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ABSTRACT

Heavy gas oil - a 345 to 525°C fraction obtained from Great Canadian Oil Sands bitumen, was catalytically hydrotreated in a continuous trickle bed reactor between 300 to 450°C temperature and 600 to 1800 psig pressures. Liquid flow rates were varied from liquid hourly space velocities of 0.5 to 4.0. Effect of operating parameters on hydrodesulfurization (HDS),hydrodenitrogenation (HDN), hydrogenolysis and hydrogenation activities of three commercial catalysts (Co-Mo-alumina, Ni-Mo-alumina and Ni-W-alumina) were investigated.

Ni-W catalyst removed up to 97% of 3.27% sulfur originally present and also gave maximum hydrogenolysis and hydrogenation activities, where as Ni-Mo catalyst gave best results in HDN (up to 82% of 0.57% nitrogen present in heavy oil). This catalyst also gave rise to more aromatics. Co-Mo catalyst gave maximum paraffins and was also effective for both nitrogen and sulfur removal. Increase in temperature and pressure and reduction in liquid flow rates had very favourable effect on all catalyst activities.

Data obtained fitted best in first order reaction models and rate constants for HDS reactions obtained values of 2.08, 1.74 and 3.0 $hr.^{-1}$ where as, reactoin rates for HDN were found to be 0.86, 1.1 and 0.5 $hr.^{-1}$ for Co-Mo, Ni-Mo and Ni-W catalysts respectively. Performance of trickle bed reactor has also been discussed.

ACKNOWLEDGEMENTS

Author is indebted to his advisor, Dr.R.S.Mann for his guidance, inspiration, co-operation and great human understanding which has made this research possible and the results to shape up in form of the present thesis. Sincere gratitude is also expressed to Dr. D. McLean, Chairman and Dr.F.D.F.Talbot, Ex-chairman of Chemical Engineering Department, for facilities and financial help. Dr. K.C.Khulbe had been a great help during the course of this investigation, and the author is sincerely thankful to him for all his assistance.

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NOMENCLATURE

B_o	Bodenstein number, $(v D_p/D)$.
C	Reactant concentration.
C_A	Concentration of element A.
C_i, C_o	Inlet and outlet concentrations.
D	Diffusivity based on empty bed volume.
D_b	Bulk diffusivity.
D_{eff}	Effective diffusivity.
D_p	Catalyst pellet size.
D_t	Inside diameter of reactor tube.
h	Height of catalyst bed.
HDS	Hydrodesulfurization.
HDN	Hydrodenitrogenation.
k	Intrinsic reaction rate constant per unit surface area of catalyst.
k_n	First order rate constant for HDN reaction.
k_p	Adsorption co-efficient of diffusing molecule on catalyst surface.
k_s	First order rate constant for HDN reaction.
L.H.S.V.	Liquid hourly space velocity.
n	Order of reaction.
N_f	% by weight of nitrogen in feed.
N_p	% by weight of nitrogen in product.
r	Radius of diffusin molecule.
$\bar{r}$	Average pore size = $2(V_g/S_g)$.
r_A	Rate of reaction for component A.
R	Pore racius.

S_f % by weight of sulfur in feed.

S_g B.E.T. surface area of catalyst particles.

S_p % by weight of sulfur in product.

S_x External area of pellet.

v Superficial velocity of the fluid.

V_g Pore volume of catalyst per unit mass.

V_p Geometrical volume of catalyst pellet.

θ Catalyst porosity.

λ Constant defined as r/R.

Φ Thiele modulus.

Γ Tortuosity factor of catalyst.

1. INTRODUCTION

One source of energy to become important in the near future is recovery and upgrading of heavy oil. Processes for converting heavy crudes and residual fractions to clean liquid products are becoming more important to refiners. Crude slates are becoming heavier, while the product slates are becoming lighter. The production of heavy crude is required to partially fill the increasing gap between the world energy demand and availability of conventional crudes. The projected constant or decreasing demand for fuel oil, the traditional outlet for residual oils, will necessitate conversion of these materials to a best end use. Generally this means " Transportation Fuel ".

In the previous two decades , there was much emphasis on the use of commercially proven technology. From this, a pattern emerged for handling the heavy oil residua. Two schemes can be identified during these years as the most acceptable ones. One the use of fluid catalytic cracker (FCC) and delayed coking, that is, fluid catalytic cracking of virgin vacuum gas oil and coker gas oil combined with delayed coking of vacuum residue. The second was fluid catalytic cracking and visbreaking consisting of fluid catalytic cracking of virgin gas oil combined with single pass visbreaking of vacuum residue. Although the economic and environmental protection pressures in the 1970's were much stronger than ever before, the conservative thinking of

the times was reflected in the limited application of certain technologies which were already in existence and which would have contributed to an increased efficiency of crude residue processing.

When residuum hydroprocessing was first developed commercially in the late 1960s, there was a growing need, especially in Japan for low-sulfur oil (LSFO). The technology was largely distillate hydrotreating applied to residua to reduce sulfur. Metal poisoning of the catalyst was minimized by running at low severities with feeds of low metal content (Ni plus V). Feeds were largely atmospheric residua from light middle eastern crudes. Sulfur in product was about 1% by weight.

Throughout 1970's , more and more capacity for residuum desulfurization (RDS) was added in Japan and other countries. During 1970's, unique RDS catalysts were developed and applied to deeper desulfurization . Very deep desulfurization (less than 0.5 wt% sulfur) is currently practiced in a number of RDS units. Some conversion of residuum (production of lower molecular weight products) has also been realized through hydroprocessing.

Also the world market of crude oil supply has been slowly shifting towards heavier crudes. Quality of crude is expected to decline further as the high API gravity, low

sulfur crudes are depleted. Two big contributing factors are the efforts of Saudi-Arabia to shift from light to heavy crude production and the increased production of heavy crudes from Canada, Mexico and Venezuela. This has been putting new demands on refiners. Existing petroleum processes have to be modified to handle the heavier crudes. Also there need to be an added thrust towards development of technology to further process the increased quantum of heavy oils and residuum which will result from heavy crude processing.

Canada has an estimate of 250 billion bbl of heavy crude as Tar Sands (1). In fact estimated recoverable reserves of 550 billion bbl in Canada and Venezuela are comparable in size to the world's total recoverable reserves of conventional crudes which have been estimated at 670 billion bbl. It is because of this reason that Canada, more than any other country needs to give more emphasis on the development of technology to tap it's vast energy source.

These heavy crudes not only give rise to increased amount of heavy and residual oils but also these heavy oils and residuum pose tougher challenge for furhter processing. The heavy crudes contain higher levels of sulfur,nitrogen and harmful metallic impurities (especially V and Ni). During the processing,these impurities get concentrated in the heavy fractions, thus making further processing of these heavy fractions more complicated. Presence of traces

of elements like sulfur can impart objectionable characteristics to finished products leading to discoloration and/or lack of stability during storage. Sulfur increases the corrosion of plant and machinery. Metallic impurities in finished products give more ash formation which can be serious danger to machinery using that product. The presence of these objectionable elements and their effects are described in more details in the next few pages.

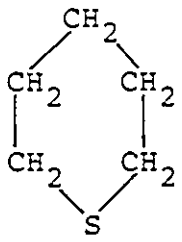
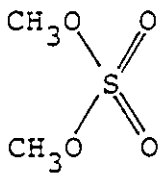
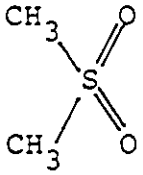
SULFUR COMPOUNDS :-

Sulfur compounds are most important of all nonhydrocarbon constituents of petroleum. During refining sequence, a great number of the sulfur compounds are concentrated in the residua and other heavier fractions. The nature of the sulfur compounds present is most important to understand for developing methods to get rid of sulfur. There are many varieties of sulfur compounds (Table-1), but the prevailing conditions during the formation, maturation and any in-situ alteration may dictate the only preferred types that exists in any particular crude oil.

Apart from the compounds listed in Table-1, free sulfur or dissolved hydrogen sulfide gas may also be present in some of the crudes. The elemental sulfur present gets evolved as hydrogen sulfide at about 150°C but it is the chemically bound sulfur that we are more concerned, as it does not easily get eliminated from the oil. Several sulfur

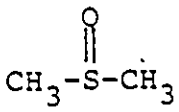
TABLE-1

Nomenclature and types of organic sulfur compounds

Types and examples	Names
Mercaptans :	
$H-S-CH_3$	Methyl mercaptan
$H-S-C_6H_5$	Phenyl mercaptan
Sulfides :	
$H-S-H$	Hydrogen sulfide
CH_3-S-CH_3	Dimethyl sulfide
$C_4H_9-S-C_4H_9$	Di-n-butyl sulfide
Disulfides :	
	Thiacyclohexane (Pentamethylene sulfide)
Alkyl sulfates :	
	Dimethyl sulfate
Sulfonic acids :	
	Methyl sulfonic acid

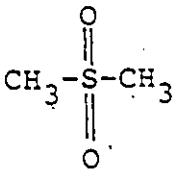
(Table-1 continued)

Sulfoxides :



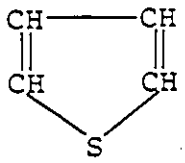
Dimethyl sulfoxide

Sulfones :

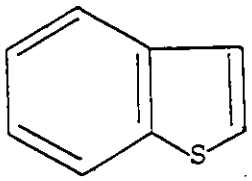


Dimethyl sulfone

Thiophenes :



Thiophene



Benzothiophene

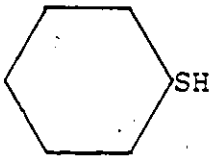
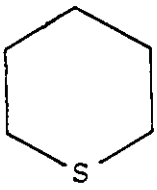
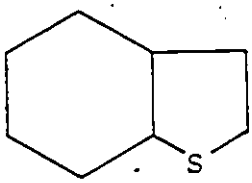
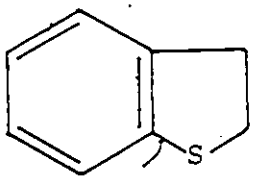
---

compounds present in oils have been identified. Some of those compounds are shown in Table-2.

The presence of sulfur compounds in finished petroleum products like gasoline will cause corrosion of engine parts, especially under winter conditions when water containing sulfur dioxide (from internal combustion) may collect in the crankcase.

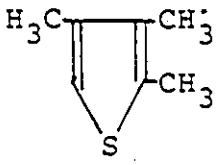
TABLE-2

Sulfur compounds identified in crude oils.

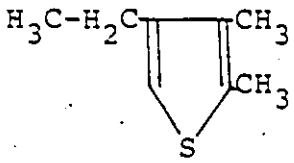
Type and examples	Names
Thiols :	
CH_3-CH_2-SH	Ethanethiol
	Cyclohexylthiol
Sulfides :	
$CH_3-CH_2-S-CH_2-CH_3$	Diethylsulfide (3-Thiapentane)
	Thiacyclohexane
	Thiahydrindane
	1-Thiaindane

(Table-2 continued)

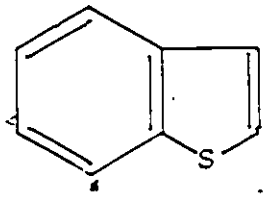
Thiophenes :



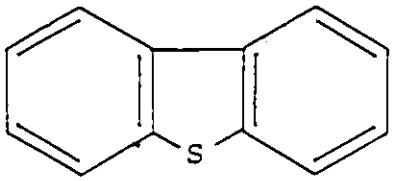
2,3,4-Trimethyl thiophene



2,3,Dimethyl-4-ethyl-thiophene



Benzyl thiophene



Dibenzothiophene

On the other hand, mercaptans cause corrosion of copper and brass in the presence of air and also have an adverse effect on the color stability of gasolines and other liquid fuels.

Free sulfur is also corrosive as are sulfides; and thiophenes which are detrimental to the octane number response to tetraethyl lead. Sulfur compounds are also detrimental to diesel fuels by increasing engine wear as well as contributing to the formation of engine deposits.

In lubricating oils, a high content of sulfur compounds, lowers resistance of oil to oxidation and increases deposition of solid material.A high content of sulfur can sometimes be tolerated in fuel oils, but current environmental regulations dictate that there should be little, if any, sulfur compounds present in the majority of fuels.

A typical distribution of sulfur originally present in crude, in to the various fractions of petroleum in a typical distillation sequence is shown in Table-3.

TABLE-3

Sulfur distribution in petroleum fractions.

Sulfur content of crude oil(wt%)	Sulfur in product (% of original sulfur in oil)			
	Naphtha (Gasoline)	Kerosene	Gas oil	Residuum
0.15	0.05	0.55	6.60	57.50
to	to	to	to	to
2.45	1.8	4.2	38.6	92.8

Generally it can be seen that the portion of sulfur will increase with the boiling point of the crude oil fraction, but if distillation is allowed to proceed at too high a temperature, thermal decomposition of the high moleculer weight sulfur compounds will ensue and, hence, the middle fractions will contain more sulfur than the higher boiling

fractions. The gas oil fractions may therefore contain even up to 60% of total sulfur present in the crude oils. Canadian Tar Sands bitumen is processed at higher temperatures than usual and therefore a substantial amount of original sulfur is present in the gas oil fractions.

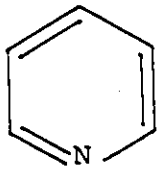
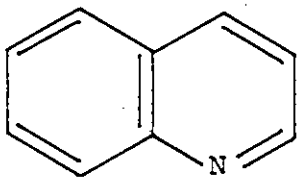
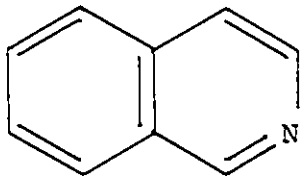
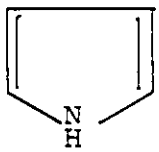
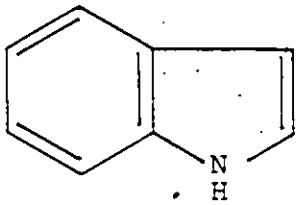
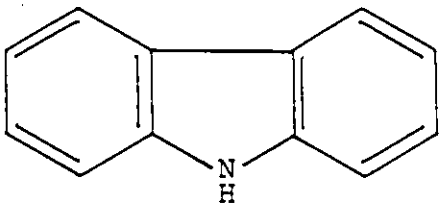
NITROGEN COMPOUNDS :

Nitrogen in petroleum is classified in two arbitrary classes - 'basic' and 'nonbasic'. Basic compounds having relatively low molecular weight can be extracted with dilute mineral acids, while equally strong bases of higher molecular weight remain unextracted because of unfavourable partition between the oil and aqueous phases. A method has been developed in which the nitrogen compounds are classified as basic or nonbasic, depending on whether they can be titrated with perchloric acid in a 50-50 solution of glacial acetic acid and benzene. Using this method it has been discovered that the ratio of basic to total nitrogen is approximately constant (0.30 ±0.5) irrespective of the source of the petroleum crude oil. Indeed, the ratio of basic to total nitrogen was found to be approximately constant throughout the entire range of distillate and residual fractions.

