

THE EFFECT OF CATALYST TEMPERATURE
ZONING ON UPGRADING A
COAL-DERIVED LIQUID

By

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PREFACE

The objective of this study was to investigate the advantages and disadvantages of hydrotreating coal-derived liquids by temperature zoning. Hydrotreating was carried out in a two-stage trickle-bed reactor, varying the top zone temperature between 400°C (752°F) and 500°C (932°F) while maintaining the lower zone temperature at 400°C (752°F). Reactor plugging became excessive when the top zone temperature was operated above 450°C (842°F).

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CHAPTER I

INTRODUCTION/LITERATURE REVIEW

One of the most important realizations in the past few years has been that the world's supply of crude oil is limited. Consequently, research efforts have been focused on alternative sources of hydrocarbons. Of these alternative fuel sources, heavy oils originating from coal appear very promising due to large and widely distributed coal reserves.

Coal-derived liquids have been produced by various liquefaction processes including Solvent Refined Coal, H-Coal, Exxon Donor Solvent, and Synthoil. In each liquefaction process, the liquid produced must be upgraded in order to be used as a feedstock for producing heating and transportation fuels. Coal-derived liquids have high molecular weights and high carbon/hydrogen ratios which must be reduced. Additionally, coal liquids are high in nitrogen and sulfur cyclic compounds which must be removed for processing, environmental, and health reasons. Coal liquids also contain oxygen compounds which can severely inhibit catalytic cracking requirements and consume large amounts of hydrogen.

A variety of hydrotreating processes have been examined to best achieve the upgrading objectives of petroleum and coal liquids. These refining processes include multi-stage operation (Murphy, 1977; Richardson et al., 1979; Johnson et al., 1983), composite catalyst beds (Nielson, et al., 1981; Brunn et al., 1975; Bhan, 1983), guard beds reactors (Christ et al., 1979; Murphy and Treese, 1979; Frumkin et al., 1966), and temperature zoning (Bhan, 1983; Robinson and Evin, 1982; Shepherd et al., 1956). These references are discussed in the following sections.

Temperature zoning consists of operating each section in a two-stage hydrotreating reactor at different temperatures. This results in a flexible system to achieve upgrading while maintaining catalyst activity. In this study, upgrading a 15 wt% SRC solids in process solvent over a Ni-Mo-Al₂O₃ catalyst by temperature zoning addressed the following objectives:

1. Evaluation of the effect of temperature zoning on catalyst activity.
2. A study of the effect of temperature zoning on catalyst coke content and surface area changes.
3. An investigation of the possibility of temperature zoning to tune reactions and achieve optimum upgrading.

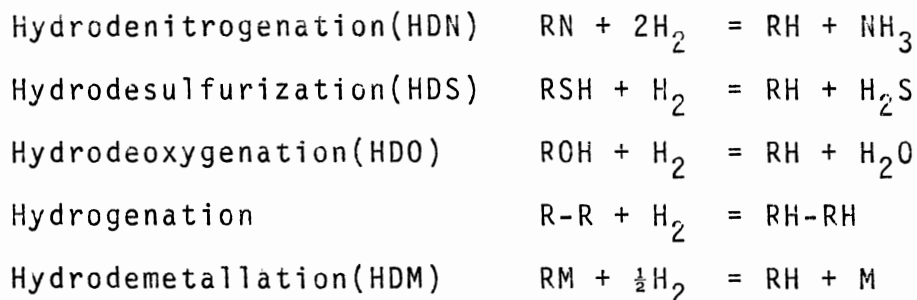
To better understand these objectives, a review of upgrading, two-stage processing, and the effect of temperature on hydrotreating will be presented.

Upgrading Coal-Derived Liquids

There are three general routes to upgrading heavy oils. The first is to add hydrogen to the molecules directly, removing inorganic material, and decreasing molecular weight by hydrotreating. The second is to remove lighter components by high-pressure extraction. The third method is a pyrolysis type where a coke is produced with inorganic impurities leaving behind a clean, lighter oil. Of these three methods, the most commonly preferred is hydrotreating (Laine and Trimm, 1982).

Hydrotreating

Hydrotreating coal-derived liquids is typically carried out in trickle-bed reactors operating in temperature and pressure ranges of 300-425°C (572-797°F) and 10-20 MPa (1,450-2,900 psig), respectively (Satterfield and Yang, 1983; Dohles et al, 1983). A history of the performance of trickle-bed reactors is presented by Bhan (1981). Bhan discusses the gas-liquid distribution, catalyst wetting, and axial dispersion and mass transfer effects in trickle-bed operations. Hydrotreating in trickle-bed reactors has successfully achieved the desired reduction of nitrogen, sulfur, and oxygen cyclic compounds as well as the desired reduction of molecular weight and metal contaminants. These reductions occur according to the following generalized, simplified reactions:



These equations are global simplifications of the complex reactions that occur during the upgrading process. Laine and Trimm (1982) present a more detail explanation of the reaction mechanisms involved in hydrotreating.

Several studies have been made to assess the function of the operating parameters on hydrotreating. It has been reported (Fu et al., 1978; Stein et al., 1978; Wilson and Kritz, 1984) that pressure increases from 3.4 MPa (500 psig) to 13.8 MPa (2,000 psig) have a positive effect on hydro-treating. Satchell (1974) reported that for raw anthracene oil, increases in hydrogen flow rate from 267 std m³/m³ (1,500 SCF/bbl) to 3,562 std m³/m³ (20,000 SCF/bbl) oil showed little effect on hydrotreating. Space time, however, has a definite effect on upgrading coal-derived liquids. Increasing space times, in the range of 0.2 to 5.0 h, improves nitrogen, sulfur and metal removal (Ternan and Brown, 1982). Wilson and Kritz (1984) found increased conversions of aromatics to naphthenes when space times were increased from 0.4 to 1.25 h. An extensive review of operating parameters effect on hydrotreating has been collected by Stein et al. (1977) and Stiegel et al. (1981).

Hydrotreating Catalysts

Catalysts used in hydrotreating are generally oxides and sulfides of molybdenum, tungsten, cobalt, nickel, zinc, or manganese on alumina or silica supports. A Co-Mo-Al₂O₃ combination is preferred for HDS while a Ni-Mo-Al₂O₃ catalyst is used when HDN is required (Dac Vong Do, 1982; Kondo et al., 1984). The alumina support typically has surface areas on the order of $100-300 \times 10^{-3} \text{ m}^2/\text{kg}$ ($4.8-14.6 \times 10^5 \text{ ft}^2/\text{lb}$), pore volumes of $0.3-0.6 \times 10^{-3} \text{ cm}^3/\text{kg}$ ($4.8-9.6 \times 10^{-3} \text{ ft}^3/\text{lb}$), and an average pore diameter of $5-15 \times 10^{-7} \text{ m}$ ($1.6-4.9 \times 10^{-6} \text{ ft}$) (Bhan, 1983). Increasing the pore volume decreases the surface area and vice versa.

A number of research efforts have been devoted to determining optimum hydrotreating catalyst properties. The subject of these research efforts included: support composition (Kwan et al., 1975; Brunn et al., 1975), active metal composition (Yeh, 1981; Berg et al., 1982), amount of metal loading (Stiegel et al., 1983; Yeh, 1981), and pore size distribution (Stein et al., 1978; Kang and Gendler, 1978).

Catalyst Deactivation

Although hydrotreating in trickle-bed reactors accomplishes the desired refining, trickle-bed reactors suffer from two major drawbacks: severe reactor plugging due to interstitial deposits and rapid catalyst deactivation due to pore blockage by coke and metals. These drawbacks were

observed in several studies including Stein et al. (1977), Soni and Crynes (1981), Chang (1982), and Garg et al. (1980). In each case, hydrotreating was carried out over commercially available catalysts in an effort to remove heteroatoms in a single stage.

Catalyst deactivation occurs through two main mechanisms: coke and metals deposition. Coal-derived liquids are high in polynuclear aromatics and asphaltenes which are considered coke precursors. Coke or carbonaceous deposits on catalysts severely inhibit the catalyst activity by reducing pore volume, blocking the pore mouths and covering surface sites.

The nature and structure of coke formations are complex and not fully understood. Baker and Harris (1978) give an excellent review of carbon deposits from catalytic decomposition of hydrocarbons as well as a literature survey of projects involving the study of coking.

Shibaoka et al. (1984) reported the occurrence of carbonaceous deposits formed during hydrogenation of coal/tetralin solutions. They observed mesophase and semicokes to form when the rate of polymerization of coal-derived aromatic material exceeded the rate of stabilization of these materials by hydrogen addition. The rates were reported to be functions of temperature, time, hydrogen availability, and design parameters of the reactor system.

Ternan et al. (1979) studied coke formation of heavy residual oils from bitumen over a Ni-Mo catalyst. They

suggested that coke deposits were compromised of two species; one a reactive substance which was subsequently converted into reaction products and one being an unreactive substance which blocks catalytic sites. Furthermore, Ternan describes coke as being formed from polyaromatic compounds in the asphaltic fraction which are deficient in hydrogen but high in heteroatom content.

Ouchi et al. (1984) studied the coking mechanism during hydrotreatment of asphaltene. They explained that coking begins with thermal splitting of bridge linkage which produces radicals. These radicals, and the molecules from which hydrogen was removed, polycondense with each other to form carbonaceous deposits.

Chang (1982), in a study hydrotreating a SRC process oil, found that coking occurs rapidly at reactor start-up but attains a maximum and levels off after 40-60 h of oil contact time. Kang and Johanson (1976) also reported rapid initial coke formation which leveled off after a few days during H-Coal processing.

Metal deposition causes irreversible catalyst deactivation due to blocking pores and covering active sites. Unlike coke deposition, metal deposition is a permanent deactivation which will not allow regeneration upon combustion. Typical metals present in coal-derived liquids include Fe, Ti, Cr, Ca, and K.

Sivasubramanian et al. (1980) and Kovach et al. (1982) studied metal deposition due to processing a coal-derived

liquid. Both studies revealed a thin inorganic crust covering the catalyst pellet consisting mainly of coke, Fe, and Ti. Kang and Johanson (1976) found titanium deposits to only one-tenth of the catalyst radius but found iron to be present at the catalyst center. Bhan (1983), in a study involving a SRC oil, found similar results regarding metal deposition and its location. Deposits of metal on the catalyst particle external surface seem to occur due to the reaction of inorganic constituents, and internal pore deposits come from reactions with oil-soluble fractions, namely organometallics.

This section on upgrading coal-derived liquids can be summarized as follows:

1. Coal-derived liquids require upgrading due to their low H/C atomic ratios and high content of cyclic compounds of nitrogen, sulfur, oxygen, and various metals.
2. Hydrotreating of coal liquids in trickle-bed reactors is best achieved by operating in the range of 300-425°C (572-797°F) and 10-20 MPa (1,450-2,900 psig).
3. Space time, pressure, and temperature have definite effects on hydrotreating while hydrogen flow rates above 267 std m³/m³ (1,500 SCF/bbl) have a negligible effect.
4. Hydrotreating catalysts are generally of a Ni, Co, or Mo oxide or sulfide supported by an alumina or alumina-silica base.

5. Catalysts are rapidly deactivated by coke and metal deposition. Coke deposition is reversible by controlled combustion regeneration but metal deposition permanently poisons the catalyst.

Temperature Effect on Upgrading

One of the most important parameters in hydrotreating coal-derived liquids is the reactor operating temperature. Temperature has marked effects on hydrotreating reaction rates, coking rates, and liquid yields. Even though temperature plays an important role in upgrading, little experimental work has been done to assess its influence.

Reaction Rates

The effect of temperature on reaction rates is apparent from the Arrhenius equation (Nalitham et al., 1983). As the temperature increases, the reaction rate constant increases exponentially. This theory holds true for HDN, HDS, HDM, and HDO reactions. Ternan et al. (1979) found the weight percent sulfur removed to increase from 55 to 90% when the temperature was increased from 350°C (662°F) to 480°C (896°F) while processing a heavy residual oil. Fu et al. (1978), in a hydrotreating study involving SCR process oil and a Ni-W catalyst, reported sulfur and nitrogen removal to increase markedly for temperature increases from about 375°C (707°F) to 435°C (815°F), above which only slight HDS and HDN improvement was shown. Berg et al. (1982) hydrogenated

SRC II using a Co-Mo-Ni-W catalyst in a temperature range of 350-500°C (662-932°F). They found that the denitrogenation increased with increased temperature. Dalling et al. (1984) reported an increase in HDO activity for increases in operating temperature from 200°C (392°F) to 380°C (716°F) when processing a SRC middle distillate.

Although increasing contact temperatures increases HDN, HDS, HDM, and HDO reaction rates, increasing the operating temperature too high can be detrimental to basic hydrogenation. At elevated temperatures, thermodynamic equilibrium favors dehydrogenation (Ahmed, 1979). Ternan et al. (1982) agreed with Ahmed citing a hydrogenation decrease with increasing temperature while processing a coal liquid. In the temperature range from 380-420°C (716-788°F), the H/C atomic ratio linearly decreased with increased temperature. Ternan explains that even though reaction kinetics increase with temperature, the equilibrium becomes less favorable for hydrogenation.

Wilson and Kriz (1984) studied the effect of temperature on reaction rates while upgrading a middle distillate fraction of a syncrude from Athabasca oil sands. They hydrotreated the syncrude over Co-Mo and Ni-Mo catalysts in the temperature range of 340-440°C (644-824°F). Wilson and Kriz reported that the conversion of aromatics to naphthenes was a reversible reaction involving chemical equilibrium which is temperature dependent. They observed that at high

temperatures, above 400°C (757°F), the extent of conversion was limited by thermodynamic equilibrium.

Dalling et al. (1984) presented hydrogenation activity data during processing a SRC middle distillate over a Ni-W catalyst. They observed aromaticity to decrease and hydrogen content to increase for increasing temperatures up to 350°C (662°F); after which the reverse was true. They believed the reversal was due to a shift in the hydrogenation-dehydrogenation equilibria as well as from hydrodealkylation of hydrogen-rich alkyl groups.

