 stainless steel sheath, grounded sensor tip, 91.4 cm (36 in) long, J-type.
   Vendor: Omega Engineering Inc.
7. Wall Thermocouples: Iron-constantan, 0.159 cm (1/16 in), 304 stainless steel sheath, grounded sensor tip, 30.5 cm (12 in) long, J-type.
   Vendor: Omega Engineering Inc.
8. Multiple Selector: 40 points selector connected to a temperature indicator.
   Vendor: Omega Engineering Inc.
9. Temperature Controller/Programmers: Two controllers, one for each reactor zone. Model PC-6010-B.
   Vendor: Valley Forge Instrument Co. Inc., Phoenixville, PA.
10. Powerstats: Input 120 volts, output 0-140 volts, 10 amperes, type 116.
    Vendor: The Superior Electric Co., Bristol, Conn.
11. Heating Tapes: Briskheat heavy insulated tape, 115 volts, 2.54 cm (1 in), and 1.27 cm (1/2 in) wide, 61 cm (2 ft) to 183 cm (6 ft) long.
    Vendor: Fisher Scientific Co.
12. Insulation Material: Fiberglass.
    Vendor: ACE store, Stillwater, Ok.

13. Pressure Gauges: Heise Bourdon tube gauge, 0-20.6 MPa (0-3,000 psig).
    Vendor: Heise Bourdon Tube Company, Inc., Newtown, Conn.
    Crosby, Aschcroff, and Matheson gauges 0-20.6 MPa (0-3,000 psig).
    Vendors: Crosby, Aschcroff, and Matheson Co., respectively.
14. Pressure Regulator: Mity-Mite type, internally loaded, inlet pressure 34.5 MPa (5,000 psig), outlet pressure 20.7 MPa, (3,000 psig), 0.635 cm (1/4 in) inlet and outlet connections.
    Vendor: Whitey Co.
15. Sample Bombs: 0.3 L, 12.4 MPa (1,800 psig), 304 stainless steel, model 6-645-232.
    Vendor: Matheson Co.
16. Surge Bomb: 2.25 L, 12.4 MPa (1,800 psig), 304 stainless steel, model 806.
    Vendor: Matheson Co.
17. Rupture Disks: 0.635 cm (1/4 in), bursting pressure 12.4 and 15.9 MPa (1,800 and 2,300 psig) at 22°C (72°F).
    Vendor: Autoclave Engineering.
18. Pump: Ruska positive displacement pump, 1 L barrel capacity, feed rates from 0.0025 to 0.56 L, 82.8 MPa (12,000 psig) max. Model 2236 WII-SXTR.
    Vendor: Ruska Instrument Corporation, Houston, TX.
19. Feed Tank: 21.6 cm (8.5 in) OD, 19.1 cm (7.5 in) in

height, satinless steel tank.

20. Hydrogen Sulfide Detector: Concentration range 0 to 50 ppm, model 10HS.
    Vendor: Sierra Labs, Inc., Palo Alto, CA.
21. Hydrogen Detector: Combustible gas alarm, model I-501.
    Vendor: MSA Instrument Corporation.

Chemicals

1. Hydrogen: 99.5 % purity, 15.7 MPa (2,300 psig).
   Vendor: Sooner Supplies, Inc., Stillwater, OK.
2. Nitrogen: 99.5 % purity, 15.7 MPa (2,300 psig).
   Vendor: Sooner Supplies, Inc., Stillwater, OK.
3. Hydrogen Sulfide: 5 vol% in hydrogen. 15.7 MPa (2,300 psig).
   Vendor: Jimmie Jones, Co., Stillwater, OK.
4. Toluene: Reagent grade.
   Vendor: Fisher Scientific Co.

APPENDIX C

SULFUR DATA

The sulfur data obtained for the seven experimental runs are listed in this Appendix. The feed was a 50 wt% mixture of VR and VGO with a 0.9 wt% sulfur content. The sulfur was analyzed 3 times for each sample with the average being the reported value.

TABLE XV

SULFUR CONTENT (WT%) OF RUN 1

Catalyst B (Feed: 0.9 wt% S)	
Time on stream (h)	Total sample (wt% S)
6	0.39
12	0.34
18	0.34
24	0.33
30	0.33
36	0.38
42	0.31
48	0.28
54	0.30
60	0.30
66	0.28
72	0.30
78	0.37
84	0.42
90	0.44
96	0.44
102	0.44
108	0.44

TABLE XVI

SULFUR CONTENT (WT%) OF SINGLE BEDS

Time on stream (h) (Catalysts)	Interstage/Total sample (Feed: 0.9 wt% S) Run 4 B	Run 6 C	Run 7 B
6	0.42/0.21	0.46/0.23	0.45/0.22
12	0.43/0.22	0.46/0.26	0.45/0.23
18	0.43/0.21	0.51/0.28	0.45/0.23
24	0.43/0.23	0.50/0.29	0.46/0.25
30	0.44/0.23	0.50/0.30	0.46/0.28
36	0.46/0.23	0.51/0.34	0.46/0.29
42	0.46/0.26	0.52/0.34	0.48/0.30
48	0.47/0.29	0.55/0.35	0.48/0.33
54	0.49/0.27	0.57/0.35	0.49/0.30
60	0.52/0.27	0.57/0.37	0.51/0.31
66	0.49/0.29	0.58/0.36	0.50/0.32
72	0.50/0.31	0.61/0.37	0.53/0.32

TABLE XVII

SULFUR CONTENT OF COMPOSITE BEDS (WT%)

Time on stream (h) (Catalysts)	Interstage/Total sample (Feed: 0.9 wt% S) Run 2 B + C	 Run 3 A + C	 Run 5 A + B
6	0.45/0.24	0.50/0.29	0.50/0.26
12	0.47/0.24	0.50/0.30	0.51/0.26
18	0.48/0.25	0.49/0.31	0.51/0.27
24	0.46/0.25	0.50/0.32	0.52/0.26
30	0.49/0.25	0.51/0.32	0.52/0.29
36	0.49/0.27	0.52/0.33	0.53/0.29
42	0.51/0.29	0.52/0.33	0.53/0.32
48	0.53/0.30	0.52/0.32	0.53/0.32
54	0.51/0.29	0.51/0.34	0.54/0.32
60	0.52/0.29	0.53/0.32	0.54/0.30
66	0.54/0.30	0.52/0.33	0.55/0.32
72	0.56/0.32	0.52/0.33	0.54/0.31

VITA

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