The basic nitrogen compounds (Table-4) which are composed of mainly pyridine homologs and occur throughout the boiling ranges, have decided tendency to exist in the higher boiling fractions and residua. The nonbasic nitrogen

TABLE-4

Nomenclature and types of common organic nitrogen compounds

	Pyridine
	Quinoline
	Iso-quinoline
	Pyrrole
	Indole
	Carbazole

compounds which are usually of pyrrole, indole and carbazole types, also occur in the higher boiling fractions and residua. Basic compounds extracted from distillates were found to consist of pyridines, quinolines and isoquinolines carrying alkyl substituents, as well as a few pyridines in which the substituent was cyclopentyl or cyclohexyl group.

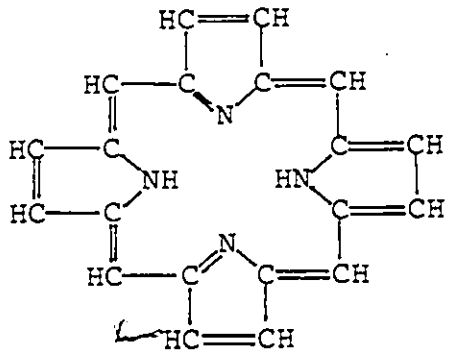
In general, the nitrogen content of petroleums is low and falls within the range 0.1 % to 0.9 % . Although early work indicates that some crudes may contain up to 2% nitrogen. However, crude oils with no detectable nitrogen or even trace amounts are not uncommon. But, in general, the more asphaltic the oil, the higher it's nitrogen content. There in fact, exists an approximate correlation between the nitrogen content and the carbon residue. The higher the carbon residue, the higher will be the nitrogen content.

The presence of nitrogen in petroleum is of much greater significance in refinery operations than might be expected from the small amounts present. Nitrogen compounds can be responsible for poisoning of cracking catalysts, and they also contribute to gum formation in such products as domestic fuel oil. The trend in recent years towards cutting deeper into the crude to obtain stocks for catalytic cracking has accentuated the harmful effects of the nitrogen compounds which are concentrated largely in to the higher boiling portions. Also the environmental protection regulations

are tightening the laws pertaining to NO_x emissions.

Porphyrins (nitrogen - metal complexes) are also constituents of petroleum and usually occur in nonbasic portion of the nitrogen compounds. Pyrrole, the chief constituent of the porphyrin molecule , is marked by high stability due to its aromatic character. As a result aromatization arising from the conjugated bond system,pyrrole is not strongly basic even though it is secondary amine. Pyrrole like other heterocyclic molecules, differs from homocyclic aromatic compounds in that it is quite reactive at the position alpha to the nitrogen atom and tend to form dimers, trimers and higher condensation products in which the fundamental pyrrole structure is preserved to a marked degree.

The simplest of porphyrins is porphine and consists of four pyrrole molecules joined by methine (-CH=) bridges as shown below :



PORPHINE

In porphines, the methine bridges astablish conjugated linkages between the component pyrrole nuclei forming a more extended resonance system. Although the resulting structure retains much of the inherent character of the pyrrole components, the larger conjugated system gives aromatic character to the porphine molecule. The reactivity of the pyrrole nuclei in porphine is greatly reduced, partially because the reactive alpha positions are occupied. These porphyrins are important in this discussion because of their complex structure which give rise to heteromolecules and because they form metal complexes. The most common metal complexes of porphyrins are those formed by replacement of two "nitrogen" hydrogens with a relatively small cation. Indeed, metal complexes of porphyrines are widespread in petroleum and its heavier fractions.

The presence of vanadium and nickel in oils, especially as metal porphyrin complexes, has focused much attention in the petroleum refining industry on the occurrence of these metals in feedstocks. It has been found that up to 40% of the total metal content of a feedstock may be existing as porphyrine complexes.

OXYGEN COMPOUNDS :

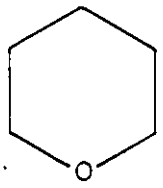
Oxygen in organic compounds can occur in variety of forms (Table-5) and it is not surprising that the more common

of the oxygen compounds occur in petroleum. The total oxygen content of petroleum is usually less than 2%, although larger amounts have been reported. But in case where the oxygen content is phenomenally high, it may be that the oil has suffered prolonged exposure to the atmosphere either during or after production. Oxygen content in various fractions of crude oil does increase with increase in boiling point, in the similar way as in case of sulfur and nitrogen. Oxygen is present mostly in the high molecular weight petroleum structures and thus , giving rise to higher oxygen contents (up to 8%) in heavy fractions. Structure of these heavy molecules is not well understood but that of lower molecular weight , the structures have been shown to contain carboxylic acids and phenols.

It has generally been concluded that carboxylic acids in petroleum with less than eight carbon atoms per molecule are almost entirely aliphatic in nature. Monocyclic acids begin at C_6 and predominate above C_{14}. This indicates that the structure of carbocyclic acids correspond with those of hydrocarbons with which they are associated in the crude oil. That is, in the range where paraffins are the prevailing type of hydrocarbon, the aliphatic acids may be expected to predominate; and similarly, in the ranges where the monocyclic paraffins and dicycloparaffins prevail, one can expect to find principally monocyclic and dicyclic acids, respectively.

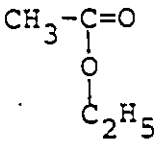
TABLE-5

Nomenclature and type of common organic oxygen compounds

Alcohols :	
CH_3-O-H	Methyl alcohol
C_6H_5-O-H	Phenyl alcohol
Ethers :	
CH_3-O-CH_3	Dimethyl ether
$C_6H_5-O-C_6H_5$	Diphenyl ether
Cyclic ethers :	
	Tetrahydropyran (Pentamethylene oxide)
Carboxylic acids :	
$CH_3-C(=O)-O-H$	Acetic acid
$C_6H_5-C(=O)-O-H$	Benzoic acid
Carboxylic acidanhydrides :	
$CH_3-C(=O)-O-C(=O)-CH_3$	Acetic anhydride

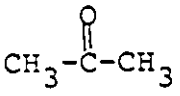
(Table-5 continued)

Carboxylic acid esters :



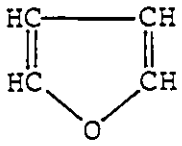
Ethyl acetate

Ketones :

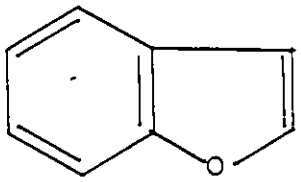


Dimethyl ketone

Furans :



Furan



Benzofuran

In addition to the carbocyclic acids and phenolic compounds, the presence of ketones, esters, ethers and anhydrides has been claimed for a variety of petroleums. However, the precise definition of these compounds is difficult as most of them occur in the non volatile, high molecular weight residua. They are claimed to be products of the air blowing of the residua, and their existance in virgin petroleum is not yet substantiated (6).

Oxygen compounds do not give any pollution problems, but their presence in finished products, generally, aid the deterioating effects which may be due to presence of other objectionable elements. Oxygen compounds are also corrosive (especially Naphthenic acids) and can promote gum formation as part of deterioration of the finished products.

METALLIC CONSTITUENTS :

The occurrence of metallic constituents in petroleum oils is of considerably greater interest to petroleum industry than might be expected from the very small amounts present. Even very minute amounts of iron, copper and especially nickel and vanadium in the charging stocks for catalytic cracking affect the activity of the catalyst and result in increased gas and coke formation and reduced yields of gasoline. In high temperature power generators, such as oil-fired gas turbines, the presence of metallic constituents, particularly vanadium in the fuel, may lead to ash deposits on the turbine blades, thus reducing clearances and disturbing balance and performance. More particularly, damage by corrosion and erosion may be very severe. The ash resulting from the combustion of fuels containing sodium and especially vanadium reacts with refractory linigs to lower their fusion points, and so cause their deterioration.

Thus, the ash residue after burning of the oil is due

to the presence of these metallic constituents. Part of these metallic constituents occur as inorganic water soluble salts (mainly chlorides and sulfates of sodium,potassium, magnesium and calcium) and these occur in the water phase of crude oil emulsions. These are removed in the desalting operation , either by evaporation of water phase and subsequent water washing or by breaking emulsion, thereby causing the original mineral content of crude to be substantially reduced. Other metals are present in the form of oil-soluble organometallic compounds either as complexes, metallic soaps, or in the form of colloidal suspensions, and the total ash from desalted crudes is of the order of 0.1 to 100 mg/litre.

Two groups of elements appear in significant concentrations in the original crude oil, associated with well defined types of compounds. Zinc, titanium, calcium and magnesium appear in the form of organometallic soaps with surface active properties, adsorbed in the water-oil interfaces, and act as emulsion stabilizers. However, vanadium, copper, nickel and part of the iron found in crude oils seem to be in a different class and are present as oil soluble compounds. These metals are capable of complexing with pyrrole pigment compounds derived from chlorophyl and homoglobin - which are certain to have been present in plant animal source materials. It is easy to surmise that the metals in question are present in such form, ending in the

ash content. Evidence for presence of several calcium and magnesium compounds have been produced in addition to vanadium,nickel,iron and copper (Table-6). Examination of the analysis of a number of crudes for iron,nickel, vanadium and copper indicates that a relatively high concentration of vanadium occurs which usually exceeds that of nickel.

Petroleum distillation concentrates the metallic constituents in heavier fractions and residua. Further processing of these heavier fraction may give rise to more concentrations of these metallic constituents even in the distillates, as there is always some volatalization of the organometallic compounds. But the majority of the vanadium,nickel,iron and copper in heavy fractions may be precipitated along with asphaltenes with n-pentane. This can reduce the concentration of especially vanadium by up to 95% with substantial reductions in the amounts of iron and nickel as well.

CHEMICAL STRUCTURE OF HEAVY OIL :

Inspite of numerous investigations, the determination of the actual molecular structure that exist in heavy oils and residua has proved to be difficult. It is no doubt, the great complexity of these materials, which are actually isolated by physical phenomena rather than by virtue of their chemical structures, which has hindered the formulation of individual molecular structures. Nevertheless, investigators

TABLE-6

Range of principal trace elements found in petroleum.

Elements	Range in petroleum (p.p.m.)
Cu	0.2 - 12.0
Ca	1.0 - 2.5
Mg	1.0 - 2.5
Ba	0.001 - 0.1
Sr	0.001 - 0.1
Zn	0.5 - 1.0
Hg	0.03 - 0.1
Ce	0.001 - 0.6
B	0.001 - 0.1
Al	0.5 - 1.0
Ga	0.001 - 0.1
Ti	0.001 - 0.4
Zr	0.001 - 0.4
Si	0.1 - 5.0
Sn	0.1 - 0.3
Pb	0.001 - 0.2
V	5.0 - 1500.0
Fe	0.04 - 120.0
Co	0.001 - 12.0
Ni	3.0 - 120.0

have discovered some significant facts about the structures that exist in heavy oils and residua. There are indications that the higher molecular weight components (the asphaltenes and resins) consist of condensed aromatic nuclei which carry alkyl and cycloalkyl (naphthenic) substituents; heteroatoms (i.e., sulfur, nitrogen and oxygen) are scattered throughout the hydrocarbon systems. In addition, it appears that with increasing molecular weight both aromaticity and proportion of the heteroatoms increase. There is also fragmentary evidence that, with increasing molecular weight the heteroatoms become incorporated into the more stable heterocyclic systems. This is especially true for sulfur where dibenzothiophene type systems are believed to predominate in the higher molecular weight asphaltics; it is presumed that similar arrangements also occur in cyclic systems or in various functional groups (6).

If, however, the heavy oil is produced by a process where thermal decomposition may have been initiated , there may be traces of thiols in the mix which would , along with any hydrogen sulfide that was generated during the process, impart an objectionable odour to heavy oil. The occurrence of thiols in heavy oils that have not been subjected to any thermal treatment is also possible but is generally not considered likely.

CHEMISTRY OF HYDROPROCESSING

Treatment of petroleum or any fraction of petroleum with hydrogen at elevated temperature, in the presence of a catalyst is called hydroprocessing or hydrotreating. Hydrotreating processes for the conversion of crude oil fractions or products may be classified as nondestructive and destructive . The destructive hydrotreatment can be imagined as one which is characterized by the cleavage of carbon to carbon linkage and is accompanied by hydrogen saturation of the fragments to produce lower boiling products. This generally need temperature in excess of 350°C. Whereas, non destructive hydrotreatment is more generally used for the purpose of improving product quality without any appreciable alteration of the boiling range. Mild processing conditions below 350°C are employed so that only more unstable materials are attacked. Thus sulfur, nitrogen and oxygen compounds liberate hydrogen sulfide, ammonia and water respectively and unsaturated materials are hydrogenated to produce the more stable hydrocarbons. Difficulties in sulfur or nitrogen removal increase in the order

paraffins < naphthenes < aromatics.

Some typical examples of various reactions that generally take place in a typical hydrotreating process are shown in Table-10.