Coke Formation

The relationship between temperature and coke formation has been highly questionable. Voorhies (1945), during fixed bed cracking of gas oil, found coke content to increase linearly with increasing temperature. Voorhies estimated that carbon formation roughly doubles for a 85°C (153°F) increase in temperature. Kang et al. (1976) also found that increasing reactor temperature increased coke formation. They carried out experiments at 10.3 MPa (1,500 psig) and 450-468°C (842-875°F) with a SRC solvent. They hypothesized that coal liquid hydrogenation was promoted by the hydrogen donors present in the solvent and that excessive processing conditions cause solvent deterioration. This deterioration lead to thermal cracking and high coke formations.

Ternan et al. (1979) reported substantial increases in catalyst coke content when the operating temperature was

increased from about 330°C (626°F) to 375°C (707°F) during hydrotreatment of bitumen. The coke content remained constant from 375-440°C (707-824°F); above the temperature of 440°C (824°F), the coke content again increased markedly.

Ahmed (1979) carried out hydrotreatment studies using an FMC oil at 10.3 MPa (1,500 psig) and 3.0 h over a Co-Mo catalyst. He reported similar coke contents (about 21 wt%) for operating temperatures of 371°C (700°F) and 427°C (800°F) but observed the coke content to jump to 38 wt% when the temperature was raised to 454°C (850°F).

However, Berg et al. (1982) found the amount of carbon deposited to be independent of temperature in processing SRC II in the temperature range of 350-500°C (662-932°F) with pressure and space times of 7.7 MPa (860 psig) and 0.25 h to 2.5 h, respectively. Berg reported catalyst coke contents of about 16 wt% when hydrotreating in this temperature range. Bhan (1983) supports Bergs finding of no dependence between coking and temperature in a study involving a feed of 15 wt% SRC solids with process solvent. Bhan found comparable coke content (4 wt% difference) on a Ni-Mo catalyst when the bed was operated at 260°C (500°F) and 400°C (752°F) at 10.3 MPa (1,500 psig) and a space time of 1.9 h.

Liquid Yields

Researchers do agree that liquid yields decrease with increasing process temperature (Kang and Johanson, 1976;

Berg et al., 1982; Shibaoka, 1984; Wilson and Kriz, 1984; and Fu, 1978). Higher contact temperatures result in higher C_1 - C_4 gas production which causes a reduction in liquid volume production.

Temperature effects on upgrading coal-derived liquids can be summarized as follows:

1. Increases in temperature increases HDN, HDS, HDM, and HD0 reaction rates.
2. Temperature increases can become detrimental to hydrogenation when elevated temperatures cause equilibria to favor dehydrogenation.
3. The relationship between coke content and temperature is disputed. Research efforts support postulates of increasing linear dependence, varying dependence, and also of no dependence whatsoever.
4. Increasing contactor temperatures will increase gas production and thus decrease liquid yields.

Two-Stage Hydroprocessing

A number of two-stage processes have been developed for the hydrotreating of heavy oils. Two-stage processing benefits from the fact that each stage can be run at different operating conditions or with different catalyst loadings and thus tune the complex reactions to achieve the desired refining.

Graded Catalyst Beds

Some hydrotreating research has been devoted to the idea of two-stage graded catalyst beds. Here, each bed is operated with catalysts of different properties including possibilities of metal loading, pore size, and pellet geometry.

Brunn et al. (1975) used the idea of graded beds with catalysts of different metal loadings. Brunn used a high HDM catalyst (Ni-Co-Mo) in the first stage and a high HDS catalyst (Co-Mo) in the second stage to hydrotreat asphaltic oil. Brunn utilized an operating temperature of about 400°C (752°F) and an operating pressure of about 13.8 MPa (2,000 psig). Most of the metal deposition occurred in the top stage and thus increased the second stage catalyst life by approximately 50%.

Krichko et al. (1984) also examined two-stage processing with different types of catalysts in each stage. They found the products from brown coal hydroliquefaction to best be upgraded by treating first with a Co-Mo catalyst (to reduce the phenol, N-compounds, and olefins content) followed by a second stage containing a Ni-Mo catalyst (to reduce sulfur content) or a Pd catalyst (to reduce aromatics content).

A 70-30 vol% mixture of SRC and creosote oil was hydrotreated over spent and fresh Shell 324 catalyst in a two-stage process by Stohl et al. (1983). They found

similar organic deposits (coke) in the first and second stages (22 and 18 wt%). The catalyst in the first stage had more Fe and Ti content than the second stage. The catalyst had a thin organic crust which contained the Fe and Ti which lead to the catalyst deactivation.

Sonnemans et al. (1984) reported on a new generation of catalyst that can most effectively be used in multi-stage hydrotreating of heavy oils. They discussed the benefits (HDS, HDN, aromatics conversion) of operating a two-stage reactor with zoning of Co-Mo and Ni-Mo catalysts. Experiments were carried out at 407°C (765°F), 5.0 MPa (725 psig), and a space time of 1.0 h.

A number of researchers have recommended the use of cheap, disposable materials as the first stage in two-stage processing of heavy oils derived from petroleum, coal, or shale (Robinson and Evin, 1982; Murphy and Treese, 1979; Kirk, 1972; Johnson et al., 1983). The different materials used in the first stage include: pyrite, clay, glass beads, and stainless steel flex-rings. In each case, little hydrogenation of the feedstock was achieved in the first stage but the first stage did remove metals, inorganics, and coke materials.

Nielson et al. (1981) studied graded catalyst beds using catalysts with different pore sizes. The study used large, medium, and small pore diameters in hydroprocessing heavy petroleum resids. Nielson found no optimum combination of pore sizes but did find that combinations of pore

sizes resulted in better HDS activity than hydrotreating over any single pore size.

Frayar et al. (1978) found zoning catalysts of different geometries to be beneficial toward upgrading oils of high metal and asphaltene content. Frayer used a catalyst with surface grooves and protrusions in the top bed and a cylindrical shaped catalyst in the lower bed. The shape of the top bed catalyst improved its HDM activity.

This section on two-stage processing can be summarized as follows:

Two-stage processing produces a flexible system which allows selective HDS, HDN, or HDM to occur in one or both stages. This processing generally occurs by operating each bed with different catalyst properties including possibilities of catalyst loading, pore size, and pellet geometry.

Temperature Zoning

Several advances in two-stage processing have been developed, one such advance is temperature zoning. Temperature zoning occurs when each stage in a two-stage reactor scheme is operated at different temperatures. Each zone may or may not contain the same type of catalyst. Temperature zoning adds another dimension of flexibility and selectivity to two-stage upgrading.

Higher Temperature in Top Zone

Fu et al. (1978) hydrotreated a 30 wt% SRC in process solvent in a two-step reactor sequence with the first step at 415°C (780°F) and the second step within a temperature range of 377-433°C (710-811°F). In the first step, the feed was hydrotreated in a rocking autoclave at 15.1 MPa (2,200 psi) for 4 h. The product was then hydrotreated at 12.4 MPa (1,800 psi) for 0.6-3.0 h. A Ni-Mo catalyst was used in both steps with the main purpose of the first stage being mild hydrotreating. They reported the percent sulfur removal to slightly increase and the C₁-C₄ production to greatly increase as the second stage temperature increased from 375°C (707°F) to 435°C (815°F). The percent nitrogen reduction increased from 30 to 60% in the temperature range of 375°C (707°F) to 415°C (780°F). However, temperature increases above 415°C (780°F) showed little effect on nitrogen removal.

Wolk et al. (1975) disclosed a process for hydrotreating high metal petroleum residual oil utilizing two ebullated beds where the first stage was a strong HDM zone and the purpose of the second stage was HDS. Both stages contained a Co-Mo catalyst and were held at about 12.4 MPa (1,800 psi). The preferred top zone space time was 1.6 h while the preferred bottom zone space time was 1.2 h. Wolk states that optimum operation occurred when the first stage was at a temperature of about 415°C (780°F) and the second stage was at a temperature of about 400°C (752°F).

Shepherd (1956) studied the desulfurization of crude oil and crude oil fractions in a two-stage reactor system where the first zone was 20-35°C (36-63°F) higher than the latter zone. He explained that this provided some needed dehydrogenation of naphthenes with maximum HDS and minimum hydrocracking. The process employed 15% of the total catalyst weight in the first zone and the remainder in the second zone. The use of short space times in the first zone was to reduce the effects of hydrocracking, namely accelerated coke deposition.

Arey et al. (1963) defined a process for hydrocracking heavy oils in two-stages. He claimed that partial conversion of fractions, HDM, HDS, and HDN occurred in the first stage while selective hydrocracking occurred in the second stage. In Arey's process, equal volume catalyst stages were used with the top stage operated at 14-28°C (25-50°F) higher than the second stage. Arey cited the need for elevated temperatures in the first stage was to compensate for its rapid catalyst deactivation.

Higher Temperature in Lower Zone

Bhan (1983) operated a temperature zoned reactor while hydrotreating an SRC coal liquid. An equal weight amount of Ni-Mo-Al₂O₃ catalyst was used in both stages (total space time of 1.9 h) with the top stage at 260°C (500°F) and the bottom stage at 400°C (752°F). Bhan found that approximately all the inorganic and heavy carbonaceous residues and

most of the metals were removed in the low temperature zone leaving the second reactor section almost residue free.

Hensley (1978) disclosed a two-stage process to treat heavy petroleum hydrocarbons. He recommended that the second section be operated at a temperature and pressure higher than that of the first section. Hensley suggested hydrotreatment in the range 343-454°C (650-850°F) and 3.4-6.9 MPa (500-1,000 psi) using a Group V, VI, or VIII metal impregnated catalyst. The main function of the first section was HDM and asphaltene reduction while the primary purpose of the second section was HDS.

Jankowski et al. (1982) hydrotreated synthetic crudes from coal using Ni-Mo-Al₂O₃ and Co-Mo-Al₂O₃ catalyst. Jankowski reported successful HDN and HDS when operating the top zone at 360°C (680°F) and the bottom zone at 390°C (734°F).

A process of desulfurization of an asphaltic oil in two-stages was developed by Brunn et al. (1975b). Normal operating conditions were in the range of 365-427°C (689-800°F) and 5.2-6.9 MPa (750-1,000 psig). The catalyst employed was a Group VI and VIII metal on a non-cracking support. Brunn utilized three times as much catalyst in the second stage as in the first stage and operated the second stage at an elevated temperature. The increased amount of catalyst was necessary because the feed to the second stage was already low in sulfur content and it required more chemical work to further reduce the sulfur content. The

elevated lower zone temperature helped meet the needed increase of chemical work by increasing the reaction rate constants.

This section on temperature zoning can be summarized as follows:

1. Temperature zoning adds flexibility to two-stage processing by allowing optimization of reactions.
2. Depending upon the feedstock and catalyst properties, successful upgrading can be achieved by operating either the top or lower zone at an elevated temperature.

Literature Summary

This literature review can be summarized as follows:

1. Coal-derived liquids seem to be a viable alternative fuel source. Coal liquids, however, are deficient in hydrogen and high in sulfur, nitrogen, oxygen, and metals content. Heteroatom and metal reduction can be achieved through hydrotreating in trickle-bed reactors.
2. Catalysts used in hydrotreating are generally oxides and sulfides of molybdenum, cobalt, nickel, or manganese on alumina or silica supports.
3. Catalyst deactivation occurs through coke and metal deposition. Coke deposition occurs rapidly upon reactor start-up and then tends to level off. Coke deposition is a process that is partially reversible by combustion. Metals tend to deposit in catalyst mouth pores and on active sites, thus permanently poisoning the catalyst.

4. Increases in operating temperature increase HDN, HDS, HDM, and HDO reaction rates yet elevated temperatures can become detrimental to hydrogenation when the temperature causes equilibrium to favor dehydrogenation. The relationship between coke content and increasing operating temperature is disputed. Research tends to support both linear dependence, varying dependence, and no dependence whatsoever between coking and temperature.

5. Upgrading heavy oils can be carried out in two stages. Graded catalyst beds occur by operating each bed with different catalyst properties including possibilities of metal loading, pore size, and pellet geometry.

6. Temperature zoning offers the advantages of flexibility and selectivity while giving the possibility of tuning reaction rates for optimum upgrading.

CHAPTER II

FEEDSTOCK AND CATALYST PROPERTIES

Liquid Feedstock

SRC-I solids and process solvent were received from Pittsburgh and Midway Coal Mining Company's pilot plant. A 15 wt% solids in process solvent mixture was prepared by slowly dissolving the solids in the liquid with constant agitation at room temperature. The solution was heated to 125°C (257°F) for 24 h and then filtered through a 50 mesh size screen. Table I presents the elemental analysis and ASTM boiling point distribution for the mixture. This feedstock was chosen because it was typical of coal liquids such as Synthoil or mixtures of H-Coal. These oils all have similar boiling point ranges and high percentages of asphaltenes, sulfur, and nitrogen compounds.

Fresh Catalyst

The catalyst was a commercially available Ni-Mo-Al₂O₃ catalyst, Armak KF-153-S. This catalyst has the following qualities: small pore size, high surface area, cylindrical geometry, and an alumina-silica base. Table II presents the catalyst chemical composition, physical properties, and pore

TABLE I
FEEDSTOCK PROPERTIES

15 wt% SRC (solid) in 85 wt% Process Solvent		
<u>Elemental Analysis</u>		<u>Mixture (wt%)</u>
C		87.2
H		7.3
N		1.1
S		0.5
Ash		0.1
 <u>Boiling Point Analysis</u>		
Volume Distilled	Temperature	
	(°C)	(°F)
IBP	250	482
10	275	527
20	291	555
30	305	581
40	323	613
50	337	638
60	360	680
70	395	743
80	450	842
wt of 450°C (842°F) residues	21.7 x 10 ⁻³ kg	

TABLE II
CATALYST PROPERTIES

Armak Commercial KF-153-S	
<u>Chemical Composition</u> *(wt%)	
NiO	3.3
MoO ₃	15.5
SiO ₂	4.1
Al ₂ O ₃	Balance
 <u>Physical Properties</u>	
Shape	1.6 mm (1/16 in) Extrudate
Surface Area (x 10 ⁻³ m ² /kg)	295.0
Pore Volume (x 10 ⁻³ cm ³ /kg)	0.48
Pore Diameter (nm)	4.8
Pore Distribution (x 10 ⁻³ cm ³ /kg)	
0-3.0 x 10 ⁻⁷ m	0.00
3.0-8.0	0.42
8.0-10.0	0.01
10.0-20.0	0.02
20.0	0.48

*vendor data

size distribution. This catalyst was chosen because in an eariler study by Bhan (1983) it was found to have good HDN activity for a SRC feedstock. Also, the same catalyst and feedstock as used by Bhan were chosen to serve as a reference point for the data in the present study.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A special trickle-bed reactor system was used to hydro-treat heavy oils. The system was designed for two-stage processing with an interstage sampling device. The experimental equipment and procedure used in this study were the same as used by Bhan (1983). Bhan gave a detailed description of the equipment and how it was used, thus only a brief mention will be made here.