TABLE-10

Typical hydrotreating reactions

A. Hydrodesulfurization (HDS) :

1.Mercaptans:

$$R\text{-}SH + H_2 \longrightarrow RH + H_2S$$

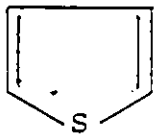
2.Disulfides:

$$R\text{-}SS\text{-}R' + 3H_2 \longrightarrow RH + R'H + 2H_2S$$

3.sulfides(aromatic,naphthenic and alkyl):

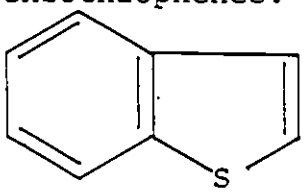
$$R\text{-}S\text{-}R' + 2H_2 \longrightarrow RH + R'H + H_2S$$

4.Thiophenes:

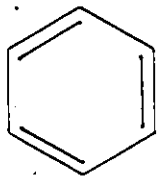


$$+ 4H_2 \longrightarrow CH_3CH_2CH_2CH_3 + H_2S$$

5.Benzothiophenes:

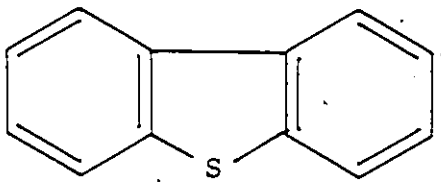


$$+ 3H_2 \longrightarrow$$

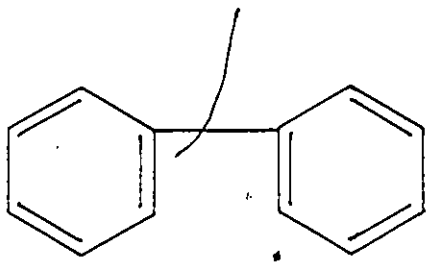


$$+ H_2S$$

6.Dibenzothiophenes:



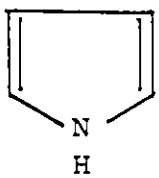
$$+ 2H_2 \longrightarrow$$



$$+H_2S$$

B. Hydrodenitrogenation (HDN) :

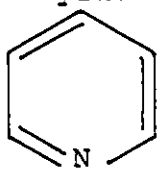
1.Pyrrole:



$$+ 4H_2 \longrightarrow CH_3CH_2CH_2CH_3 + NH_3$$

(Table-10 continued)

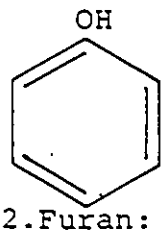
2.Pyridine:



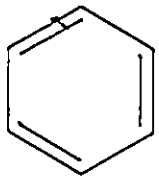
$$+ 5H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_3 + NH_3$$

C. Hydrodeoxygenation (HDS) :

1.Phenol:

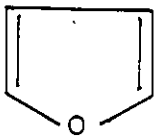


$$+ H_2 \longrightarrow$$



$$+ H_2O$$

2.Furan:



$$+ 4H_2 \longrightarrow CH_3CH_2CH_2CH_3 + H_2O$$

D. Hydrogenation :

$$CH_3CH_2CH_2CH{=}CH_2 + H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_3$$

E. Hydrocracking :

$$C_{10}H_{22} + H_2 \longrightarrow C_4H_{10} + C_6H_{14}$$

HEAVY OIL USED IN THIS INVESTIGATION :

Heavy oil which was used in this investigation, was a 650°F (345°C) to 975°F (524°C) heavy gas oil fraction from hydrocracking of Athabasca bitumen. The bitumen contains 51.5% by weight of pitch (material boiling above 524°C) and about 0.6% by weight of ash. Other properties of the bitumen are shown in Table-7 (2).

TABLE-7

Properties of bitumen of Great Canadian Tar Sands.

Specific gravity (60/60°F)	1.010
Sulfur (wt.%)	4.73
Ash (wt.%)	0.56
Viscosity (cst. at 210°F)	175.8
Conradson carbon residue (wt.%)	13.7
Pentane insoluble (wt.%)	15.6
Benzene insoluble (wt.%)	0.57
Nickel (p.p.m.)	68
Vanadium (p.p.m.)	211

Table-8 gives the distillation analysis of the Great Canadian Tar Sands bitumen.

The process of bitumen hydrotreating is quite complex and exact details are not available. However, from the available information , it is known that the bitumen is hydro-

cracked at temperatures of about 450°C with hydrogen pressure of around 2000 psig. Liquid hourly space velocities (L.H.S.V.) in the reactor are of the order of 1.0. Heavy fraction of the product oils are recycled to minimize the coke formation. Coke formation in the process reduces if ash content in the liquid feed increases and recycle heavy oil is used for the same reason. Upward flow ebulated bed type reactor is used . There is substantial reduction in concentration of sulfur, nitrogen as well as the metallic impurities during the thermal hydro-cracking of bitumen. The heavy gas oil derived from this process constitutes about 35% of the total liquid products.

TABLE-8

Distillation analysis of bitumen.

Equivalent distillation range at 1 atms. Temp. °C (°F)	Fraction (wt.%)	Cumu-lative (wt.%)	Sp.Gr. of fraction	Sulfur wt. % in fraction
IBP-200(IBP-392)	1.4	1.4	0.816	1.52
200-250(392-482)	2.2	3.6	0.856	1.02
250-333(482-632)	9.7	13.3	0.904	1.78
333-418(632-785)	17.7	31.0	0.955	2.98
418-524(785-975)	17.5	48.5	0.989	3.80
+524(+975)	51.5	100.0	1.073	6.39

The heavy oil was tested for its physical properties, elemental analysis and ASTM D-86 distillation (these tests

TABLE-9

Properties of Heavy Gas Oil.

Specific gravity	(60/60°F)	0.983
API gravity	(°API)	12.4
Viscosity (at 25°C)	(cp)	240
"	(cst)	244
Equivalent Saybolt Universal viscosity (100°F)	(sec.)	1128
Asphaltenes	(wt.%)	1.0
Aniline point	(°C)	47.2
Cetane index		26.8
Elemental analysis * :		
	C (wt.%)	85.77
	H (wt.%)	10.76
	N (wt.%)	0.57
	S (wt.%)	3.27
C/H ratio		0.67

ASTM D-86 Distillation analysis :

Distillate volume collected (wt%)	Temperature (°C)
IBP	296
5	327
10	337
20	349
30	357
40	361
50	361
60	369

* -Oxygen was not traceable.

are described in details in the analytical section). The results are tabulated in Table-9. Concentration of metallic constituents were not found as demetallization studies were not intended in this investigation.

AIM OF THIS STUDY

The following were a few of the aims of the present investigation :

(a) To catalytically hydrotreat the above mentioned heavy gas oil.

(b) Study the performance of the three most commonly used catalysts.

(c) Study the effect of operating parameters on hydrotreatment of heavy gas oil.

(d) And to evolve experimental as well as analytical schemes to achieve the goals of this investigation as well as for future work on synthetic fuels.

2. LITERATURE SURVEY

Gary (3) in his book has described the present practices in petroleum industry. As per this, the light atmospheric and vacuum gas oils are further processed in hydrocracker or catalytic cracker to produce gasoline, jet and diesel fuels. The heavier vacuum gas oil can also be used as feed stocks for lubricating oil processing units.

Wittington et al.(4) have also described the recent trends in processing schemes using fluid catalytic crackers, delayed coking and visbreaking methods. Some of these have already been mentioned in the introduction. A part of the discussion presented by Green et al. (5) is also an indication of statistics and recent trends in residual oil processing. They have also discussed pore size distribution effects on residuum desulfurization activity and demetallization activities of catalysts. These indicate that catalysts having micropores in the 100-200°A range would be best for desulfurization reactions. The catalyst deactivation appears to be due to metallic impurities (mainly vanadium and nickel). Sosnowski et al. (1) have given a scheme of upgrading the heavy crude oils in which hydrocracking is proposed for both hydrogenation and partial conversions of virgin gas oils to get controlled product slates.

Furimsky (7) has shown that removal of sulfur,

nitrogen and oxygen from heavy gas oil is affected by the chemical composition of supported molybdate catalysts. When cobalt and nickel are added to these catalysts, they have a promoting effect on the catalyst activity. However, the relative rates always follow the same trend; that is, the hydrodesulfurization (HDS) is the fastest , followed by hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). He used pure alumina supports without any catalytic metallic impregnations and reported that pure alumina did not show any HDS,HDN or HDO activity. In his work concentrations of molybdate on alumina are varried from 0 to 9% and some trials have been made by addition of up to 4.4% CoO and up to same amounts of NiO separately. Addition of these have shown that these metals act as promoters and they improve all the catalyst properties. In his experiments, temperature of 400°C , pressure of 2000 psig and L.H.S.V. of 2.0 were used . It has also been reported that the selectivity and activity of catalysts can also be controlled to some extent during the catalyst preparation.

Similar work has been reported by Parsons and Ternan (8). They have found that low concentrations of 2.2 to 3% of MoO_3 on γ-alumina have significant HDS activity but on the other hand , it can be seen from their work that HDN activity of this catalyst increases with increase in MoO_3 concentration up to 18%. This catalyst gave a sharp increase in cracking activity with concentration of MoO_3 up-

to 9% and the increase in cracking activity was lower after this point. They also studied the promoting effects of Ti,V, Cr,Mn,Fe,Co,Ni,Cu and Zn oxides on 2.2% MoO_3 on gama-alumina catalysts. It was found that Ni, as promoter , was best suited for enhancing HDN activity as well as to give better cracking results. Ni also substantially increased the HDS activity but with Co as promoter this increase was slightly more.Next to these two was Ti as promoter. Fe and Cu showed least promoter activity.Operating conditions used were similar to those used by Furimsky (i.e., 380 to 420°C temperature, 2000 psig pressure and L.H.S.V. of 2.0).

Similar studies were carried out by Frost et.al (9), Eberline et al.(10), Mirza et al.(11) and Ahuja et al. (12). Data from these studies show that reactions like HDS, HDN, hydrogenation and hydrogenolysis can be performed satisfactorily , mainly with the help of catalysts made of metallic sulfides from group VIII and VIB of the periodic table (mainly Co, Ni, Fe, Mo and W). Sulphides are usually made by sulfiding the respective oxides of these metals. Alumina , silica and alumina-silica have been reported as the support materials , with majority of investigators working with alumina supports. Generally a ratio of group VIII metal to group VIB metal in the range of 0.25 to 0.33 is found to be most suitable for such applications.

Hass (13) tried 27 different commercial catalysts

for catalytic hydrotreatment of Pittsburg and Midway Company's Solvent Refined Coal. He also used about 28 catalysts which were locally prepared by using different alumina-silica supports. He found that Co-Mo on alumina catalyst, out of all commercial catalysts, performed the best for HDS as well as HDN . In the locally prepared catalysts he used different concentrations of Ni,Co,Mo,W and Cr metal oxides. All the catalysts were sulfided before use and a trickle bed reactor was used. Out of all the catalysts tested, catalyst containing 0.26% NiO,1.15% CoO and 13.1% MoO_3 on alumina-silica support gave best HDN results. The catalyst having 0.2% NiO, 1.1% CoO and 15.5% MoO_3 and alumina-silica support gave best HDS results.

Some of the publications referred to earlier deal with the fitting of kinetic equations to describe the catalytic activities with respect to one of the elements. Some of the data do appear to fit quite close in to the proposed mathematical correlations. However, such equations can not be generalized to cover other aspects of the same catalyst or to cover the same aspect with different liquid feed stocks. Such equations, therefore, can only find a very limited use.

TRICKLE BED REACTORS :

Trickle bed reactors are fixed catalyst bed reactors where liquid flows down over the catalyst particles and gas

can either flow co-current or counter-current to the liquid. The counter current flow gives better distribution of liquid than co-current flow, but liquid handling rates are limited by flooding conditions. This type of reactors are in use in modern refinery in variety of sizes and shapes. Liquid hourly space velocities (L.H.S.V. = volume of liquid feed/ (volume of catalyst X hours)) in the range of 0.5 to 10 are commonly used for various purposes. Trickle bed reactors have one big advantage over the fluidized or ebulated bed reactors, that their operation is very simple.

One topic that is still under discussion is the effect of the ratios of reactor diameter to catalyst particle size. Porter et.al. (14) report that in bench-scale trickle-bed reactors, liquid migrates to the wall and the fraction flowing down the wall increases to a steady state value at about one foot down the bed. These steady state wall fractions correspond to as much as 30 to 60% of total liquid flow rates at ratios of reactor diameter to particle diameter of as high as 10. In this particular investigation a ratio of $\simeq 7$ was used. Also the catalyst particles are mixed with inert particles in ratio of 1:1. This allows more area for gas -liquid film transport so that gas could get diffused in to the liquid phase before it actually reaches the active sites of catalyst particles.

3. EXPERIMENTAL

APPARATUS :

Schematic diagram of the apparatus used in this study is shown in Fig.1. It consisted of a trickle bed reactor , reactor heater, temperature controller, metering pump, feed reservoir, catchpots , back pressure regulator and other accessories. The reactor was a stainless steel type 316 tube, 25.4 mm O.D., 17.5 mm I.D. and 450 mm long (Cat.No. SF 1000 CX) of Autoclave Engineers. 1/4" swagelok fitting were welded to both end adapter fittings. Heater was a 480 watts longitudinal heating elements embedded in split cylinderical ceramic enclosures. Both halves were backed up by six inches of ceramic wool insulation. These two halves of cylinderical insulation and heater assembly were hinged together at one end so that when folded , the heater surrounded the reactor tube.

Heavy oil feed reservoir was a one litre size measuring cylinder with an outlet at its bottom . This was connected to the inlet of a metering pump. The metering pump was a Milton Roy company, plunger type pump, model no.396-31 and had a manual adjustment of flow from 16 to 160 C.C./Hr. and could pump up to a maximum of 5000 psig pressure.