Reactor Operation

A simplified flow diagram of the reactor system is shown in Figure 1. A Ruska positive displacement pump was used to provide a continuous oil flow rate of $20 \text{ cm}^3/\text{h}$ ($5.2 \times 10^{-3} \text{ gal/h}$). Hydrogen, supplied from a gas cylinder, flowed through a high pressure meter and was controlled by a valve to approximately $1781 \text{ std m}^3/\text{m}^3 \text{ oil}$ (10,000 SCF/bbl). Inlet hydrogen pressure was kept at 10.3 MPa (1500 psig) by a Mity-Mite pressure regulator. The feed oil and hydrogen gas flowed co-currently down the packed reactor tubes and into a gas-liquid separator. The gas was scrubbed with a 50 vol% ethanolamine solution and vented to the atmosphere. The liquid from the separator was collected in the lower sample bomb until removal.

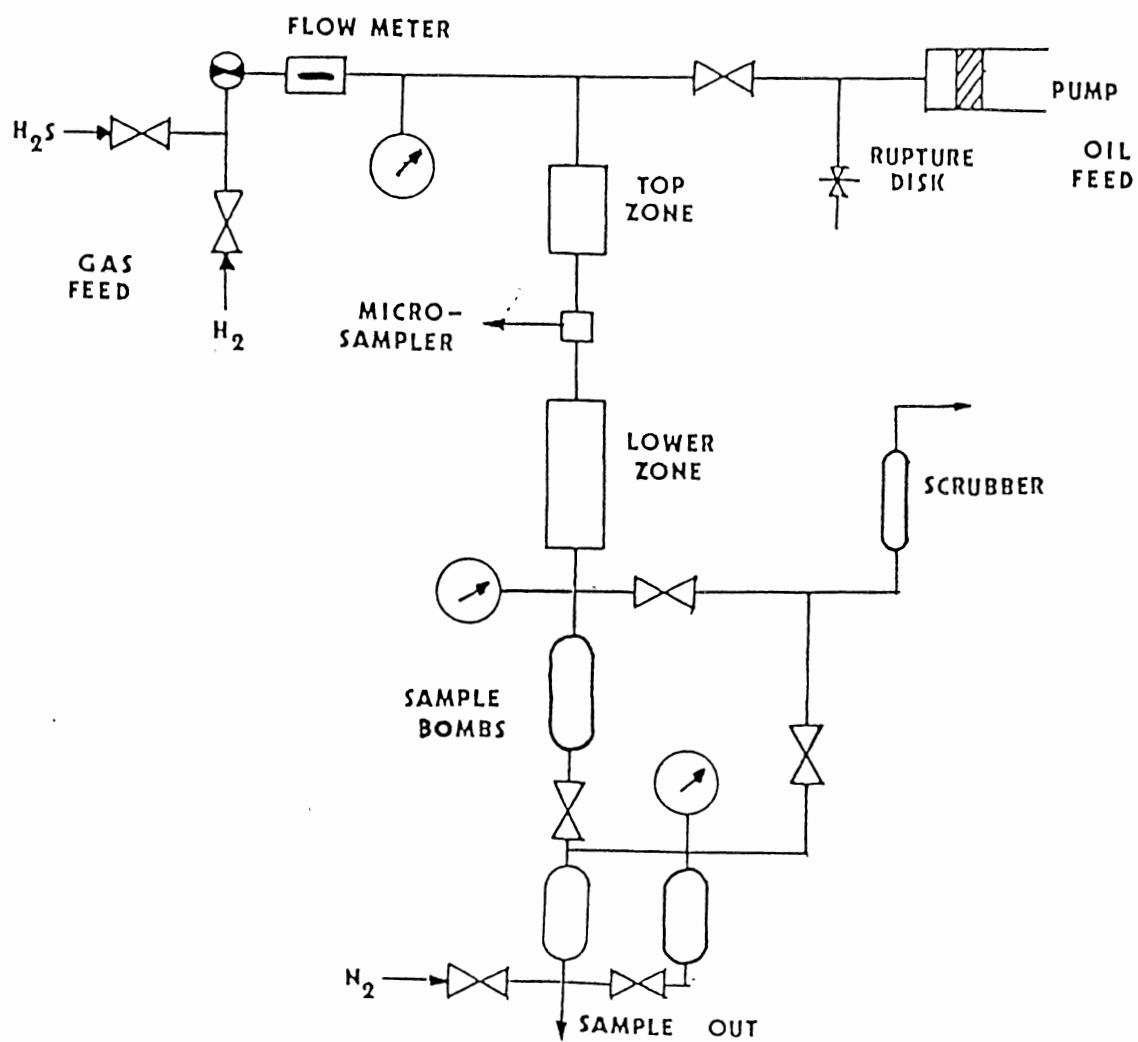


Figure 1. Simplified Flow Diagram.

The reactor was heated by electrical resistance bands placed along its length. Temperature controllers and variacs were used to maintain the reactor at the desired temperature. The reactor temperature was measured by thermocouples placed inside and outside the reactor tube.

The reactor system contained a shut-off valve above the lower sample bomb so product liquid samples could be taken without disturbing normal operation. The system was also equipped with a three-way valve in between the reactor zones to provide interstage sampling.

Start Up

The top zone was packed to a catalyst height of 8.9 cm (3.5 in) with 3.8 cm (1.5 in) of glass beads before and after the catalyst section. The lower zone contained 35.5 cm (14 in) of catalyst with 2.5 cm (1 in) pre- and post-sections of 0.3 cm (0.11 in) diameter solid glassbeads. The weight of the catalyst used in each run was held constant and the reactor tube was "tapped" as the catalyst was loaded in order to obtain the desired bed height.

After the beds were packed, the reactor tubes were installed and pressure tested at the operating pressure. A pressure drop of less than 0.13 MPa (20 psig) over a 1.0 h period was considered satisfactory.

Next, the catalyst was calcinated by allowing nitrogen at 1.3 MPa (200 psig) and $200 \text{ cm}^3/\text{h}$ ($6.9 \times 10^{-3} \text{ ft}^3/\text{h}$) to flow through the system for 3.5 h as the temperature was

raised approximately 120-160°C/h (216-288°F/h) to a final temperature of 400°C (752°F). After calcination the catalyst was sulfided with a 5 vol% H₂S gas in hydrogen at 0.52 MPa (80 psig) and 500 cm³/hr (1.7 x 10⁻² ft³/h) for 2.5 h at 400°C (752°F).

During pre-sulfiding, the feedstock was charged to the Ruska pump and heated to approximately 100°C (212°F). After pre-sulfiding, the reactor temperature was allowed to drop 20°C (36°F) and the oil and hydrogen feeds were started. Over the next hour, the reactor was brought up to operating conditions and the run was considered to begin at that point in time.

Shut Down

After the experiment had operated for 72 h, the last interstage and product samples were taken. Next, the oil pump was turned off and de-pressurized. The heaters were turned off and the reactor insulation was removed for rapid cooling. The hydrogen flow was allowed to pass through the system until ambient temperature was reached.

Liquid Sample Analysis

Liquid samples taken every 6-12 h were analyzed for nitrogen, carbon, and hydrogen content by a Perkin-Elmer Elemental Analyzer Model 240 B.

The feedstock and product samples taken at 60 h on stream were distilled according to ASTM D-1160 procedures.

100 cm³ (2.6×10^{-2} gal) of the sample was fractionated at 2.0×10^{-3} MPa (0.3 psia) while recording the vapor temperature and volume distilled. Temperatures were corrected to atmospheric pressure using ASTM D-2892 charts for petroleum hydrocarbons.

Catalyst Sample Analysis

Catalyst pellets were taken from three sections in the upper reactor zone (top, middle, and bottom) and from four sections in the lower reactor zone (top, upper middle, lower middle, and bottom). The catalysts were extracted for 24 h with tetrahydrofuran in a Soxhlet extraction unit to remove any residual oil.

Spent catalysts from each reactor section were analyzed for carbonaceous deposits (coke content). Coke content was defined as the percent loss in catalyst weight upon combustion at 475°C (887°F). Catalyst samples were first dried under vacuum at 100°C (212°F) for 3 h to remove any water on the pellets. The samples were cooled and weighed in a helium atmosphere to avoid water absorption. After combustion for 24 h at 475°C (887°F), the catalyst was again dried and weighed in a helium atmosphere.

Catalyst pellets were randomly selected from each reactor section and analyzed for metals content using a JEOL Model JFM-35 Energy Dispersive X-ray Analysis (EDAX) in a Scanning Electron Microscope (SEM). The concentration of surface metals by EDAX was determined as the area fraction

of the metals present with the area fraction representing the count intensity of a particular element. The catalysts were not only analyzed for metals deposited on the surface, but also some pellets were radially fractured and examined in the center and near the edge to determine metals penetration.

Selected spent and regenerated catalyst pellets were analyzed for surface area, pore volume, and pore size distribution on a Quantachrome Autoscan-60 Porosimeter.

Gas Sample Analysis

Gas samples taken at 24, 36, and 60 h on stream were analyzed on a Hewlett-Packard 5880A Gas Chromatograph (flame ionization detector). Each sample was run three times and the results were averaged.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental Parameters

Six experimental runs were conducted in the two-stage trickle-bed reactor. The sixth run was a duplicate of the fourth and will be discussed in the section on precision and reproducibility. In each run, the operating pressure was maintained at 10.3 MPa (1,500 psig). The reactors were loaded with 20 wt% of the total catalyst in the top zone and the remainder in the lower zone. The temperature in the top zone was operated in 25°C (450°F) increments from 400°C (752°F) to 500°C (932°F) while the temperature in the lower zone was maintained at 400°C (752°F). The space time (based on total bed volume of both zones) was held at 1.9 h and the hydrogen flow rate was kept at 1781 std m³/m³ of oil (10,000 SCF/bbl).

Table III summarizes the experimental run conditions and gives a brief comment on operating experience. Run TZE was shut down after only 6 h of operation due to excessive reactor plugging; no liquid, catalyst, or gas analysis was made of this run. Excessive plugging due to interstitial deposits indicate that 500°C (932°F) was too high a temperature to attempt hydrotreating this feedstock.

TABLE III
EXPERIMENTAL RUN PARAMETERS

Reactor: two-stage trickle bed Pressure: 10.3 MPa				Hydrogen flow rate: 1781 std m ³ /m ³ Space time: 1.9 h
Run Name	Temperature (°C)		Time on Oil (h)	Comments on Operation
	Top Zone	Bottom Zone		
TZA	400	400	72	no problems during run
TZB	425	400	72	no plugging problems, maximum pressure drop across reactor was 0.4 MPa
TZC	450	400	72	slight plugging problems occurred at about 58 h, maximum pressure drop across reactor was 0.7 MPa
TZD	475	400	72	slight plugging at about 30 h, progressively worse plugging, maximum pressure drop across reactor was 5.5 MPa
TZE	500	400	6	severe reactor plugging caused shut down after 6 h, maximum pressure drop across reactor was 10.3 MPa
TZF	475	400	72	slight plugging at about 36 h, progressively worse plugging, maximum pressure drop across reactor was 6.9 MPa

Liquid Sample Analysis

HDN and Hydrogenation Activity

Liquid samples taken every 6-12 h were analyzed for nitrogen, hydrogen, and carbon content. Figures 2-5 show the percent nitrogen content for each sample as a function of time on stream. Table IV lists the liquid product hydrogen content for all runs. In each case, the catalysts lost a significant amount of their HDN and hydrogenation activity. Rapid activity loss occurred until 48-60 h, after which the activity loss leveled off. Similar loss in HDN activity when processing coal liquids was observed by Chang (1982), Stiegel et al. (1983), Ahmed (1979), and Bhan (1983). The catalyst activity loss can be attributed to coking; consistent with the activity loss reported by Chang (1982). Chang reported rapid coke deposition up to 40-60 h of operation, after which the coking rate stabilized and only gradually increased.

The HDN activity of the catalyst showed a strong dependence on the top zone temperature. As the temperature in the top zone increased from 400°C (752°F) to 450°C (842°F), the wt% nitrogen in the liquid product decreased. However, for the temperature increase to 475°C (887°F), the final nitrogen content increased. Initially, TZD contained low amounts of nitrogen but after 30-36 h on stream, the nitrogen content was greater than that of the lower temperature runs (see Figure 6 for a comparison of all experimental runs).