The outlet of the metering pump was connected to one

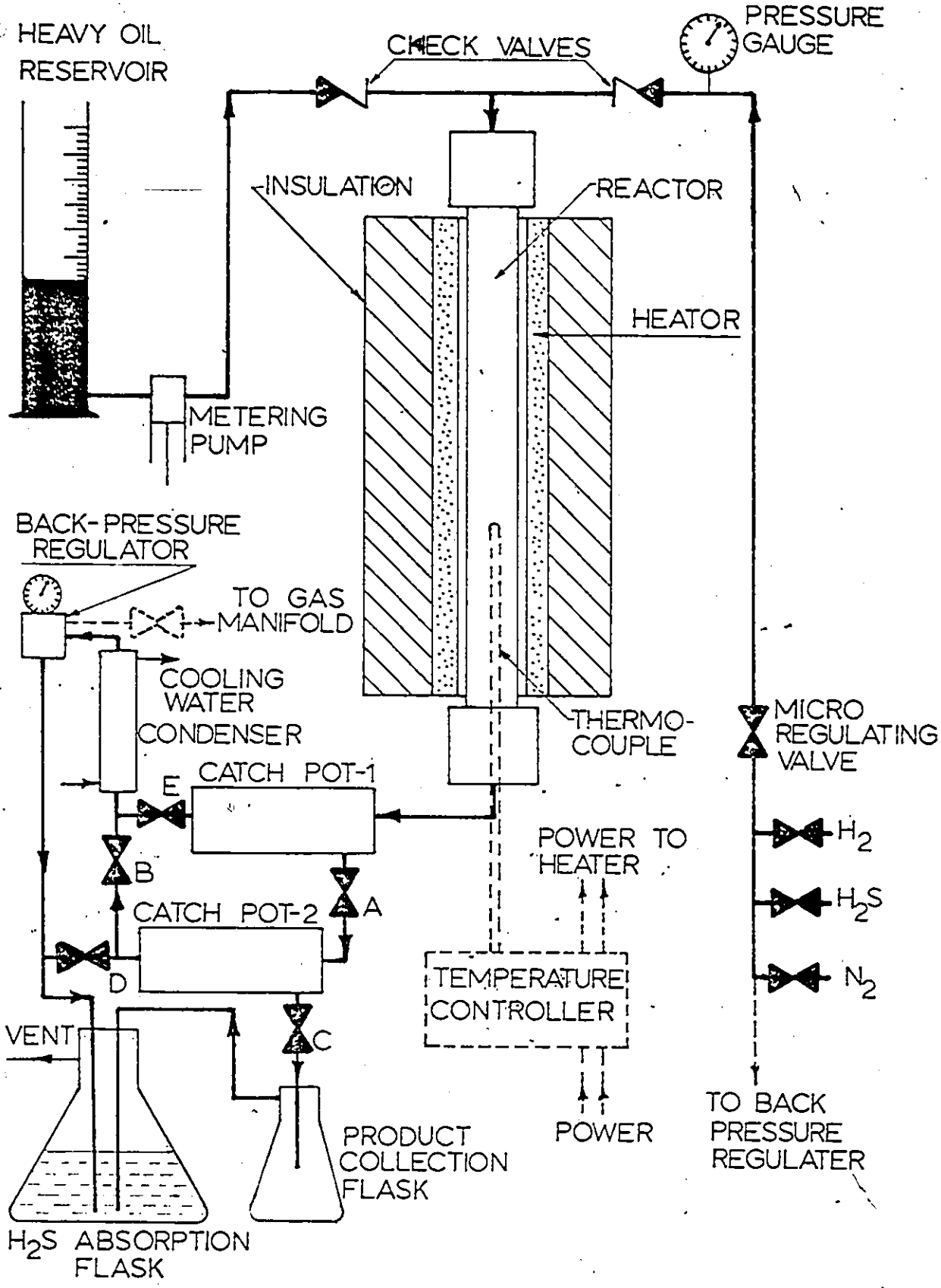


FIG.1 SCHEMATIC OF HYDROTREATMENT SYSTEM.

side of a T-joint on the top end of the reactor tube through a one way check valve. The gas manifold was connected to the other end of the T-joint . Another one way check valve was placed in the gas line before the T-joint . A 6" dial Matheson company's precision pressure gauge with all parts coming in contact of gas made of stainless steel, was placed on that gas line, to monitor the system pressure. Hydrogen , Nitrogen and Hydrogen sulfide cylinders were connected to the gas manifold with their respective pressure reducing valves. Flow of gas was regulated with the help of a microregulating valve.

Another T-connection was connected to the bottom end of the reactor tube. A Thermoelectric company's iron-constanton thetmocouple was inserted through the T-connection so as to get the tip of the thermocouple in the middle of the catalyst zone of the reactor tube. This thermocouple was connected across Honeywell R7350A temperature controller. Power to the heater element of the reactor heater was controlled by this temperature controller to keep the reactor at the desired temperature.

The outlet from the T-connection at bottom end of reactor was connected to two liquid catchpots of 800 C.C. capacity each. The purpose of these catchpots was the separation of the liquid from gases and to enable sample withdrawl without disturbing the reaction system. The

effluent gases were cooled in a vertical condensor to remove all low boiling components which might otherwise would have escaped. The outlet of condensor is connected to the Back-pressure regulator, model S-91XW of m/s Grove Valve and Regulator Company . This regulator holds the desired pressure inside the system and allows the effluent gases to escape . It needs a pressure signal of same pressure as that desired inside the system . Therefore, a separate 1/8 " tube was connected with a valve, between back-pressure regulator and the gas manifold. (Refer Appendix-B for more details)

The effluent gases coming out of back pressure regulator as well as the gases escaping during the sample collection in the sample collection flask, were passed through a H_2S absorption flask. This was done to remove H_2S gas from the effluent gas stream before venting it to the atmosphere. The whole apparatus was installed inside a fume hood so as to prevent obnoxious smell of H_2S from spreading out.

CATALYSTS :

Three commercial catalysts of Harshaw company were used in this study. They were Co-Mo on Alumina (Harshaw no: 400), Ni-Mo on Alumina (Harshow no.100) and Ni-W on alumina (Harshow no.4303). Detailed description of these catalysts is given in Table-11.

As already discussed earlier, it was decided to dilute

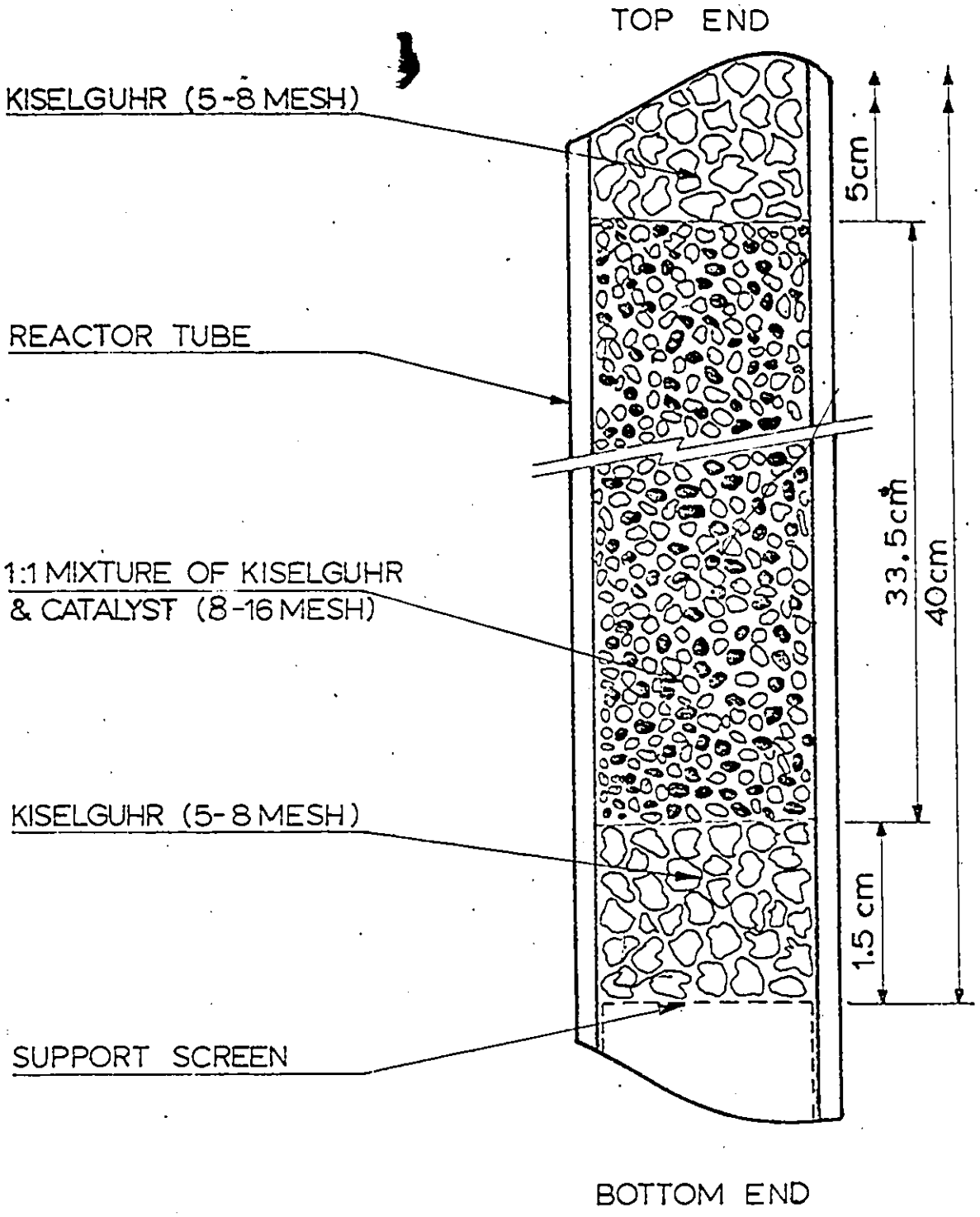


Fig. 2 CATALYST FILLING

TABLE-11

Specification of catalysts used.

Harshow No.	Description	Surface area M^2/gm	Pore volume ml./gm	Av. pore size °A
400	1/8" extrusions, 3%CoO, 15%MoO_3 on alumina.	220	0.5	91.0
100	1/8" extrusions, 3.8%NiO, 16.8%MoO_3 on alumina.	190	0.54	113.6
4303	1/16" extrusions, 6%NiO, 19%WO_3 on alumina.	152	0.54	142.2

the catalysts with the inert material in 1:1 proportion. Kiselguhr was used as inert material. Catalyst and Kiselguhr were packed in reactor tube as shown in Fig.2. A stainless steal 30 mesh screen was placed at around five centimeters from bottom end of reactor tube. On the top of this , 1.5 cm layer of coarse kiselguhr particles of 5-8 mesh size were placed. It was followed by 33.5 cms of 1:1 mixture of catalyst and kiselguhr particles of 8-16 mesh size. 5 cms of coarse kiselguhr particles of 5-8 mesh were packed in the top part of the catalyst bed. This top layer of particles was placed to act as a preheating zone.

Each catalyst bed was sulfided before using the catalyst beds for actual hydrotreatment runs. The sulfiding procedure is described in the Operating Procedures.

ANALYSIS OF PRODUCTS :

Original heavy oil as well as the product oil samples were tested for their physical properties - density and viscosity, elemental analysis - percentage by weight of C,H, N and S, ASTM D-86 distillation analysis, Aniline point, Cetane index and Diesel index. Gas chromatography, Infra-red spectroscopy and silica gel column separation were also performed on some of the samples.

Specific gravity bottle was used to measure the density of samples. To get accurate volume of specific gravity bottle mercury was cleaned and weighed in that bottle. Density values were converted to °API values using regular petroleum tables. Viscosity of oil samples was measured with the help of a Brookfield Syncro-electric viscometer model LV with a UL adapter. For most of the samples the UL adapter was used for better accuracies. But for some samples of higher viscosities , like original heavy oil, UL adapter could not be used. Therefore, the regular spindles were used by putting the oil in a 600ml beaker. Kinematic viscosity was calculated using these viscosity and density values and ASTM D-2161 conversion tables were used to convert the kinematic viscosity values to Saybolt Universal viscosity values.

Elemental analysis was done by Perkin Elmer model 240B

elemental analyzer. The equipment was first calibrated for C,H and N analysis and all samples were tested. Then the necessary changes were made for sulfur analysis by putting appropriate chemical packings in the quartz tubes. Sulfur analysis was done for all samples after the equipment was calibrated for sulfur with sample of known sulfur content.

Aniline point was measured as per ASTM D-611 method. Apparatus was fabricated locally using details given in ASTM specifications. Aniline was dreid overnight by putting sodium hydroxide pellets in aniline bottle and shaking the contents thoroughly. Then aniline was distilled under vacuum in rotavapour equipment. First and last ten percent of aniline was discarded. The purified aniline was sealed in a clean and dry bottle and was kept under nitrogen atmosphere all the time. Ten ml. of aniline and ten ml. of oil samples were used for each test and the aniline points were noted in °C.

ASTM D-86 distillation was performed on each sample including original heavy oil. Standard apparatus made by Precision Scientific Company,Chicago was used . The apparatus is built as per ASTM E-133 specifications. All accessories such as distillation flasks, measuring cylinders and thermometers were used strictly as per above mentioned specifications. 100 ml. of sample was used for each test and boiling points were noted in °C for every 10 ml. of distillate

collected.

Cetane index was estimated using ASTM D-976 method. Mid range boiling points were taken from above mentioned ASTM distillation. Aniline point values as estimated by standard method described earlier were used in this method. This procedure of estimation of cetane index is not recommended for petroleum liquids other than derived from natural petroleum base. But it was decided to use the same method for this study as there was no other method available. Also ,the results were intended to be used in comparison of qualities of different liquid samples rather than quantifying the absolute values of this particular property.

Cetane index calculations were carried out with help of following expressions :

$$\text{Cetane index} = 0.49083 + 1.06577(x) - 0.0010552(x)^2$$

where $x = 97.833(\log \text{mid-range boiling point, °F})^2 + 2.2088(\text{°API})(\log \text{mid-boiling point, °F}) + 0.01247(\text{°API})^2 - 423.51(\log \text{mid-range boiling, °F}) - 4.7808(\text{°API}) + 419.59.$

Diesel index values were calculated using °API values and aniline point values,using the following expression:

$$\text{Diesel index} = \frac{\text{°API} \times \text{Aniline point (°F)}}{100}$$

Gas chromatographic analysis was performed using Hewlett-Packard model No.5700A gas chromatograph. Two different columns were used in gas chromatographic studies for these oil samples. 5 ft. long and 1/8 inch O.D. column, packed with 1.5% V-101 on 100-120 mesh chromosorb-G was used for the high boiling components. Where as components of the oil samples having boiling points below 150°C were best resolved by 1.5 M long and 0.33 cm O.D. , OPN/Porasil-C column. Thermal conductivity detector was used in both cases. Temperatures of detector, injection port and auxillary systems was kept at 250°C. The oven temperature was programmed to stay at 80°C for first two minutes after injection, and then reach a maximum of 250°C at a steady rate of 4°C/minute, for V-101 column which was used for high boiling components. For OPN/Porasil-C column , oven temperature programming of 60°C for first two minutes and then to reach a maximum of 130°C at a steady rate of 4°C/minute and detector, injection port and auxillary temperatures of 150°C were used. Helium flow rates of 25 ml./hour were used for both columns and 2 microlitre quantity of oil sample was injected each time.

With OPN/Porasil-C column many of components showing on the chromatogram were identified by injecting small amounts of known pure chemicals with the oil samples. About seventy five pure chemicals,which were expected to be present, were tried and out of them twenty compounds did correspond to the peaks of chromatographs obtained with oil samples.