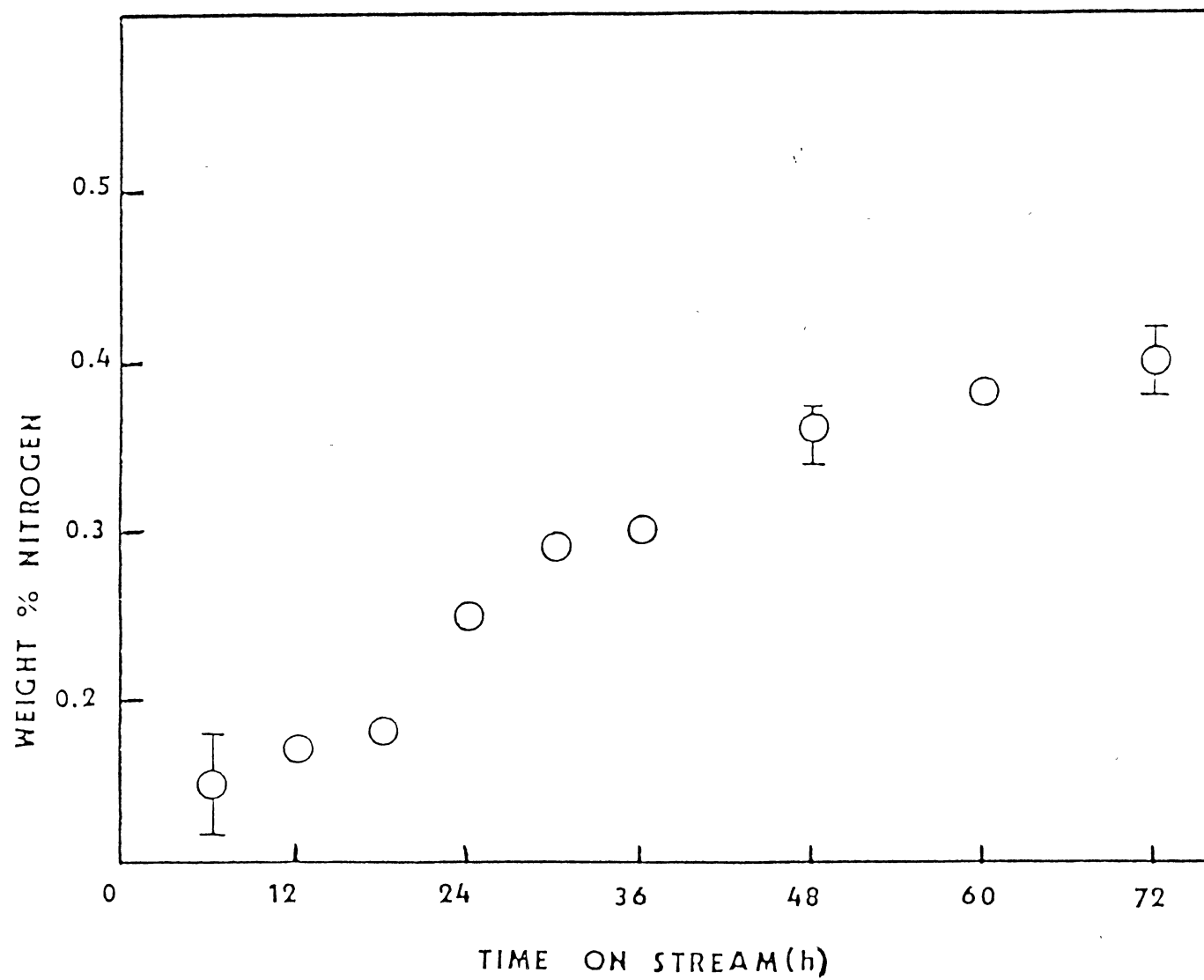


Figure 2. Run TZA Time on Stream versus Nitrogen Content.

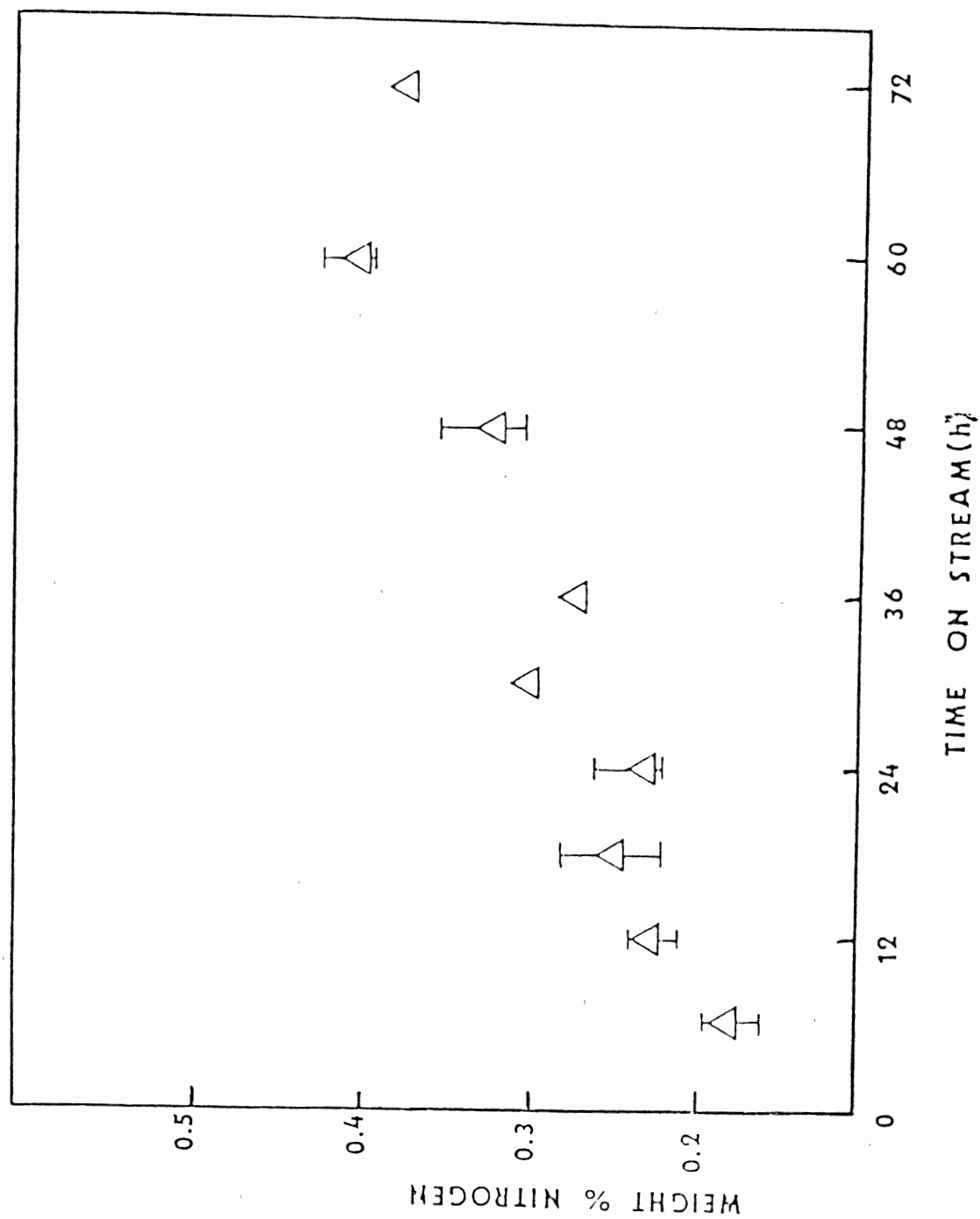


Figure 3. Run TZB Time on Stream versus Nitrogen Content.

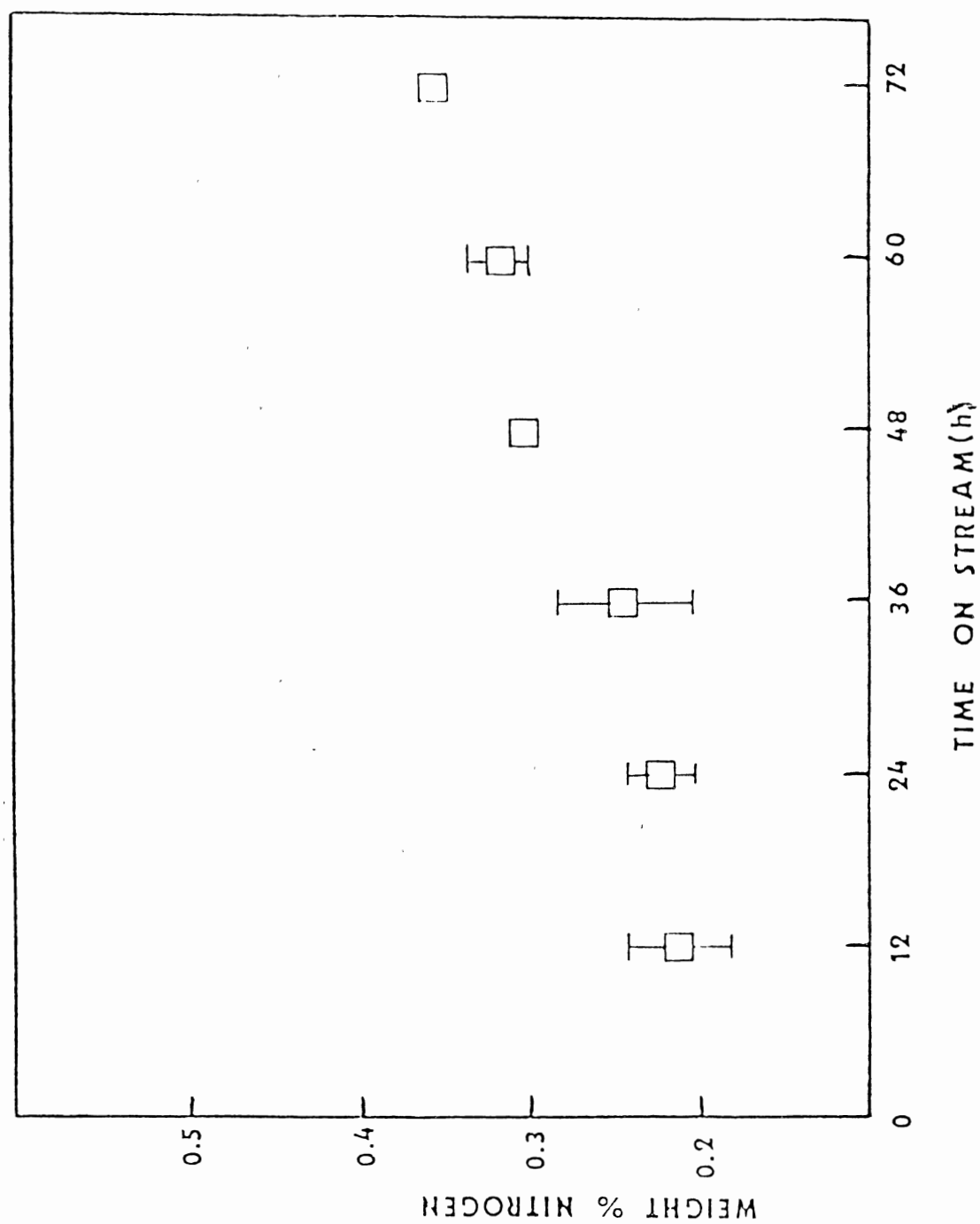


Figure 4. Run TZC Time on Stream versus Nitrogen Content.

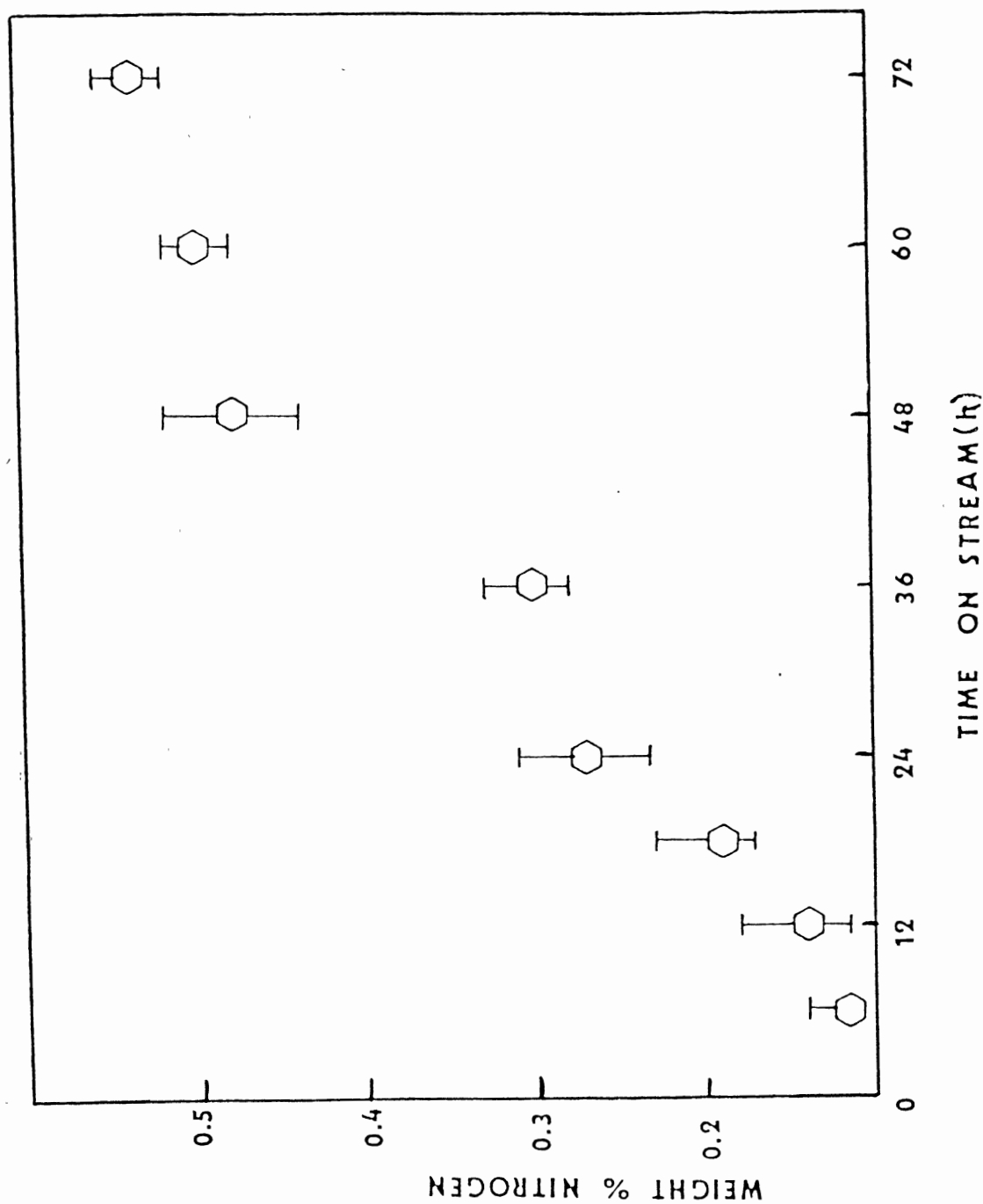


Figure 5. Run TZD Time on Stream versus Nitrogen Content.

TABLE IV
HYDROGEN CONTENT OF LIQUID SAMPLES
(wt%)

<u>Time on Stream (h)</u>	<u>TZA (400°C)</u>	<u>TZB (425°C)</u>	<u>TZC (450°C)</u>	<u>TZD (475°C)</u>
6	10.5	10.3	--*	10.6
12	10.8	9.9	10.3	10.8
18	10.6	9.8	---	10.2
24	10.0	10.1	10.5	10.2
30	10.3	10.0	---	9.9
36	9.3	9.6	10.2	9.7
48	10.0	9.3	10.0	9.2
60	10.1	10.1	10.1	9.2
72	9.8	10.0	10.0	9.5

* Samples taken every 12 h
Feedstock contained 7.3 wt% hydrogen.

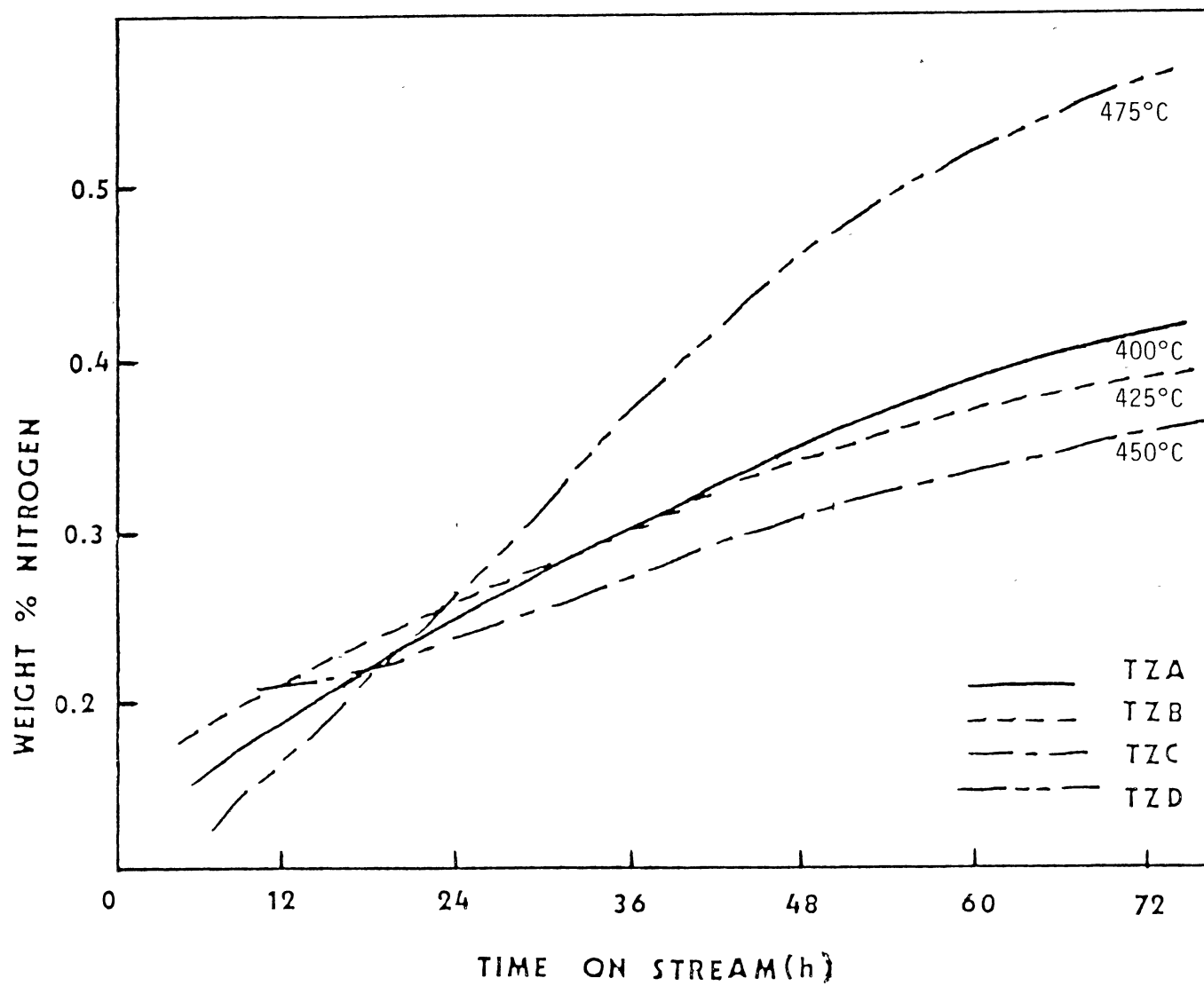


Figure 6. All Runs Time on Stream versus Nitrogen Content.

Ahmed (1979) reported a similar activity profile during hydrotreatment of FMC oil (1.1 wt% nitrogen) in a trickle-bed reactor at 10.3 MPa (1,500 psig) and 3.0 h over a Co-Mo catalyst. He ran experiments at 371°C (700°F), 427°C (800°F), and 454°C (850°F). Ahmed found that up to about 100 h on oil, the nitrogen content decreased with increasing temperature but after 100 h, the HDN activity of the 454°C (850°F) run was worse than that of the 371°C (700°F) or 427°C (800°F) run.

The inversion effect of temperature on HDN can be explained by poor mass transfer and dehydrogenation-hydrogenation equilibrium. Mass transfer effects in a trickle-bed reactor occur through two mechanisms: 1) external - diffusion from the bulk phase of the fluid up to the external surface of the catalyst pellet and 2) internal - diffusion from the pellet surface to the active internal sites. The top zone of TZD contained large amounts of interstitial deposits. These deposits glued the catalyst pellets together which caused the blockage of the liquid flow pattern and thus poor external mass transfer. The top zone of TZD was also high in coke and metals deposition which cover the catalyst surface and pore mouths and thus inhibit internal diffusion.

Dehydrogenation-hydrogenation equilibrium effects HDN since the removal of nitrogen from heterocyclic compounds occurs through a reaction network where the ring is first saturated with hydrogen followed by opening of the ring and

subsequent removal of nitrogen in the form of ammonia (Gates et al., 1979). To achieve nitrogen removal, the heterocyclic ring must be completely hydrogenated.

Ahmed (1979), Ternan et al. (1982), and Wilson and Kriz (1984) reported during hydrotreatment of syncrudes that operating temperatures too high can cause dehydrogenation due to unfavorable thermodynamic equilibrium. Dautzenberg and Yeung (1984) reported that the saturation of aromatics to naphthene was a reversible reaction. Furthermore, they stated that dehydrogenation was endothermic and was favored by high temperatures. They observed aromatic conversion to be kinetically and thermodynamically controlled. As temperature increased, the hydrogenation activity increased due to kinetics. At a given temperature, the increase in hydrogenation was countered by dehydrogenation as the reaction became thermodynamically limited.

The effect of excessive operating temperature causing poor catalyst wetting and unfavorable equilibrium was also evident in the liquid interstage samples. Table V shows the nitrogen content and Table VI lists the hydrogen content for the interstage samples. TZA, TZB, and TZC showed slight HDN (16-30 wt% nitrogen removal) and failed to exhibit catalyst deactivation. Low nitrogen removal can be attributed to the low reactor space time, only 0.3 h. The interstage samples did contain more hydrogen than the feedstock (7.3 wt%) indicating that some hydrogenation took place.

Interstage samples of TZD showed almost no hydrotreating activity after about 48 h on stream. Nitrogen and

TABLE V
NITROGEN CONTENT OF INTERSTAGE SAMPLES
(wt%)

<u>Time on Stream (h)</u>	<u>TZA (400°C)</u>	<u>TZB (425°C)</u>	<u>TZC (450°C)</u>	<u>TZD (475°C)</u>
6	1.03	0.93	-	0.77
12	0.89	0.97	0.90	0.81
18	0.89	0.89	-	0.94
24	0.98	0.83	0.98	1.00
30	1.03	0.85	-	1.01
36	0.96	0.90	0.99	1.02
48	1.00	0.96	0.85	1.09
60	0.96	0.96	0.90	1.06
72	0.95	0.93	1.01	1.10

*Feed contained 1.1 wt% nitrogen.

TABLE VI
HYDROGEN CONTENT OF INTERSTAGE SAMPLES
(wt%)

<u>Time on Stream (h)</u>	<u>TZA (400°C)</u>	<u>TZB (425°C)</u>	<u>TZC (450°C)</u>	<u>TZD (475°C)</u>
6	7.5	9.1	--	8.7
12	8.1	8.2	8.1	8.3
18	7.9	8.6	--	8.1
24	8.0	8.6	8.4	8.1
30	8.0	8.1	--	8.1
36	8.0	8.2	8.6	8.0
48	7.7	8.5	8.8	7.8
60	8.0	8.3	8.5	8.3
72	8.1	8.2	8.5	7.8

* Feedstock contained 7.3 wt% hydrogen.

hydrogen contents were on the order of 1.1 and 8.0 wt%, respectively (the feedstock contained 1.1 wt% nitrogen and 7.3 wt% hydrogen). This observation coincides with the total liquid product nitrogen content increase and hydrogen content decrease after 30-36 h on stream. Thus, the inter-stage sample data support the total liquid product nitrogen and hydrogen profiles which indicate that elevated temperatures can cause poor mass transfer (due to interstitial, coke, and metal deposition) and dehydrogenation (due to unfavorable thermodynamic equilibrium).

ASTM Distillation

Liquid samples collected between 48-60 h on stream were vacuum distilled according to ASTM D-1160 procedure. Liquids distilled were categorized as light oil (normal boiling point below 216°C [420°F]), middle-distillate (normal boiling point between 216°C [420°F] and 343°C [650°F]), and heavy ends (normal boiling point greater than 343°C [650°F]). Also, the weight of residues left in the boiling pot (solids boiling above 450°C [842°F]) were recorded. Table VII presents the normal boiling point distributions, liquid volume percents, and 450+°C (842+°F) residue weights for each run as well as for the feedstock.

Figure 7 shows that as the top zone temperature increased, the normal boiling point curve slightly shifted. This shift was due to increased cracking and hydrocracking. This effect was also illustrated in the volume percents of

TABLE VII

DISTRIBUTION OF LIQUID SAMPLES AS A
FUNCTION OF BOILING POINT RANGE

<u>Volume % distilled</u>	Temperature (°C)				<u>FEED</u>
	<u>TZA</u>	<u>TZB</u>	<u>TZC</u>	<u>TZD</u>	
initial	195	160	150	155	250
10	250	245	237	237	275
20	273	270	265	271	291
30	290	286	280	287	305
40	305	297	295	298	323
50	323	310	310	313	337
60	343	328	328	332	360
70	378	350	355	352	395
80	425	385	395	393	450
wt residues (x 10 ⁻³ kg)	9.9	11.0	5.0	8.1	21.7
light oil (vol%) T<216°C	2.0	5.5	7.0	7.5	0.0
mid-distillate (vol%) 216<T<343°C	58.0	62.5	60.0	60.5	52.0
heavy ends (vol%) T>343°C	40.0	32.0	33.0	32.0	48.0

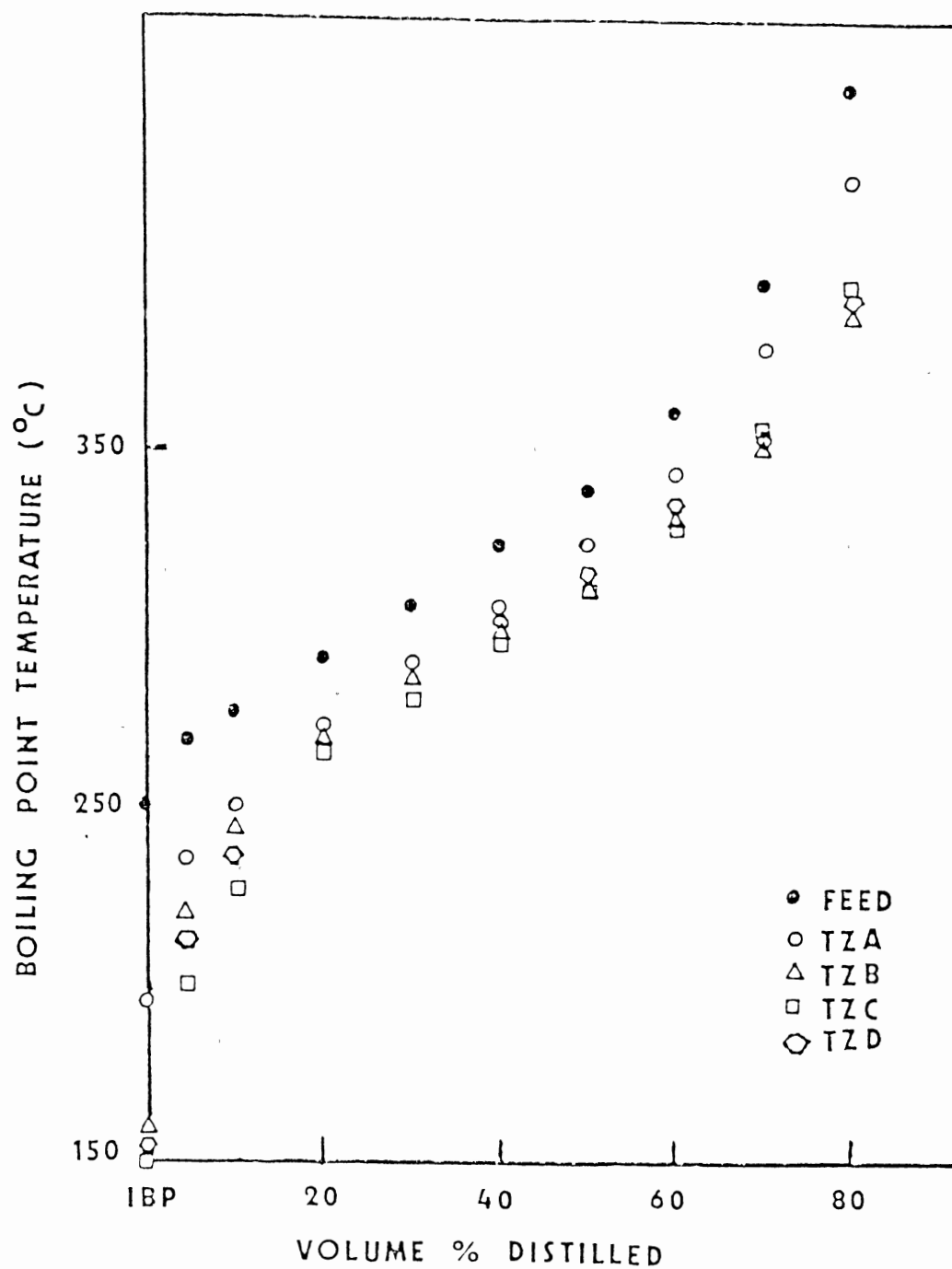


Figure 7. Boiling Point Distribution of Runs TZA, TZB, TZC, and TZD.

the three distillate cuts. As the top zone temperature increased, the volume percent of light oils increased from 2 vol% to 8 vol%. Also, for the temperature zone increase from 400°C (752°F) to 475°C (887°F) the heavy ends decreased from 40 vol% to 30 vol%. The shift in the normal boiling point curve and changes in volume percent light oil and heavy ends were not excessive. This can be attributed to the fact that only 20 wt% of the total catalyst (0.3 h LVHST) was subject to the increases in temperature.