Infra-red spectra of a few samples was taken on Perkin-Elmer model 267 Infra-red spectroscope. 0.5% by wt. solution of each liquid sample was made in carbon tetrachloride (spectroscopic grade). 0.2 mm thick calcium flouride cells were used for both samples and reference liquids. Pure carbon tetrachloride was used as the reference liquid. Spectra were taken with Infra-red wavenumbers from 4000 to 800(cm^{-1}).

Different fractions from heavy oil and product oil samples were separated by silica-gel column . 22 mm I.D. and 500 mm long glass column was used. Baker grade 60-200 mesh size silica-gel particles were used. Silica-gel was prepared in a separating funnel in pentane. Glass column was cleaned and dried before use. A glass wool plug was placed at the bottom end and then the column was filled with silica gel slurry. At top end another 1cm layer of glass wool was packed. Care was taken that the whole column, thus prepared, did not have any air bubble and was always kept full of liquid. A weighed amount of asphaltene free oil (approx. 20 ml.) was dissolved in toluene and was poured at top of the column.

First fraction was eluted with n-pentane. This fraction was a colourless oil fraction. Excess pentane was evaporated on a water bath and the liquid thus obtained was dried of pentane in rotavapor apparatus at 60°C under vacuum. The residue was wax type and was collected and weighed. The second fraction that came out after white oil was yellow in color and was designated as "yellow oil". This fraction was

also dried in rotavapor and was weighed. This fraction was like oil. The column was then eluted with mixture of n-pentane and chloroform. Dark brown coloured liquid was collected and evaporated in rotavapor . This fraction was very viscous and was designated as "Dark oil". Next fraction was "Chloroform resin" which was eluted with chloroform. The last one which was eluted with tetrahydrofuran was designated as "Tetrahdrofuran resin ". All these fractions were also evaporated in rotavapor and weighed.

OPERATING PROCEDURES :

Before starting the experiment the metering pump was calibrated at different pressures to check any flow rate variations at different pressures. The micro-regulating valve on gas line was also calibrated to achieve the gas flow rates of between 0.5 to 6.0 scf/hr. Experimental set up was checked for any leakage with help of soap solution at 2000 psig.

Each catalyst bed was sulfided before use. Mixture of 10% H_2S and 90% H_2 were passed through the reactor for 12 hours. The reactor temperature was kept at 350°C during sulfiding and after that, only H_2 gas was allowed to flow through the reactor for one hour at the same temperature. The reactor was then cooled.

The following sequence of steps were followed while starting and shutting the experiment and withdrawl of samples :

start of Experiment :

1. Fill heavy oil in feed reservoir.
2. Adjust pump setting and start pump.
3. Close valves C,D and E and keep A and B open.
4. 10 minutes after step 2 open valve on hydrogen cylinder and adjust pressure regulator for desired pressure and adjust micro-regulating valve for desired flow.
5. Fold the reactor heator around the reactor tube and set the required temperature on temperature controller. Start heating five minutes after gas starts bubbling through the H_2S absorption flask.
6. Draw all liquid collected (ref. Sample Withdrawl) in catch pot-2 one hour after the reactor attains set operating conditions.
7. Check liquid samples every 15 minutes after step 6 and stop these checks after consistant quality of samples observed.
8. Let the process run for sufficient time to get about 250 ml. of product oil.
9. Withdraw the sample and change operating conditions for next run and then go to step 6 or shut down the experiment.

Shut Down :

1. Put off reactor heater and open-up the heater assembly. Start reactor cooling by blowing compressed air.
2. When reactor cools to room temperature, close the hydrogen supply.
3. Open valve D slightly to bleed out all pressure inside the reactor system.
4. Shut the pump when pressure inside the system comes

to atmospheric.

5. Flush the whole system with N_2 gas.
6. Open the top end of reactor and flush the reactor and catch-pots with acetone till the system is clean.

Sample Withdrawl :

1. Open valve E and close valves A and B.
2. Just slightly open valve C to let liquid flow to collection flask at very slow rate.
3. Close valve C when all liquid is out of catch pot-2 and open valves A and B. Close valve E.

The above mentioned procedures took care of some of very important precautions that were taken in course of experiments. For example, liquid was never poured over dry hot catalyst particles. Catalyst particles were wetted with liquid before heating. Pump was started before pressurising the system so as to avoid any air-lock in pump.

Operating conditions were changed in the following sequence for all catalysts :

	Temperature (°C)	Pressure (psig)	L.H.S.V.
Temperature variation:	300,350, 400,450.	1000	2
Pressure variation :	450	600,1000 1400,1800.	2
Oil feed rate variation :	450	1000	0.5 to 4.0

4. RESULTS

The experimental data were obtained by means of an isothermal trickle bed reactor at temperatures 300 to 450°C and at pressures 600 to 1800 psig. Steady state was not only realized from the operating conditions but also from the product analysis. The effect of various variables, namely temperature, pressure and liquid feed rates on conversion and product distribution were investigated.

EFFECT OF TEMPERATURE :

Effect of temperature on the catalytic hydrotreatment of heavy oil was studied at 1000psig and between 300 and 450°C temperature. The flow rate of oil was kept between 82 to 87 ml./Hr. (L.H.S.V. of approx. 2) for all the three catalysts . Densities of product samples decreased with increase in temperature (Fig. 3). While Ni-W catalyst gave the lowest density , the decrease in densities was the least with Co-Mo catalyst. Another noticeable difference between the Co-Mo and other two catalysts was at temperature greater than 400 °C. In this range densities dropped at a much faster rate in case of Ni-W and Ni-Mo than in case of Co-Mo.

Viscosities of product oils also showed a similar trend. Increase in temperatures gave rise to lower viscosities

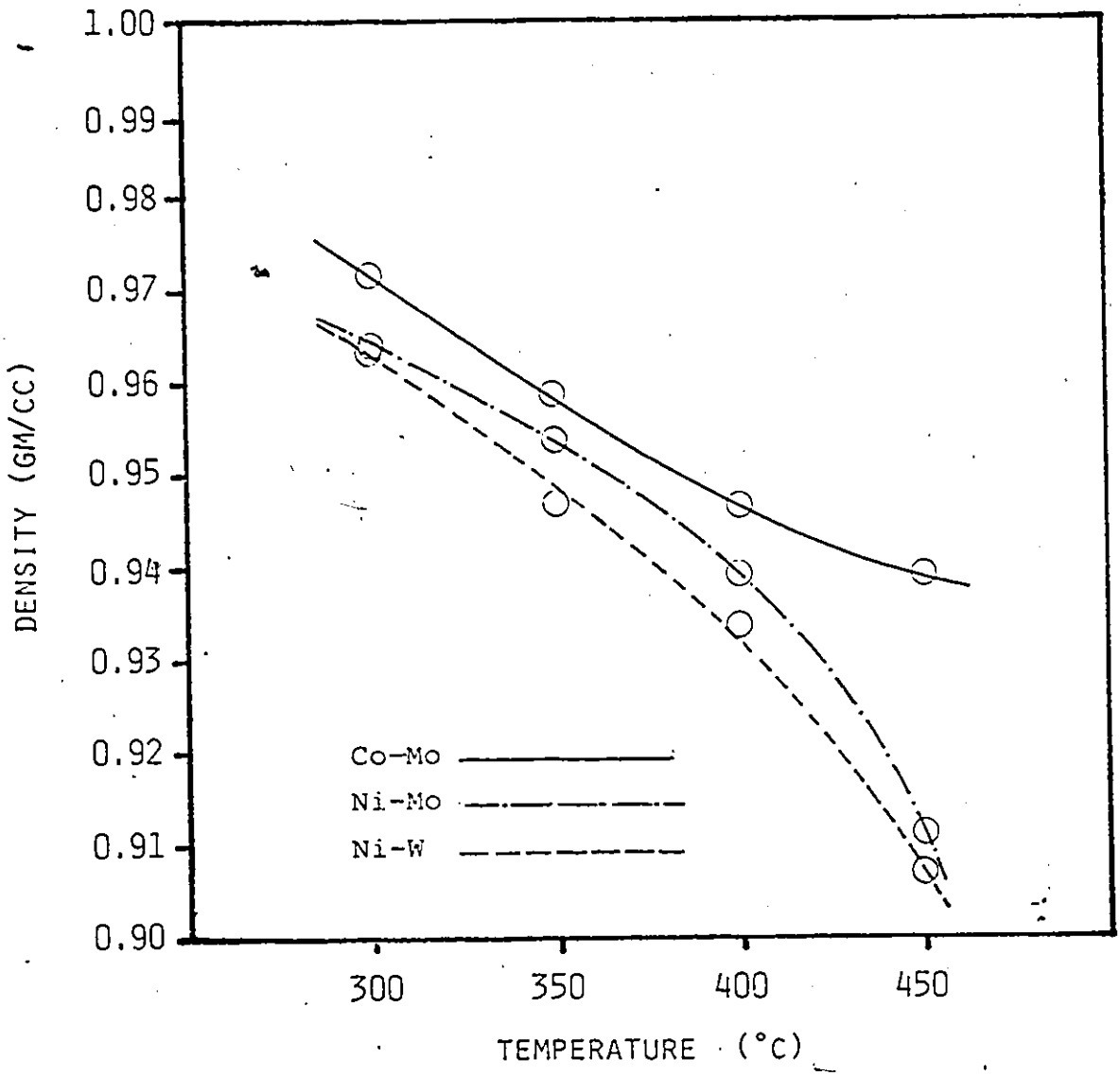


FIG.3 TEMPERATURE EFFECT ON DENSITY

(Fig. 4). Again Ni-W catalyst gave lowest viscosities except at low temperature of 300°C. At 300°C Co-Mo catalyst gave better results where as at temperatures higher than 300°C the viscosities of product oil derived from this catalyst were higher than with the other two catalysts. Also the rate of decrease in viscosities with increase in temperature was much more in case of Ni-W and Ni-Mo catalysts than that in case of Co-Mo catalyst.

Therefore hydrogenolysis of heteromolecules was more pronounced at higher temperatures. Ni-W catalyst showed the maximum hydrogenolysis activity at all temperatures where as Co-Mo showed the least activity out of the three catalysts. Ni-W catalyst was most sensitive to temperature changes and Co-Mo was least sensitive.

The effect of temperature on cetane index, C/H atomic ratio and aniline point of product liquid samples is shown in Figures 5,6 and 7 respectively. Cetane index values increased slightly with increase in temperature. Ni-W catalyst gave rise to products of maximum cetane index values (Fig.5) at all temperatures and Co-Mo catalyst gave the least cetane index values. However, increase in cetane index values with temperature was least pronounced in case Ni-W catalyst.

C/H atomic ratio (Fig.6) also decreased as the

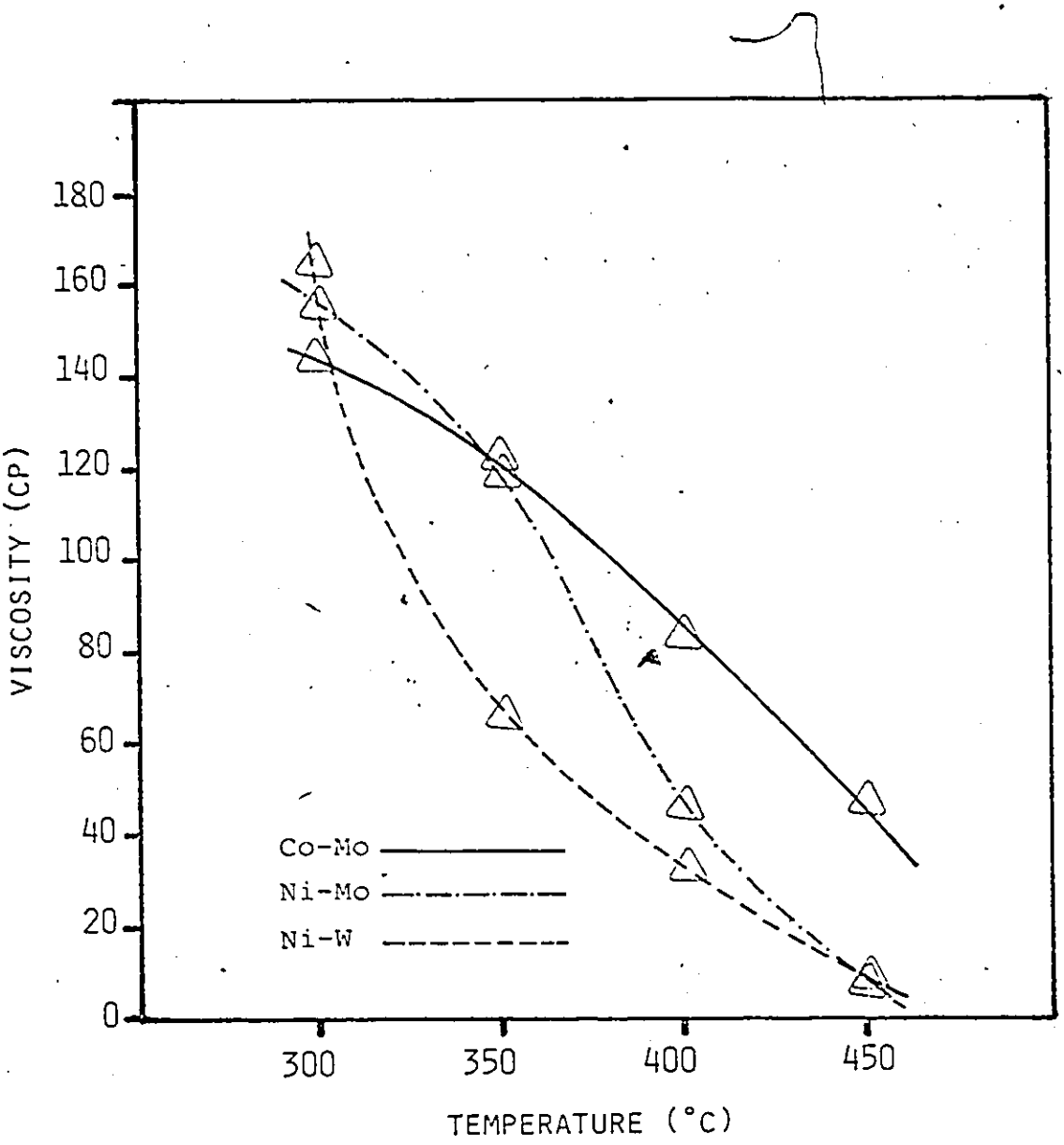


FIG.4 TEMPERATURE EFFECT ON VISCOSITY.

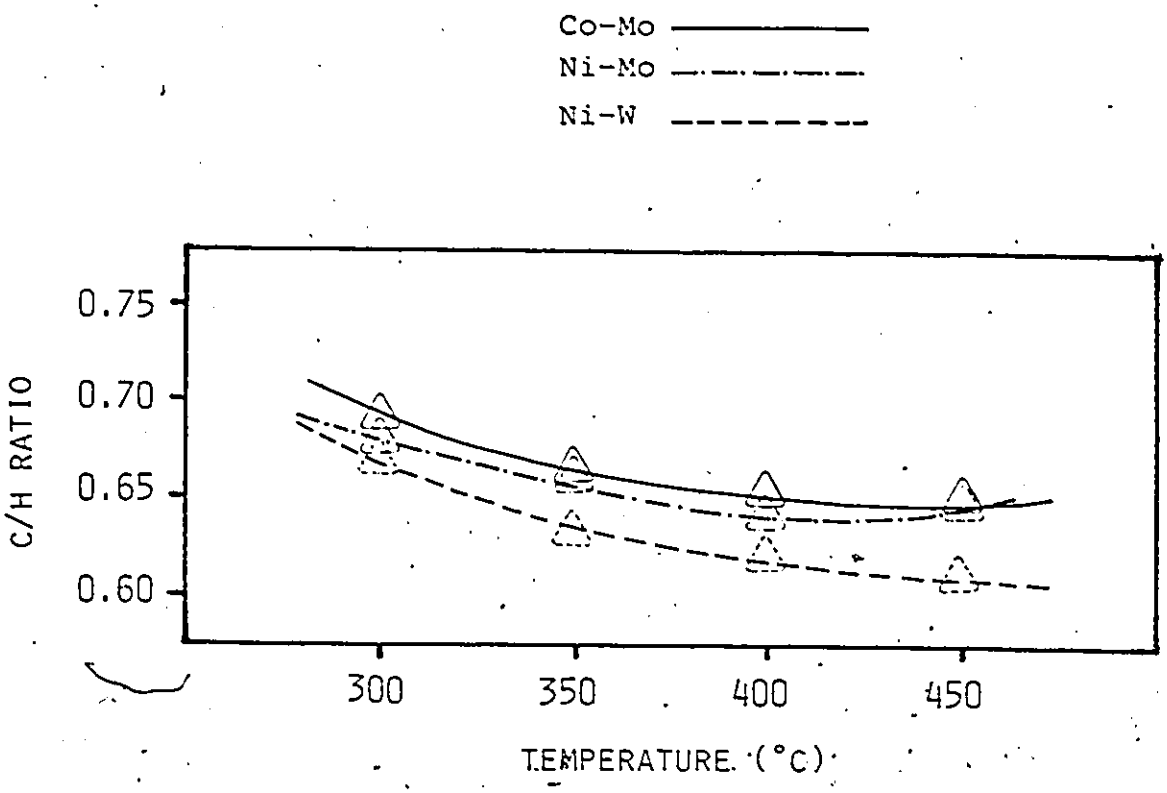


FIG.6 TEMPERATURE EFFECT ON C/H RATIO.

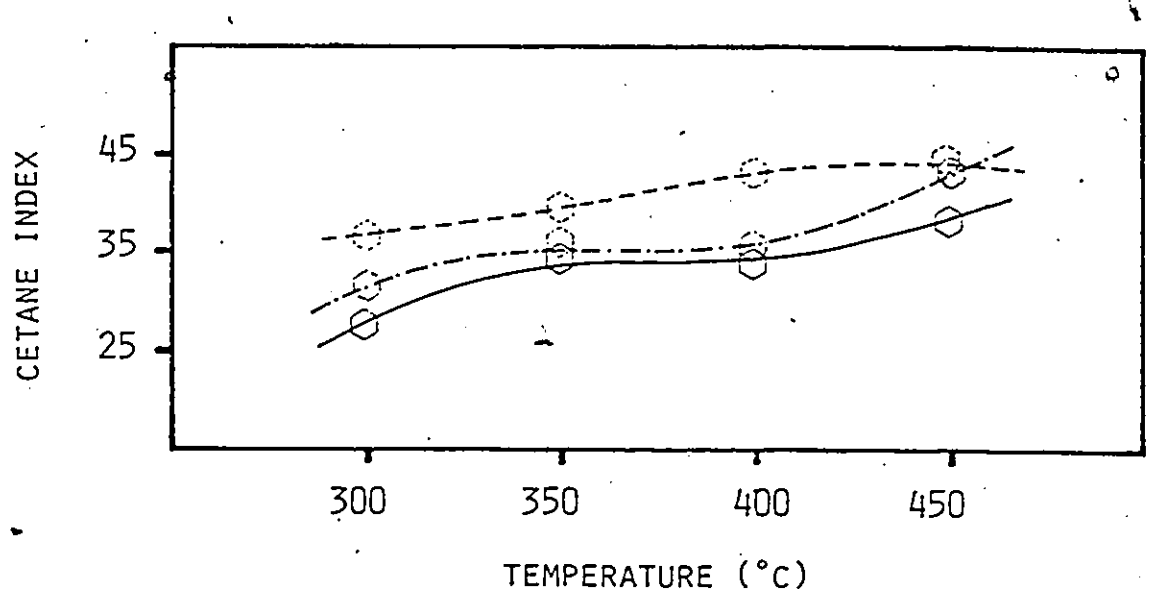


FIG.5 TEMPERATURE EFFECT ON CETANE INDEX.

temperature increased in all cases. Ni-W catalyst gave the lowest C/H ratios at all temperatures. Also the decrease was much steeper in case of Ni-W catalyst than in case of other two. C/H ratio study proves that Ni-W catalyst gave best hydrogenation activity and a significant improvement took place in hydrogen content in oil as the temperature was increased. Aniline point (Fig. 7) also leads to an important conclusion. Aniline point values do not show much of a decrease with increase in temperature from 300 to 400°C except in case of Co-Mo catalyst where aniline point fall at 350°C and increased to the original value at 400°C. In case of Ni-Mo and Ni-W catalysts the aniline point fall as temperature was increased beyound 400°C. This change, to some extent, may be attributed to the decrease in average molecular weight of product oils. It mainly indicates a lesser paraffinicity. Combining this information with results obtained from C/H ratios, it can be concluded that Ni-Mo catalyst gave rise to more aromatics than Ni-W or Co-Mo catalyst . Ni-W catalyst enhanced the production of olefins in this range.

Hydrodesulfurization (HDS) and hydrodenotrogenation (HDN) were another important factors in this study. The effect of temperature on HDS and HDN capabilities of the three catalysts is shown in figure numbers 8 and 9 respectively. HDS activity significantly increased for all catalysts with temperature (from 20 to 30% at 300°C to up to 88% at 450°C)

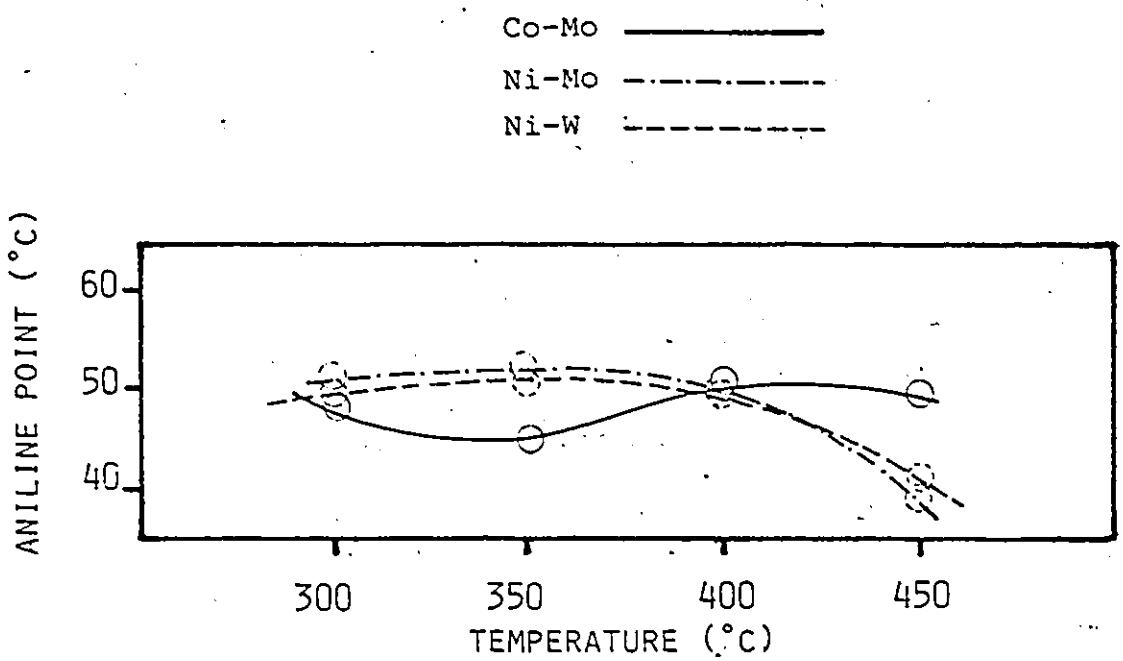


FIG.7 TEMPERATURE EFFECT ON ANILINE POINT

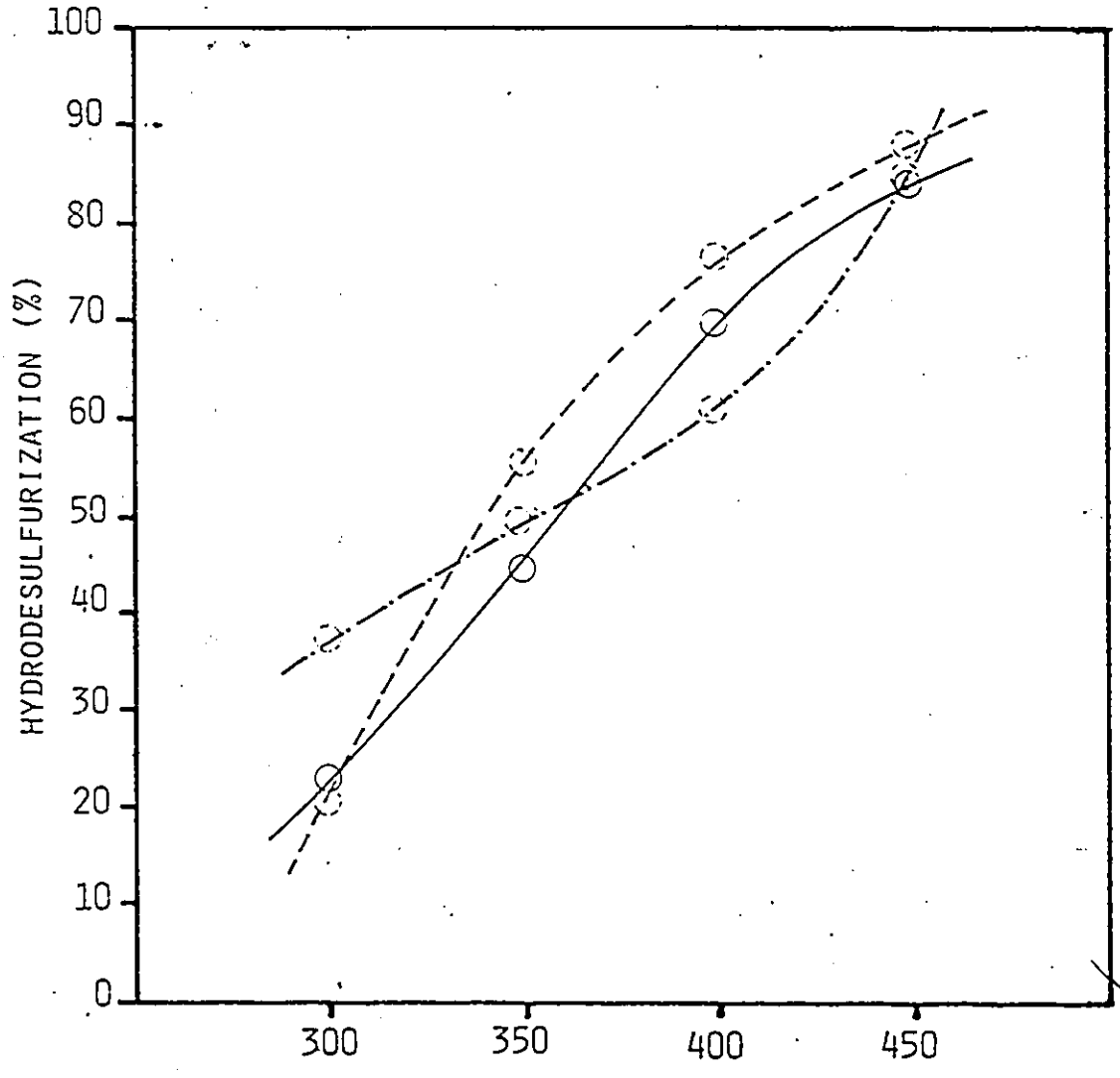


FIG.8 TEMPERATURE EFFECT ON HYDRODESULFURIZATION.