This section on liquid sample analysis can be summarized as follows:

1. In each run, substantial HDN and hydrogenation activity was lost. The catalyst rapidly lost activity during the first 40-60 h of operation; the activity loss was gradual over the remaining time.

2. The liquid product wt% nitrogen content decreased and wt% hydrogen increased with increasing top zone temperature until 450°C (842°F). Above this temperature, the wt% nitrogen increased and wt% hydrogen decreased with increasing temperature. HDN and hydrogenation increased with temperature as reaction rates increased until a temperature of 475°C (887°F) was reached where thermodynamic equilibrium became unfavorable. Also, at 475°C, large amounts of interstitial deposits caused poor catalyst wetting which decreased the hydrotreating activity.

3. Increasing the top zone temperature from 400°C (752°F) to 475°C (887°F) slightly increased the amount of

cracking and hydrocracking as evident by the shift in normal boiling point curves and changes in the amount of light oils and heavy ends present.

Catalyst Sample Analysis

Coke Deposition

Aged catalyst samples were analyzed for coke content which was defined as the percent loss in catalyst weight upon combustion at 475°C (887°F). Aged catalyst sample weight reduction occurs due to the combustion of carbonaceous deposits on the catalyst surface. Weight reduction also occurs due to the oxidation of the active metal sulfides (Ni, Mo) and oxidation of the deposited metals sulfides (Fe, Ti). Bhan (1983) reported a 3.3% reduction in weight due to active metal oxidation for the KF-153-S catalyst. Catalyst coke content data are reported with the correction for active metal sulfides oxidation; no estimate could be made for the weight reduction associated with deposited metal sulfides oxidation.

Table VIII presents the coke content of the aged catalyst for each run. Coke content was reported for seven sections (three from the top zone and four from the lower zone) as well as an average coke content for each zone.

The coke content for each individual zone from top to bottom was relatively constant. Chang (1982) reported that coke content was greater at the top section of his reactor zone if the coking rate was still rapidly increasing. Once

TABLE VIII
CATALYST COKE CONTENT

<u>Section</u>	Weight Percent			
	<u>TZA (400°C)</u>	<u>TZB (425°C)</u>	<u>TZC (450°C)</u>	<u>TZD (475°C)</u>
<u>TOP ZONE</u>				
Top	28.6	29.0	29.6	35.8
Middle	25.5	29.1	31.2	41.5
<u>Bottom</u>	<u>27.1</u>	<u>25.3</u>	<u>31.2</u>	<u>36.8</u>
Average	27.0	27.8	30.7	38.0
<u>LOWER ZONE</u>				
Top	23.6	23.9	25.8	26.8
Upper Middle	23.5	19.2	24.3	25.5
Lower Middle	19.1	24.1	24.8	26.4
<u>Bottom</u>	<u>21.1</u>	<u>19.7</u>	<u>24.5</u>	<u>28.0</u>
Average	21.8	21.8	24.8	26.6

a maximum coking rate had been attained and the rate leveled off, the reactor zone showed constant coke content in each section. This result, along with the profile of HDN activity loss, confirms that in each run the maximum coking rate was attained before 72 h and probably began leveling off at 40-60 h.

The hydrotreating temperature of the top zone showed definite effects on the catalyst coke content in the top zone (Figure 8). For the temperature range of 400-450°C (752-842°F) only a small increase in coke content was reported (3.7 wt%). However, for the change in top zone temperature from 450°C (842°F) to 475°C (887°F), a large increase in the catalyst coke content was observed (7.3 wt%). This same effect of temperature on carbon laydown was reported by Ternan et al. (1979). Ternan hydrotreated heavy gas oil from hydrocracking bitumen. Ternan found the coke content to increase with temperature up to approximately 375°C (707°F); the coke content remained constant from 375°C (707°F) to 440°C (824°F); above 440°C (824°F), the coke content increased markedly with temperature. Ternan hypothesized that the "flat" spot in the coking profile was related to a phenomenon of adsorption or reactivity of hydrogen on the catalyst surface counteracting the tendency for increased coke formation.

Ahmed (1979) hydrotreated a FMC oil over a Co-Mo catalyst at 371°C (700°F), 427°C (800°F), and 454°C (850°F). He reported the 371°C (700°F) and 427°C (800°F) runs to have

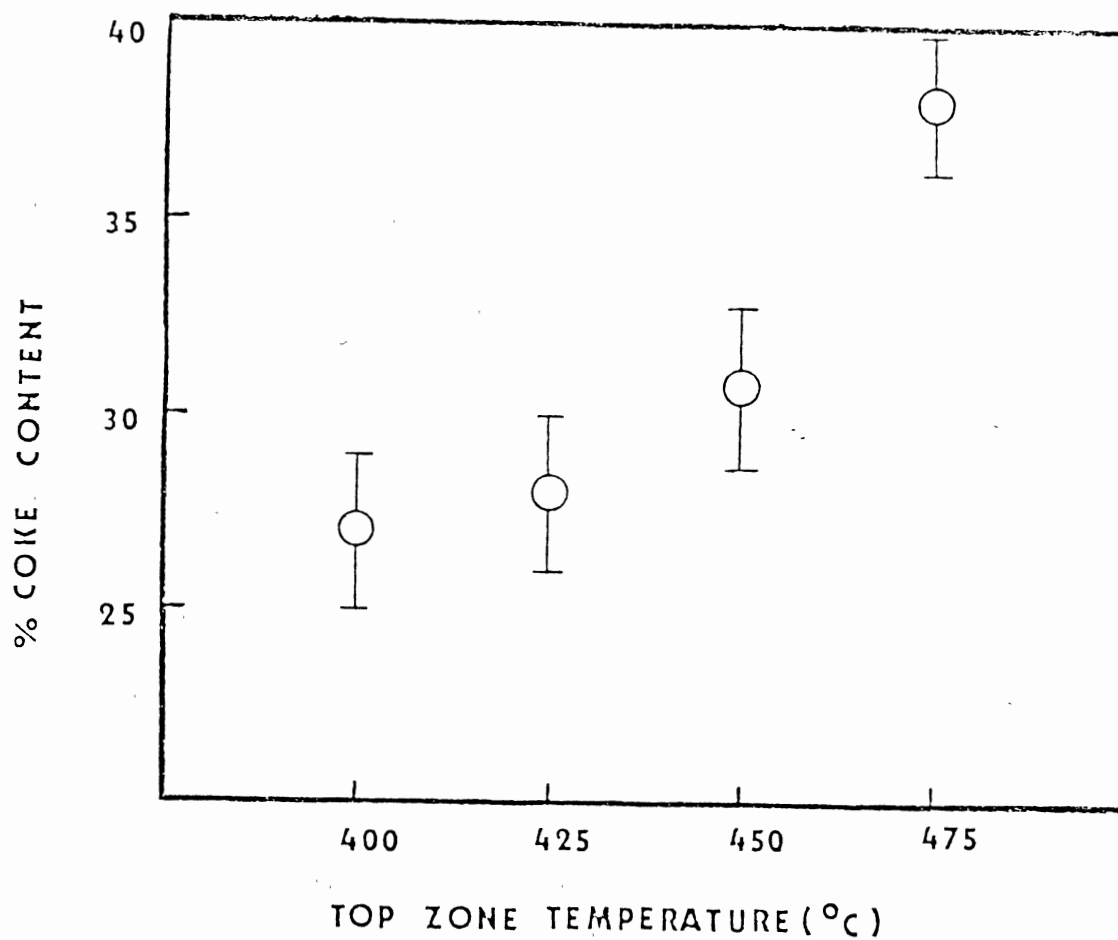


Figure 8. Effect of Top Zone Temperature on Catalyst Coke Content.

similar coke contents (about 21 wt%). When the reaction temperature was increased to 454°C (850°F), the coke content rose to 38 wt%. Ahmed offered no explanation of coke content variation with temperature.

The effect of temperature on coke formation in the present study can be explained in terms of hydrogenation. For top zone temperature increases from 400°C (752°F) to 450°C (842°F), the hydrogenation rate was enhanced. When the top zone temperature was increased to 475°C (887°F), a thermodynamic limitation was reached and dehydrogenation reactions dominated. Ternan et al. (1979) reported one specie of coke to be a reactive material which could be hydrogenated into reaction products. Shibaoka et al. (1984) reported coke to form when the rate of polymerization of aromatic material exceeded the rate of stabilization by hydrogen addition. Thus, excessive operating temperatures cause dehydrogenation which fails to hydrogenate reactive coke species, slows aromatic stabilization rates, and subsequently increases coke formation.

The catalyst coke content of the lower zone slightly increased with increasing top zone temperature. For a top zone temperature of 400°C (752°F) the coke content was 21.8 wt% while at a top zone temperature of 475°C (887°F), a coke content of 26.6 wt% was reported. This indicated that even though the top bed hydrotreated some of the coke precursors, the feed to the second stage was still high in polynuclear aromatic compounds.

Metal Deposition

EDAX analyses are only semi-quantitative, but they are helpful in determining the types of metals present and where the deposits concentrate. Table IX presents the average metal content of the top and lower zones for the major metals found (Fe, Ti, and Cr). The amount of Fe deposited was relatively independent of the top zone temperature. All runs showed about 27-32 area% Fe. The amount of Ti deposited, however, was dependent on the top zone temperature. Ti concentration increased from 0.8 area% to 7.4 area% for the temperature increase from 400°C (752°F) to 475°C (887°F). The increase in top zone temperature increased the HDM of the Ti organometallic compound. Tamm et al. (1981) hydro-treated Arabian heavy oil and found organometallic compounds to follow the Arrhenius law where increases in temperature exponentially increase HDM rates. No relationship between Cr deposition and top zone temperature was evident.

Appendix C contains the raw data from the EDAX analysis. All experimental runs showed that metals tended to deposit nearer the reactor entrances than at the middle or exit sections. Additionally, a thin crust of inorganic material was found on the catalyst pellets. The crust was thickest in the upper sections of the reactor zones. These observations are also consistent with those reported by Tamm et al. (1981).

Catalyst pellets were radially fractured and examined for metals in the center and near the edge. Fe, Ti, and Cr

TABLE IX
AVERAGE METAL DEPOSITION IN REACTOR ZONES

Run	Zone	Fe	Area Percent	
			Ti	Cr
TZA (400°C)	Upper	26.8	0.8	3.6
	Lower	9.8	3.5	0.6
TZB (425°C)	Upper	30.1	2.3	5.3
	Lower	10.2	1.9	0.4
TZC (450°C)	Upper	32.3	3.9	5.1
	Lower	9.5	2.6	0.2
TZD (475°C)	Upper	32.4	7.4	2.0
	Lower	11.9	6.0	0.1

were found near the pellet edge but only substantial amounts of Fe was found at the catalyst center. This indicates that diffusion of organometallic compounds to the catalyst interior was limited (probably due to blockage of pores by coke). Similar reports of metal deposition and location were reported by Bhan (1983) and Kang and Johanson (1976).

Surface Area and Pore Volume

Table X presents the surface areas and pore volumes of spent and regenerated catalysts for each run. All catalysts lost a considerable amount of surface area and pore volume but each run regained more than 80% of its original value after regeneration. Spent catalyst from the 400°C (752°F) and 425°C (797°F) runs showed similar decreases in surface area (about a 60% reduction) and pore volume (about a 73% reduction). Raising the top zone temperature to 450°C (842°F) and 475°C (887°F) caused severe decreases in surface area (91% reduction) and severe decreases in pore volume (89% reduction). The excessive reduction in catalysts properties was due to the increased amount of coke and metal deposition of TZC and TZD.

The surface areas and pore volumes of the lower zones showed the same trend as the top zones. Runs TZA and TZB had similar but greater surface areas and pore volumes than TZC and TZD. This difference can be attributed to coking since the coke content increased from 21.8 wt% (TZA) to 26.6 wt% (TZD). The top zone of TZD was severely deactivated so the feed to the lower zone was high in coke precursors.

TABLE X
SURFACE AREA AND PORE VOLUME FOR ALL RUNS

	Run	Spent		Regenerated	
		Surface Area ($\times 10^{-3} \text{ m}^2/\text{kg}$)	Pore Volume ($\times 10^{-3} \text{ cm}^3/\text{kg}$)	Surface Area ($\times 10^{-3} \text{ m}^2/\text{kg}$)	Pore Volume ($\times 10^{-3} \text{ cm}^3/\text{kg}$)
	Fresh	295.0	0.48	295.0	0.48
Top Zone	TZA (400°C)	115.3	0.11	285.4	0.47
(middle	TZB (425°C)	128.3	0.15	270.5	0.49
section)	TZC (450°C)	30.1	0.01	242.8	0.41
	TZD (475°C)	26.2	0.02	262.2	0.47
Lower Zone	TZA (400°C)	181.9	0.21	263.0	0.44
(upper	TZB (400°C)	187.5	0.16	287.3	0.49
middle	TZC (400°C)	96.7	0.08	287.9	0.48
section)	TZD (400°C)	60.2	0.04	293.6	0.46

The lower zone catalysts tended to regain more surface area and pore volume upon regeneration than the top zone catalysts. This supports the EDAX analysis showing that the top zones contained more deposited metals. Several researchers have reported catalysts to lose a considerable amount of surface area and pore volume when processing coal liquids (Stiegel et al., 1983; Kang and Johanson, 1976; Shibaoka et al., 1984;). These authors report coke deposits to be removed during combustion but deposited metals permanently poisoned the catalyst.