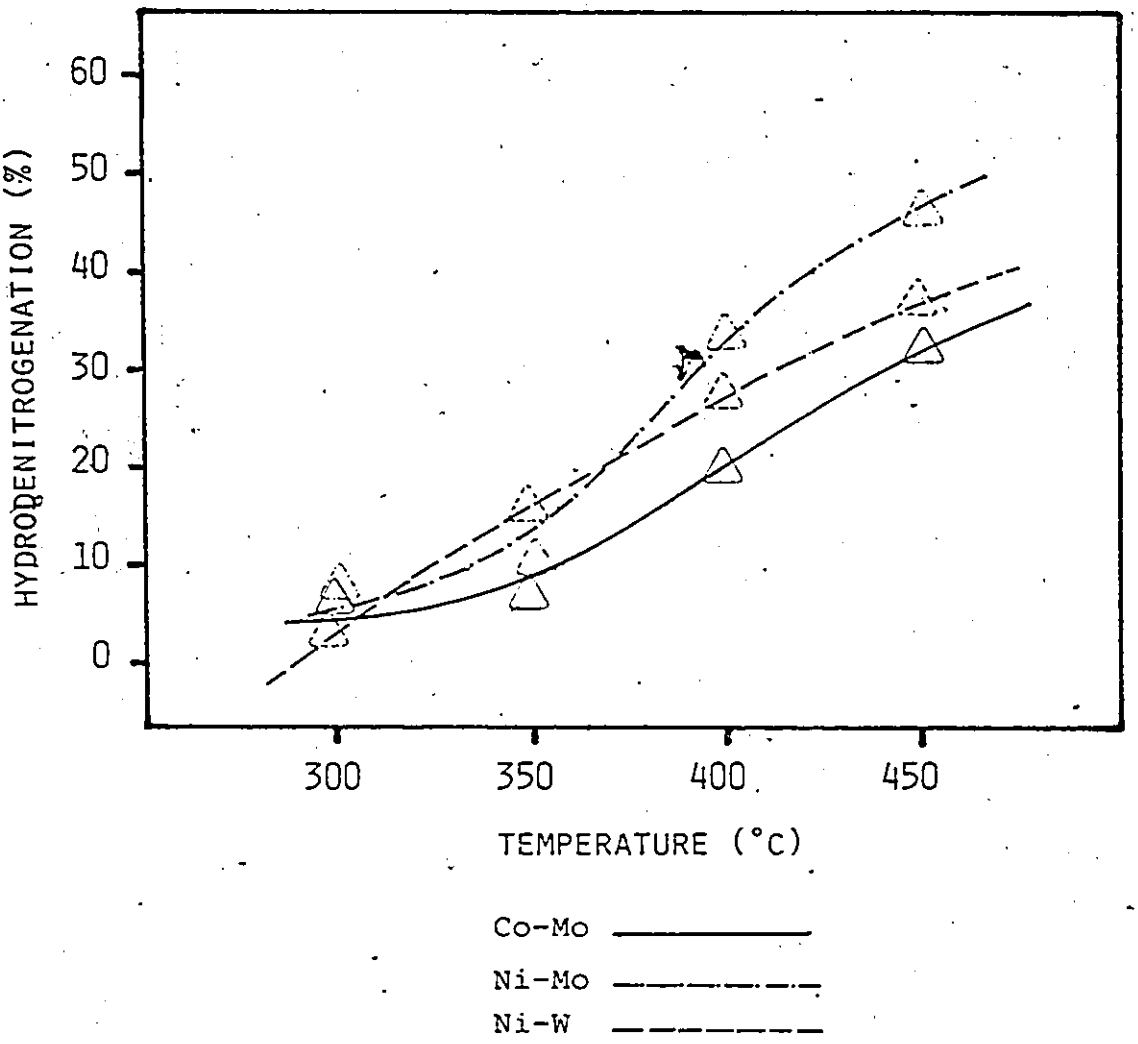


FIG.9 TEMPERATURE EFFECT ON HYDRODENITROGENATION

while Ni-W catalyst showed best HDS activity at temperatures more than 350°C. Ni-Mo and Co-Mo show approximately same performance in this range. However, at temperatures less than 350°C Co-Mo showed better sulfur removal activity. These results indicate that sulfur was present mainly in the complex macro-molecules in the heavy oil and for better desulfurization of this heavy oil, more hydrogenolysis of macro-molecules is very essential.

The improvement in HDN activity with temperature was not as much as that for HDS activity. This result is in line with the well known fact that nitrogen removal is comparatively more difficult than sulfur removal in all hydrotreatment processes. The performance of Ni-Mo catalyst for the nitrogen removal (HDN) was best (46% at 450°C as compared to 38% for Ni-W and 32% for Co-MO).

PRESSURE EFFECT :

The effect of pressure on product distribution was studied between 600 and 1800 psig. Liquid flow rates were kept constant around 80 ml./hr. (L.H.S.V. of 2.0) and temperature at 450°C. Due to limitations of the apparatus, higher pressures could not be tried. However, very important features of hydrotreating reactions with these catalysts are highlighted with this study.

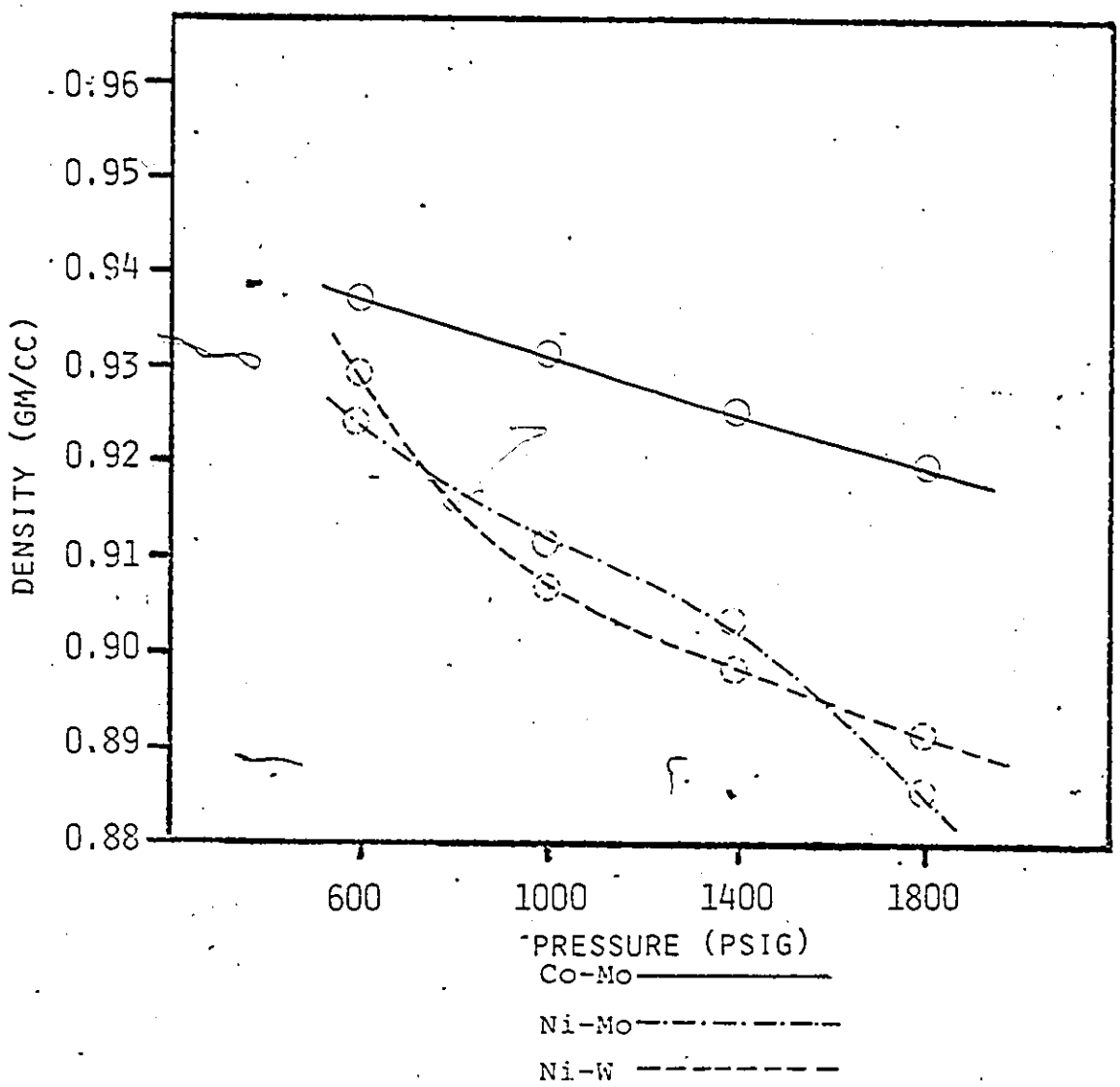


FIG.10 PRESSURE EFFECT ON DENSITY.

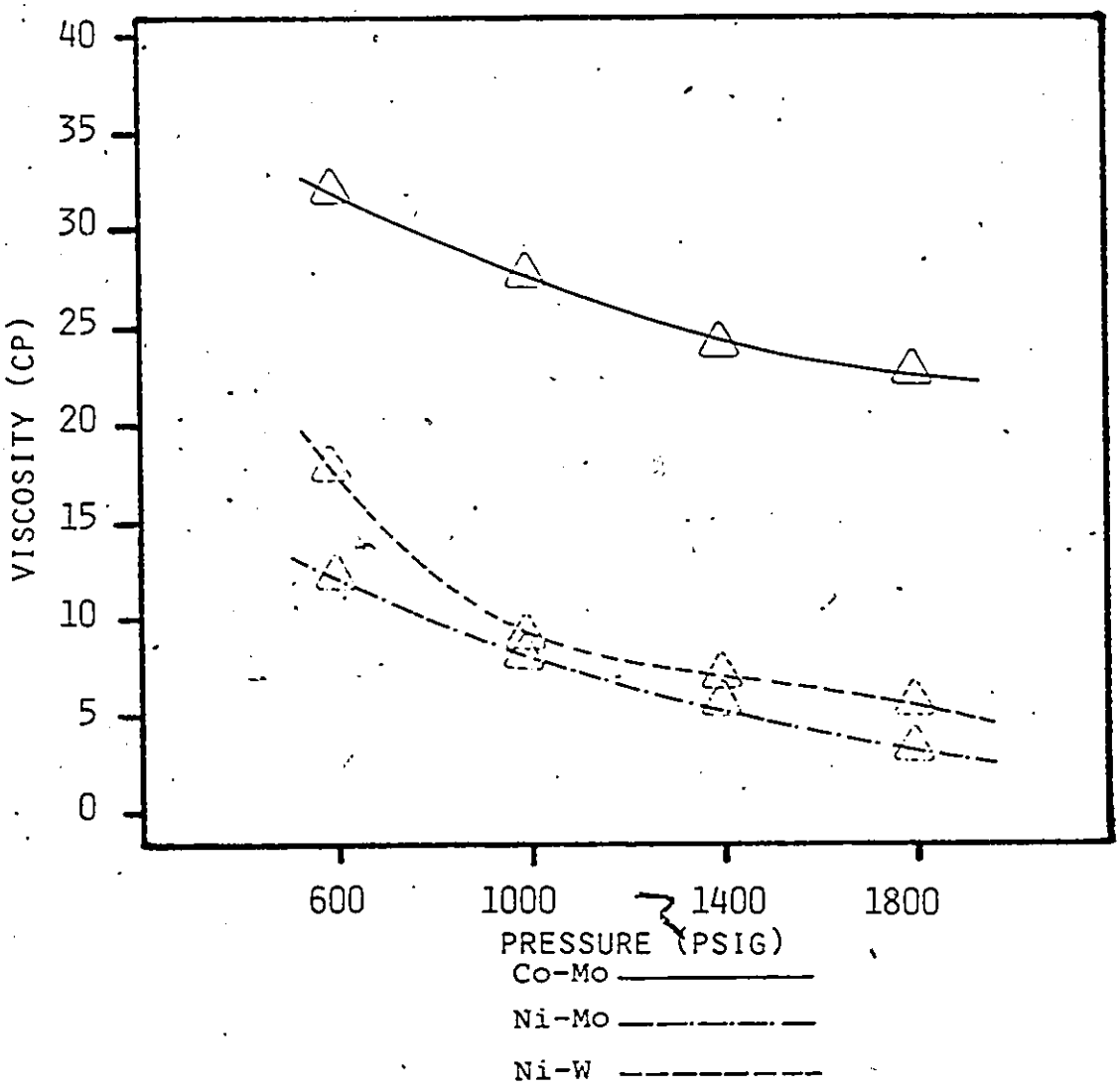


FIG.11 PRESSURE EFFECT ON VISCOSITY.

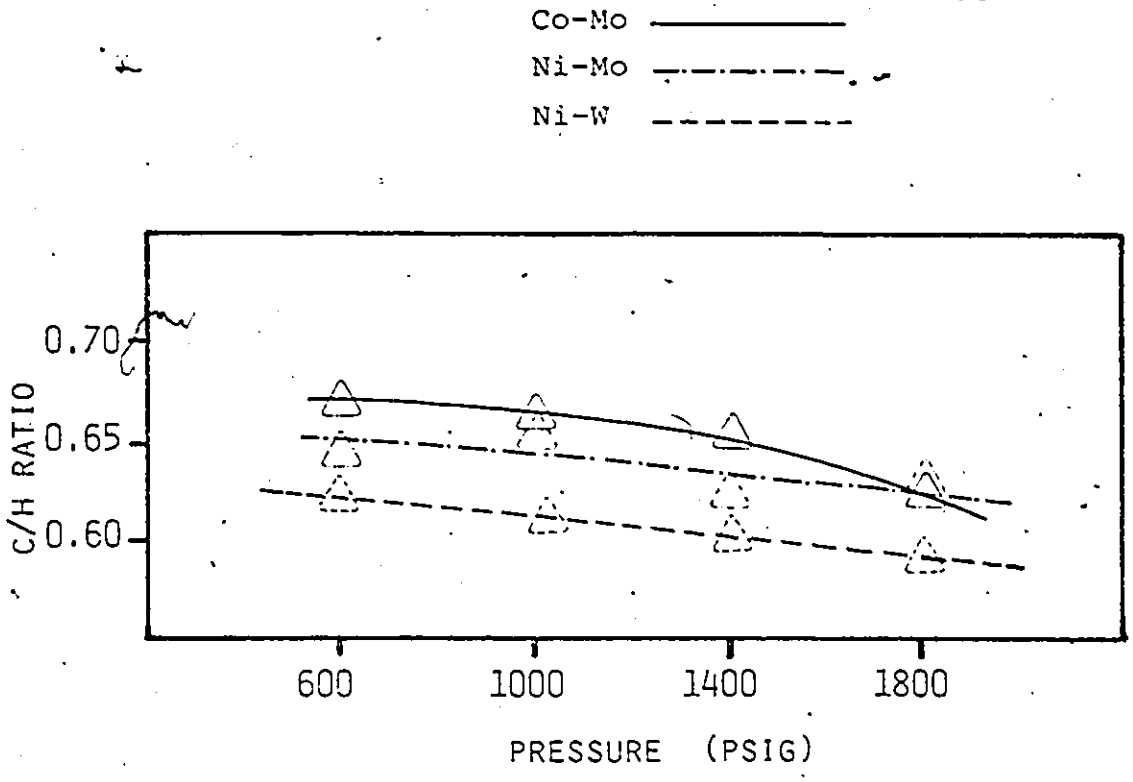


FIG.13 PRESSURE EFFECT ON C/H RATIO.