Bhan (1983) conducted a hydrotreating study using the same catalyst and feedstock as used in the present study. He reported surface area reductions to about $171 \times 10^{-3} \text{ m}^2/\text{kg}$ ($8.3 \times 10^5 \text{ ft}^2/\text{lb}$) and pore volume reductions to about $0.19 \times 10^{-3} \text{ cm}^3/\text{kg}$ ($3.0 \times 10^{-3} \text{ ft}^3/\text{lb}$) when operating at 400°C (752°F), 11.7 MPa (1,700 psig) and at 1.9 h. These numbers are fairly consistent with those reported in Table X for TZA (400°C [752°F]).

This section on catalyst sample analysis can be summarized as follows:

1. Catalyst coke content remained fairly constant for the top zone temperatures of $400\text{--}450^\circ\text{C}$ ($752\text{--}842^\circ\text{F}$). Increasing the temperature to 475°C (887°F) caused a marked increase in coking.
2. The amount of Fe deposited was independent of the top zone temperature. The amount of Ti increased with increasing temperature.

3. All catalysts lost a considerable amount of surface area and pore volume during hydrotreatment. More than 80% of the original surface areas and pore volumes were recovered upon regeneration.

Gas Sample Analysis

Gas samples taken at 24, 36, and 60 h on oil were analyzed for composition by a gas chromatograph. Table XI lists the compositions of the samples taken for each run. No apparent relationship can be found between top zone temperature and gas formation (chromatographic analysis was only semi-quantative). However, most of the gas formed was methane and propane with traces of ethane, normal-, and isobutane indicating severing of alkyl groups from the rings but not much breaking of the rings themselves.

Precision of Experimental Techniques

The experimental data reported in this study are affected by the performance of the reactor system and the precision of the liquid and catalyst sample analysis. One experimental run condition was duplicated to check the overall reproducibility of the study.

Reactor System Operation

The performance of the reactor system depended on four main components: liquid feed rate, gas feed rate, reactor pressure, and operating temperature. The liquid feed rate was held at $20 \text{ cm}^3/\text{h}$ ($5.3 \times 10^{-3} \text{ gal/h}$) by a Ruska positive

TABLE XI
GAS SAMPLE COMPOSITION

<u>NAME/h on oil</u>	Volume percent				
	<u>C₁</u>	<u>C₂</u>	<u>C₃</u>	<u>i-C₄</u>	<u>n-C₄</u>
TZA/30	9	6	85	-	-
/36	70	-	30	-	-
/60	36	2	60	-	2
TZB/24	16	17	62	2	3
/36	34	7	53	6	-
/60	46	3	49	-	-
TZC/24	74	12	14	-	-
/36	94	3	3	-	-
/60	100	-	-	-	-
TZD/24	45	13	33	2	7
/36	16	22	48	5	9
/60	21	19	57	3	-

displacement pump. Positive displacement pumps deliver smooth flow rates with almost no fluctuations. A check on the flow rate was made by collecting oil in a graduated cylinder for 3 h. For this time period, less than a 1.0 cm^3 ($3 \times 10^{-4} \text{ gal}$) deviation from 60.0 cm^3 ($1.5 \times 10^{-2} \text{ gal}$) was observed (accuracy was limited by the difficulty of reading less than 1.0 cm^3 [$3 \times 10^{-4} \text{ gal}$] differences in a graduated cylinder).

The hydrogen gas flow rate was held at $600 \text{ cm}^3/\text{h}$ ($2.1 \times 10^{-2} \text{ ft}^3/\text{h}$) by a micrometering valve. A high pressure flow meter was calibrated by observing flow through a 0-500 cm^3 (0-0.1 gal) bubble meter. A flow rate of $600 \text{ cm}^3/\text{h}$ ($2.1 \times 10^{-2} \text{ ft}^3/\text{gal}$) was maintained by throttling the metering valve until the desired flow meter reading was obtained. Occasional fluctuations varied between 200-800 cm^3/h ($0.7\text{-}2.8 \times 10^{-2} \text{ ft}^3/\text{h}$). Wan (1974) and Sooter (1975) reported negligible effect on hydrotreating when varying hydrogen flow rates between 89-1187 cm^3/h ($2.3\text{-}31.3 \times 10^{-2} \text{ gal/h}$). Thus, the occasional gas flow rate fluctuations in this study should have little or no effect on the hydrotreating data.

The reactor pressure was controlled by a "Mity-Mite" pressure regulator and was observed by a 0-20.6 MPa (0-3,000 psig) Heise gauge. System pressure was maintained at $10.3 \pm 0.14 \text{ MPa}$ ($1,500 \pm 20 \text{ psig}$).

The operating temperature of the reactor was maintained by temperature controllers and variacs. The interior and exterior reactor temperatures were reported by Omega J-type

(iron-constantan) thermocouples. Variations in top and lower zone temperatures were $\pm 1.8^{\circ}\text{C}$ (3.2°F) and $\pm 3.5^{\circ}\text{C}$ (6.3°F), standard deviation, respectively. The lower zone deviation was due to the top and bottom sections of the reactor being a few degrees lower than the middle section. This small deviation from isothermal reactor operation should have a negligible effect on the hydrotreating data.

Liquid Sample Analysis

Each liquid product sample was analyzed for elemental analysis three times with the average being the reported value. The nitrogen content of the samples varied between 0.11 wt% and 1.13 wt% with standard deviations of ± 0.01 wt% to ± 0.05 wt%. The hydrogen content of the samples varied between 7.3 wt% and 10.8 wt% with standard deviations of ± 0.06 wt% to ± 0.57 wt%. These deviations are consistent with those reported by Bhan (1983).

Liquid samples taken between 48-60 h on stream were vacuum distilled according to ASTM-1160 procedures. Due to the large amount of liquid required, these samples were only analyzed once. However, the feedstock was distilled three times. The normal boiling point curves for these the three runs never showed more than 3°C (5.4°F) deviation from each other.

Catalyst Analysis

Aged catalyst samples were analyzed for coke content by controlled combustion at $475 \pm 10^\circ\text{C}$ ($887 \pm 18^\circ\text{F}$). Coke contents ranged between 19.1 wt% and 41.5 wt%. One section of the lower zone of TZC was analyzed three times and found to have an average coke content of 25.8 wt% with a standard deviation of ± 1.6 wt%.

Surface area and pore volume of aged and regenerated catalyst samples were determined by a Quantachrome Porosimeter. Surface areas and pore volumes ranged between $23.2\text{--}295.0 \times 10^{-3} \text{ m}^2/\text{kg}$ ($1.1\text{--}14.6 \times 10^5 \text{ ft}^2/\text{lb}$) and $0.003\text{--}0.48 \times 10^{-3} \text{ cm}^3/\text{kg}$ ($4.8\text{--}770.0 \times 10^{-5} \text{ ft}^3/\text{lb}$). Fresh KF-153-S was analyzed three times with a reported surface area of $295.0 \pm 14.1 \times 10^{-3} \text{ m}^2/\text{kg}$ ($14.6 \pm 0.7 \times 10^5 \text{ ft}^2/\text{lb}$) and a pore volume of $0.475 \pm 0.007 \times 10^{-3} \text{ cm}^3/\text{kg}$ ($770.0 \pm 11 \times 10^{-5} \text{ ft}^3/\text{lb}$).

Reproducibility

A sixth run (TZF) was made to check the experimental reproducibility. This run was operated at a top zone temperature of 475°C (887°F) and was conducted with procedures identical to those of run TZD. Both runs showed similar plugging problems after about 30-48 h on stream. Also, both top zones contain large amounts of interstitial deposits which glued the catalyst pellets together.

Figure 9 shows the HDN activity of the duplicate runs. TZD and TZF showed similar HDN activity loss. Small devia-

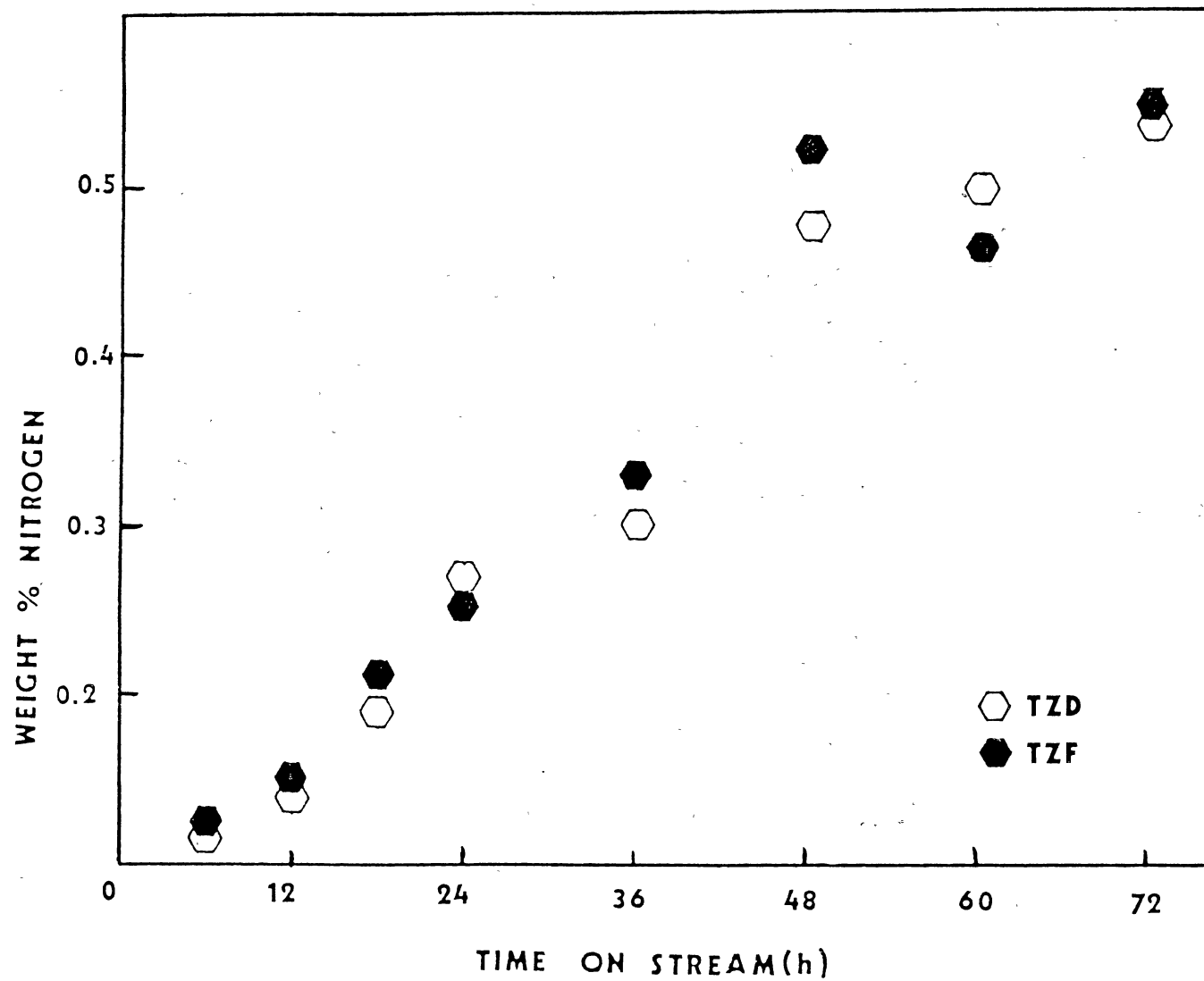


Figure 9. Runs TZD and TZF Time on Stream versus Nitrogen Content.

tions between the reported nitrogen contents can be attributed to non-ideal catalyst wetting and mass transfer caused by the interstitial deposits and are within analytical precision.

Table XII lists the liquid product hydrogen content as well as the interstage sample nitrogen and hydrogen contents. The product hydrogen contents of TZD and TZF were in good agreement and the wt% nitrogen and hydrogen of the interstage samples were fairly consistent. Again, the small difference in concentrations can be assumed to be due to the disruption of ideal flow by the interstitial deposits. Also, variations in the interstage sample data could have been caused by liquid hold-up in the microsampling device. A small amount of liquid hold-up could greatly affect the 2-3 cm³ interstage sample.

Table XIII lists the catalyst coke content of TZD and TZF. These runs were reported to have an average top zone coke content of 38.0 wt% and 38.9 wt% for a standard deviation of 0.6. The average lower zone coke contents were 26.6 wt% and 26.7 wt% with a standard deviation of 0.1.

Table XIV presents the surface area and pore volume of spent and regenerated catalyst samples. Run TZD and TZF showed similar reductions in surface area and pore volume. Also, both runs regained about the same amount of surface area and pore volume after regeneration.

The good agreement between HDN and hydrogenation activity, excellent agreement between coke contents, and

TABLE XII
 PRODUCT HYDROGEN CONTENT AND INTERSTAGE
 HYDROGEN AND NITROGEN CONTENT
 (wt%)

<u>Time on Stream (h)</u>	<u>Product Hydrogen</u>		<u>Interstage Hydrogen</u>		<u>Interstage Nitrogen</u>	
	<u>TZD</u>	<u>TZF</u>	<u>TZD</u>	<u>TZF</u>	<u>TZD</u>	<u>TZF</u>
6	10.6	10.6	8.7	8.2	0.77	0.87
12	10.8	10.7	8.3	7.9	0.81	0.85
18	10.2	10.6	8.1	8.7	0.94	0.85
24	10.2	9.8	8.1	7.4	1.00	0.99
30	9.9	10.2	8.1	8.7	1.01	1.00
36	9.7	9.8	8.0	7.8	1.02	0.98
48	9.5	9.3	7.8	7.8	1.09	1.20
60	9.7	9.4	8.3	7.6	1.06	1.03
72	9.3	9.2	7.8	7.8	1.10	1.14

TABLE XIII
CATALYST COKE CONTENT OF TZD AND TZF

<u>Section</u>	<u>TZD (475°C)</u>	<u>TZF (475°C)</u>
<u>TOP ZONE</u>		
Top	35.8	38.5
Middle	41.5	38.1
<u>Bottom</u>	<u>36.8</u>	<u>40.3</u>
Average	38.0	38.9
Standard Deviation	0.6	
<u>LOWER ZONE</u>		
Top	26.8	26.0
Upper Middle	25.5	26.2
Lower Middle	26.4	28.9
<u>Bottom</u>	<u>28.0</u>	<u>25.8</u>
Average	26.6	26.7
Standard Deviation	0.1	

TABLE XIV
SURFACE AREA AND PORE VOLUME OF TZD AND TZF

	Run	Spent		Regenerated	
		Surface Area ($\times 10^{-3} \text{ m}^2/\text{kg}$)	Pore Volume ($\times 10^{-3} \text{ cm}^3/\text{kg}$)	Surface Area ($\times 10^{-3} \text{ m}^2/\text{kg}$)	Pore Volume ($\times 10^{-3} \text{ cm}^3/\text{kg}$)
Top Zone (middle section)	TZD (475°C)	26.2	0.022	262.2	0.47
	TZF (475°C)	23.2	0.027	259.3	0.45
Lower Zone (upper middle section)	TZD (400°C)	60.2	0.04	293.6	0.46
	TZF (400°C)	48.7	0.01	297.5	0.47

excellent agreement between surface areas and pore volumes of TZD and TZF show that the experimental and analytical techniques are highly reproducible.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A two-stage trickle-bed reactor has been successfully used to study the effects of hydrotreating coal-derived liquids by temperature zoning. The following conclusions can be drawn from this study:

1. Excessive reactor plugging occurred when the top zone was operated at 500°C (932°F). Temperatures in this range caused large amounts of interstitial deposits and thus should be considered an upper limit in processing temperature for this feedstock.

2. All temperature zoning combinations showed a loss in catalyst activation over the experimental run duration of 72 h. Activity loss was rapid for the first 30-40 h and gradual for the remainder of the run. Activity loss was attributed to coke and metal deposition.

3. Increasing the top zone temperature from 400°C (752°F) to 450°C (842°F) had a beneficial effect on the catalyst HDN and hydrogenation activity. This increase in activity occurred without any severe increase in catalyst coke content. The temperature increase in this range

increased reaction kinetics without promoting excessive coke or interstitial deposition.

4. Increasing the top zone temperature to 475°C (887°F) had a detrimental effect on the catalyst HDN and hydrogenation activity. The increase in reactor temperature greatly increased the coke content and amount of interstitial deposits. The decrease in hydrotreating activity was attributed to the elevated temperature causing thermodynamically unfavorable equilibrium and the poor catalyst wetting due to interstitial and coke deposits.

5. As the top zone temperature was increased, the amount of light oil produced increased and the amount of heavy ends produced decreased. Also, this temperature increase showed a shift in the normal boiling point distribution signifying that more cracking and hydrocracking occurred as the temperature increased.

6. The amount of Fe deposited was independent of the top zone temperature while the amount of Ti deposited increased with increasing temperature.

7. All catalysts lost a considerable amount of surface area and pore volume upon hydrotreating. Reductions were severe for temperatures above 450°C (842°F). All catalysts recovered more than 80% of their original surface area and pore volume upon regeneration.

8. Hydrotreating coal liquids produces a gas consisting mainly of methane and propane with traces of ethane, and normal and iso-butane. No definite correlation between top zone temperature and composition of gas was evident.

In summary, operation of the top zone of a two-stage reactor in the range of 425-450°C (797-842°F) while maintaining the lower zone at 400°C (752°F) was beneficial. This combination of temperatures had many advantages over an isothermal operation at 400°C (752°F) including: increased HDN and HDM activity, better hydrogenation, and less heavy ends at no cost of increased coke content nor gas formation. However, unacceptably rapid catalyst deactivation was still a problem.

Recommendations

This study on hydrotreating coal liquids by temperature zoning produced the following recommendations:

1. The effects of temperature on hydrotreating coal liquids are still not fully understood. A study with a different type of reactor system (to avoid the problems of plugging and poor catalyst wetting) should further investigate temperature effects on coking and hydrogenation.
2. Rapid catalyst deactivation occurs during the first 30-60 h on stream. A study to minimize initial start-up deactivation needs to be conducted.
3. The effect of space time on hydrotreating by temperature zoning should be examined. Different percentages of catalyst loadings in each stage should be examined to assess its effect on hydrotreating by temperature zoning.
4. Metal deposition permanently poisons the catalyst. A study to investigate effective methods for metals removal needs to be conducted.

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APPENDIX A

LIST OF MAJOR EQUIPMENT AND CHEMICALS

The equipment and chemicals used were the same as those used by Bhan (1983) with the following exceptions:

Reactor System

1. Reactor - 316 stainless steel, seamless, 1.3 cm (0.5 in) diameter, 0.088 cm (0.035 in) wall thickness, heat treated, top zone was 42.5 cm (17 in), bottom zone was 45.0 cm (18 in).
2. Aluminum Heating Block - two blocks, each 10.0 cm (4 in) diameter, one 37.5 cm (15 in) long and one 40.0 cm (16 in) long.

Chemicals

1. Hydrogen - 99.5% purity, 15.7 MPa (2,300 psig) (Jimmie Jones Co., Stillwater, OK).
2. Nitrogen - 99.5% purity, 15.7 MPa (2,300 psig) (Jimmie Jones Co., Stillwater, OK).

APPENDIX B

DATA FROM EDAX ANALYSIS

Figures XV-XVIII list the data from EDAX analysis for runs TZA, TZA, TZB, TZC, and TZD.

TABLE XV
METAL DEPOSITION FROM RUN TZA

Location/Type	Area Percent							
	Al	S + Mo	Ca	Fe	Ti	Cr	Ni	Si
Upper zone top/surface	0.9	25.0	-	63.9	-	1.3	0.8	0.4
/center	1.1	44.2	-	49.2	-	4.9	-	0.7
/edge	35.6	40.7	1.5	16.9	0.9	3.0	1.8	1.5
Upper zone middle/surface	22.6	39.6	-	19.2	2.3	5.3	6.8	0.7
/center	2.2	34.5	-	51.7	-	10.1	1.9	0.5
/edge	40.7	36.7	1.2	9.7	1.2	4.9	4.2	1.3
Upper zone bottom/surface	36.4	38.6	-	13.5	2.5	3.3	4.3	1.3
/center	50.3	31.6	-	5.3	-	-	12.8	-
/edge	33.9	22.2	-	13.2	-	-	30.7	-
Lower zone top/surface	48.1	37.2	-	2.2	4.6	1.5	5.1	1.2
/center	44.8	35.2	1.3	2.5	4.0	1.0	8.3	0.5
/edge	53.3	31.3	1.3	3.2	4.1	-	6.0	0.8

TABLE XV (Continued)

Location/Type	Area Percent							
	Al	S + Mo	Ca	Fe	Ti	Cr	Ni	Si
Lower zone upper middle/surface	52.5	34.0	1.0	0.8	6.4	-	4.1	1.2
/center	10.6	17.1	-	53.8	-	-	4.6	1.6
/edge	53.0	33.9	-	3.3	1.3	-	6.3	1.1
Lower zone lower middle/surface	55.8	31.6	-	1.9	1.7	-	4.9	0.8
/center	28.6	27.9	1.4	8.6	19.9	1.3	12.6	0.3
/edge	47.3	34.1	0.5	3.3	6.4	0.6	6.9	0.8
Lower zone bottom/surface	32.7	29.7	-	10.6	13.6	2.8	10.1	0.4
/center	9.2	10.8	-	25.9	-	-	13.5	2.9
/edge	62.7	27.8	-	1.9	0.6	-	5.9	1.1

TABLE XVI
METAL DEPOSITION FROM RUN TZB

Location/Type	Area Percent							
	Al	S + Mo	Ca	Fe	Ti	Cr	Ni	Si
Upper zone top/surface	10.2	15.7	-	60.1	1.9	8.7	3.1	0.4
/center	1.1	50.0	3.4	41.2	-	2.3	1.2	0.8
/edge	38.2	43.1	-	12.7	0.2	3.7	-	2.1
Upper zone middle/surface	32.6	35.4	-	15.7	2.1	10.1	4.1	-
/center	3.2	39.8	5.7	20.6	0.3	4.3	25.6	0.5
/edge	30.7	12.0	-	50.7	5.1	-	-	1.5
Upper zone bottom/surface	34.4	23.8	-	18.7	8.9	13.3	-	0.9
/center	40.1	22.6	-	8.1	-	-	28.1	1.1
/edge	20.1	17.1	-	63.7	2.2	5.3	-	0.5
Lower zone top/surface	51.1	33.2	-	10.6	2.5	-	1.6	1.0
/center	14.7	18.3	1.3	44.1	-	-	20.4	1.2
/edge	27.8	54.8	-	0.8	1.7	1.5	12.5	0.8

TABLE XVI (Continued)

Location/Type	Area Percent							
	Al	S + Mo	Ca	Fe	Ti	Cr	Ni	Si
Lower zone upper middle/surface	55.3	16.6	1.4	7.4	4.6	1.7	12.1	0.9
/center	30.1	52.8	-	3.5	-	-	13.6	-
/edge	47.8	28.9	2.9	10.0	-	-	9.5	0.3
Lower zone lower middle/surface	48.6	7.6	-	40.1	1.8	0.6	-	1.3
/center	8.4	33.4	2.0	19.2	0.9	0.5	32.7	2.9
/edge	53.3	30.6	0.3	1.6	6.4	-	7.5	0.6
Lower zone bottom/surface	62.3	16.2	-	2.2	10.1	1.0	5.7	2.5
/center	15.3	67.6	-	2.5	-	-	11.2	3.4
/edge	47.9	41.9	-	4.6	0.5	0.3	4.8	-

TABLE XVII
METAL DEPOSITION FROM RUN TZC

Location/Type	Area Percent							
	Al	S + Mo	Ca	Fe	Ti	Cr	Ni	Si
Upper zone top/surface	27.0	35.6	2.6	11.8	7.6	9.7	4.4	1.2
/center	10.9	21.6	-	67.2	-	-	-	-
/edge	3.3	-	-	50.1	3.4	14.0	29.1	-
Upper zone middle/surface	48.9	33.9	3.3	1.9	4.3	1.0	5.3	1.2
/center	0.4	38.4	-	48.9	-	6.4	0.2	-
/edge	4.8	45.4	0.9	43.9	1.3	7.3	0.7	0.7
Upper zone bottom/surface	25.1	26.4	1.2	2.1	38.0	1.7	4.4	0.9
/center	15.5	13.7	-	56.8	-	-	14.0	-
/edge	30.9	29.1	1.6	8.4	18.5	5.8	3.7	2.1
Lower zone top/surface	33.3	38.6	-	15.1	8.1	-	-	4.9
/center	29.0	35.7	-	18.3	5.6	-	11.4	-
/edge	50.7	34.5	0.5	3.2	4.3	-	5.8	0.9

TABLE XVII (Continued)

Location/Type	Al	S + Mo	Ca	Fe	Area Ti	Percent Cr	Ni	Si
Lower zone upper middle/surface	49.3	34.9	0.5	4.3	4.2	0.4	5.0	1.2
/center	38.8	37.3	-	3.2	3.2	-	13.0	-
/edge	52.5	38.5	-	2.6	1.6	-	4.8	1.2
Lower zone lower middle/surface	48.6	32.5	-	4.7	1.8	1.6	9.9	0.7
/center	8.4	20.4	-	71.2	-	-	-	-
/edge	56.3	35.2	-	1.1	0.8	-	5.2	1.2
Lower zone bottom/surface	51.6	37.8	-	3.1	0.9	-	5.4	1.2
/center	15.1	21.3	-	54.8	-	-	6.2	2.5
/edge	53.9	32.6	-	3.5	1.3	-	7.5	1.0

TABLE XVIII
METAL DEPOSITION FROM RUN TZD

Location/Type	Area Percent							
	Al	S + Mo	Ca	Fe	Ti	Cr	Ni	Si
Upper zone top/surface	12.1	10.1	3.1	22.5	18.2	8.9	2.0	4.0
/center	10.7	36.0	-	20.3	18.0	3.7	-	11.1
/edge	37.7	32.8	2.8	9.0	12.3	2.3	2.8	8.9
Upper zone middle/surface	23.7	28.6	-	19.1	18.6	-	3.7	6.1
/center	13.3	32.0	-	47.5	-	-	-	7.2
/edge	7.5	17.6	-	18.1	-	-	51.8	5.0
Upper zone bottom/surface	28.1	23.3	2.2	10.2	27.0	2.5	2.4	4.3
/center	27.0	16.5	-	38.8	-	-	9.2	8.6
/edge	30.9	-	-	60.5	-	-	-	8.5
Lower zone top/surface	35.5	38.0	-	9.5	8.4	-	7.2	1.3
/center	11.9	10.8	-	57.0	-	-	20.2	-
/edge	33.8	30.3	-	19.1	5.8	-	11.0	-

TABLE XVIII (Continued)

Location/Type	Area Percent							
	Al	S + Mo	Ca	Fe	Ti	Cr	Ni	Si
Lower zone upper middle/surface	47.7	29.7	0.9	3.8	11.4	-	4.4	2.2
/center	25.1	-	-	74.9	-	-	-	-
/edge	24.1	26.1	-	10.0	11.4	-	26.8	-
Lower zone lower middle/surface	54.8	31.6	0.9	2.8	2.2	1.2	5.2	1.3
/center	32.6	29.8	-	14.4	14.1	-	8.4	0.7
/edge	32.5	30.6	1.0	11.8	13.1	-	8.8	1.0
Lower zone bottom/surface	54.8	32.9	-	3.5	2.4	-	4.2	2.2
/center	41.8	37.7	-	7.4	2.1	-	9.9	0.9
/edge	55.9	33.1	0.5	2.4	1.4	-	5.2	1.3

VITA¹

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