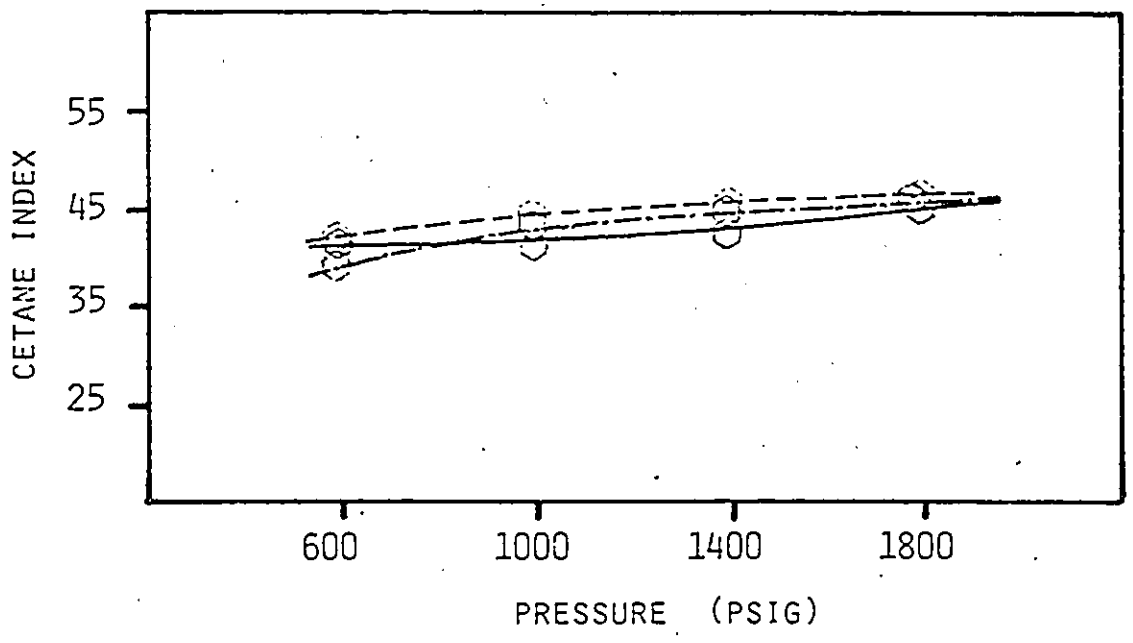


FIG.12 PRESSURE EFFECT ON CETANE INDEX.

The effect of pressure on density of liquid products is shown in Figure 10. A fairly good decline in density values was obtained with increasing pressures. This indicated that liquid products were lighter in quality at higher pressures. Similar trend was observed in case of viscosities of product oils (Figure 11). At higher pressures less viscous products are obtained with all catalysts. It can be concluded that the pore diffusion did play an important role in hydrogenolysis reactions.

Figure 12 shows the effect of pressure variation on cetane index. For all the catalysts, cetane index improved (i.e., increased) marginally on increasing the pressure. C/H atomic ratio (Figure 13) also indicates that increase in pressure did lower C/H values further. In case of Ni-Mo catalyst, a little leveling of C/H ratios at pressures greater than 1400 psig was observed. This may be due to its tendency of producing more aromatics in comparison to the other two catalysts. This is further confirmed when we observe aniline point (Figure 14)

The three catalysts gave rise to varying trends in aniline point of products at different pressures (Figure 14). In case of Co-Mo catalyst aniline point values increased with increase in pressure where as in case of Ni-Mo catalyst there was a decrease in aniline points values. Ni-W catalyst gave fairly uniform aniline point values at all

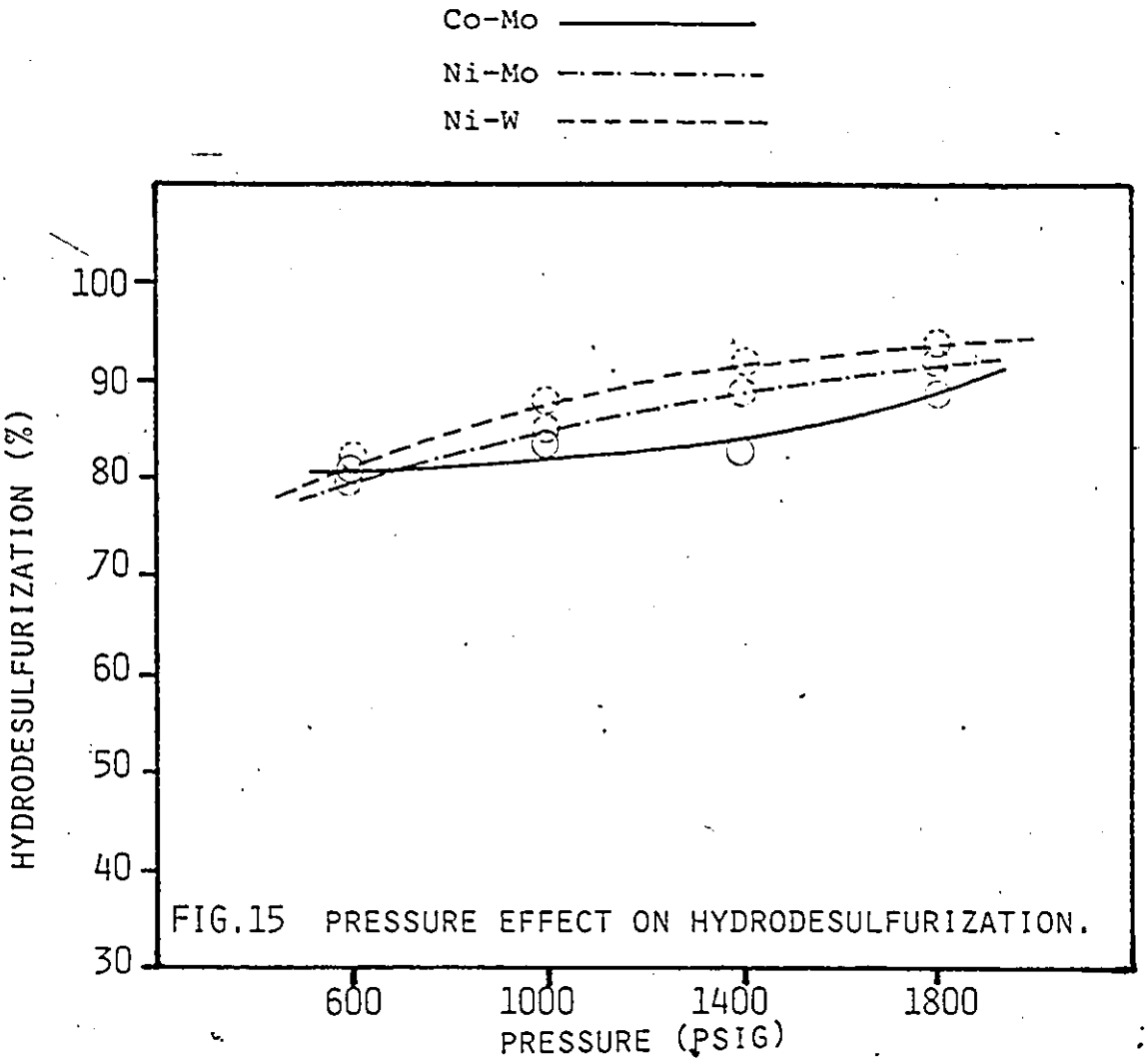


FIG.15 PRESSURE EFFECT ON HYDRODESULFURIZATION.

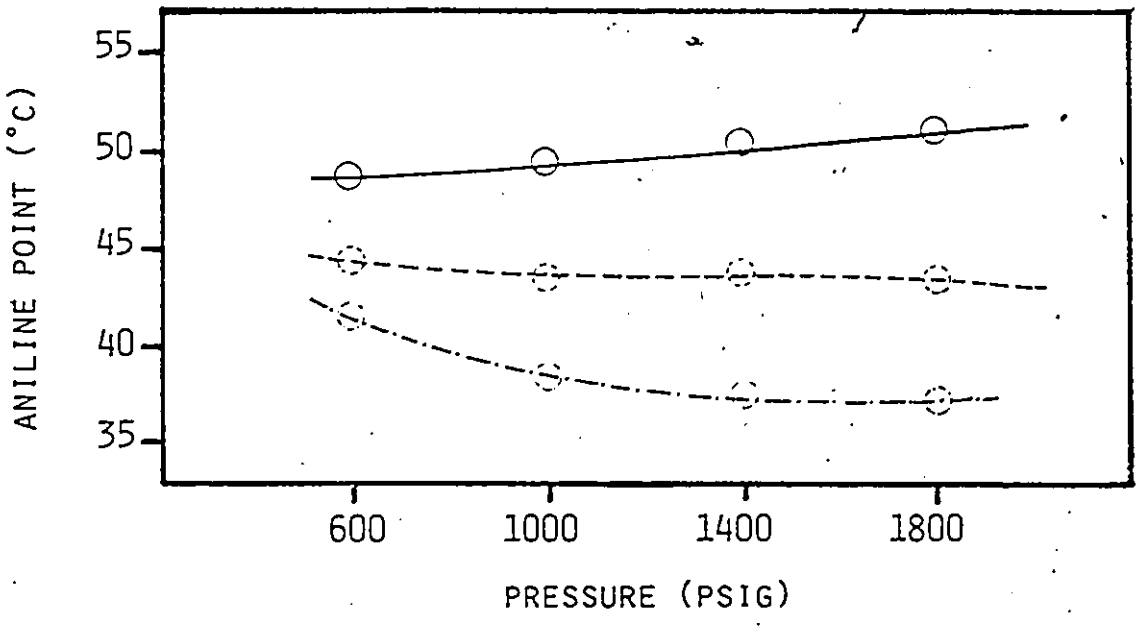


FIG.14 PRESSURE EFFECT ON ANILINE POINT.

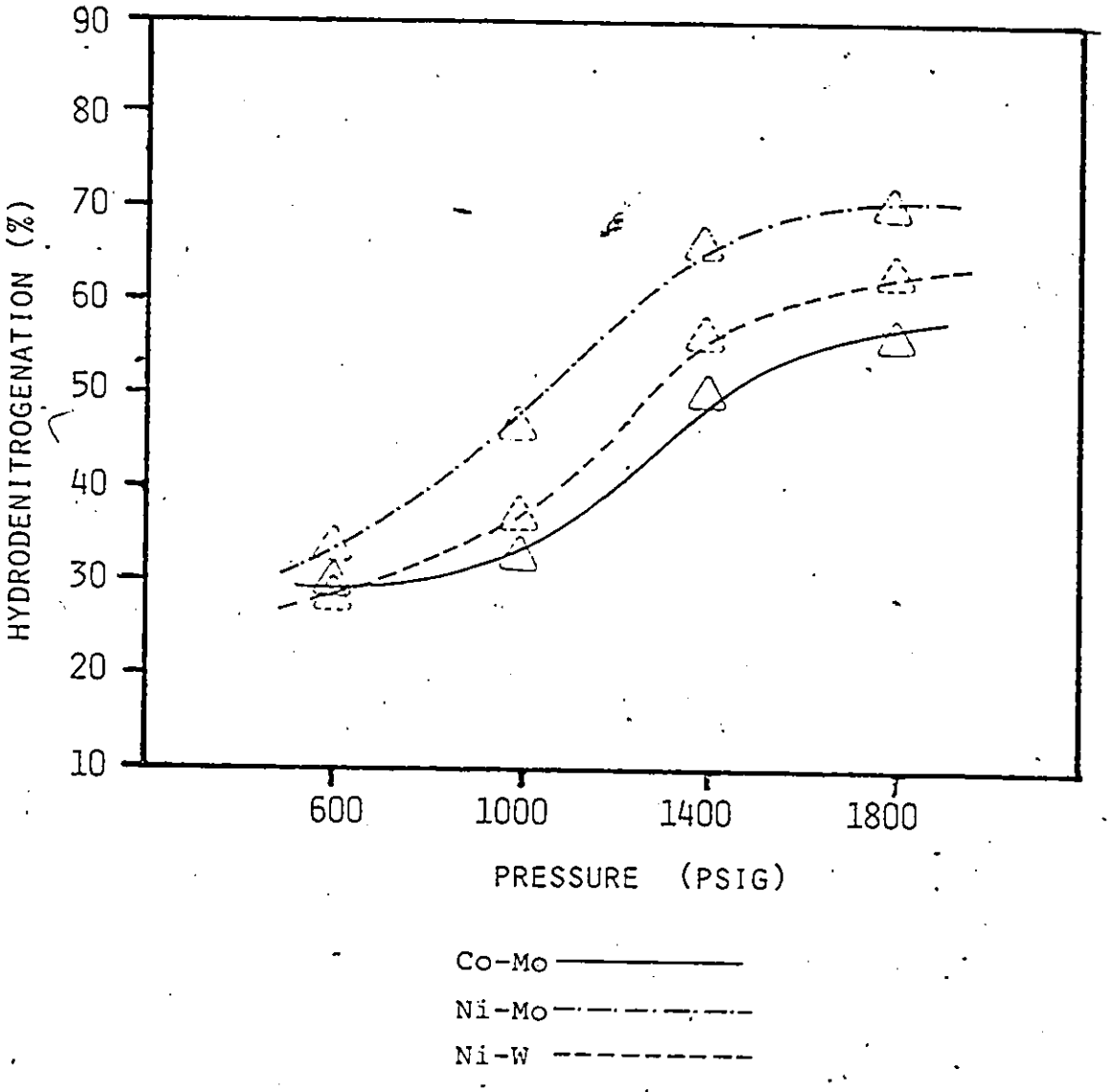


FIG.16. PRESSURE EFFECT ON HYDRODENITROGENATION.

pressures in the operating range. This shows that in case of Co-Mo catalyst paraffinicity increased with increasing pressures where as with Ni-MO catalyst more aromatics were formed. In case of Ni-W there might had been a slight increase in paraffinicity which probably was compensated by slight decrease in average molecular weight as is indicated by the effect of pressure on physical properties.

HDS and HDN activities of all catalysts showed improvements with increase in pressure. Figures 15 and 16 show the increase in HDS and HDN activities, respectively. Significant difference between the increase in HDS and HDN activities is that only HDN activity got a substantial boost because of increase in operating pressure. Improvement in HDS activity was of the order of 10% where as HDN activities has improved by about 35%. This is reverse of what was observed in case of temperature effect. It can be concluded from the foregoing analysis that HDN was more sensitive to increase in operating pressures than to the operating temperatures.

EFFECT OF LIQUID FEED RATES :

Effect of changes in feed rates of heavy oil was studied at 1000 psig pressure and 450°C temperature. The flow rates of heavy oil were varied between 20 ml./hr. and

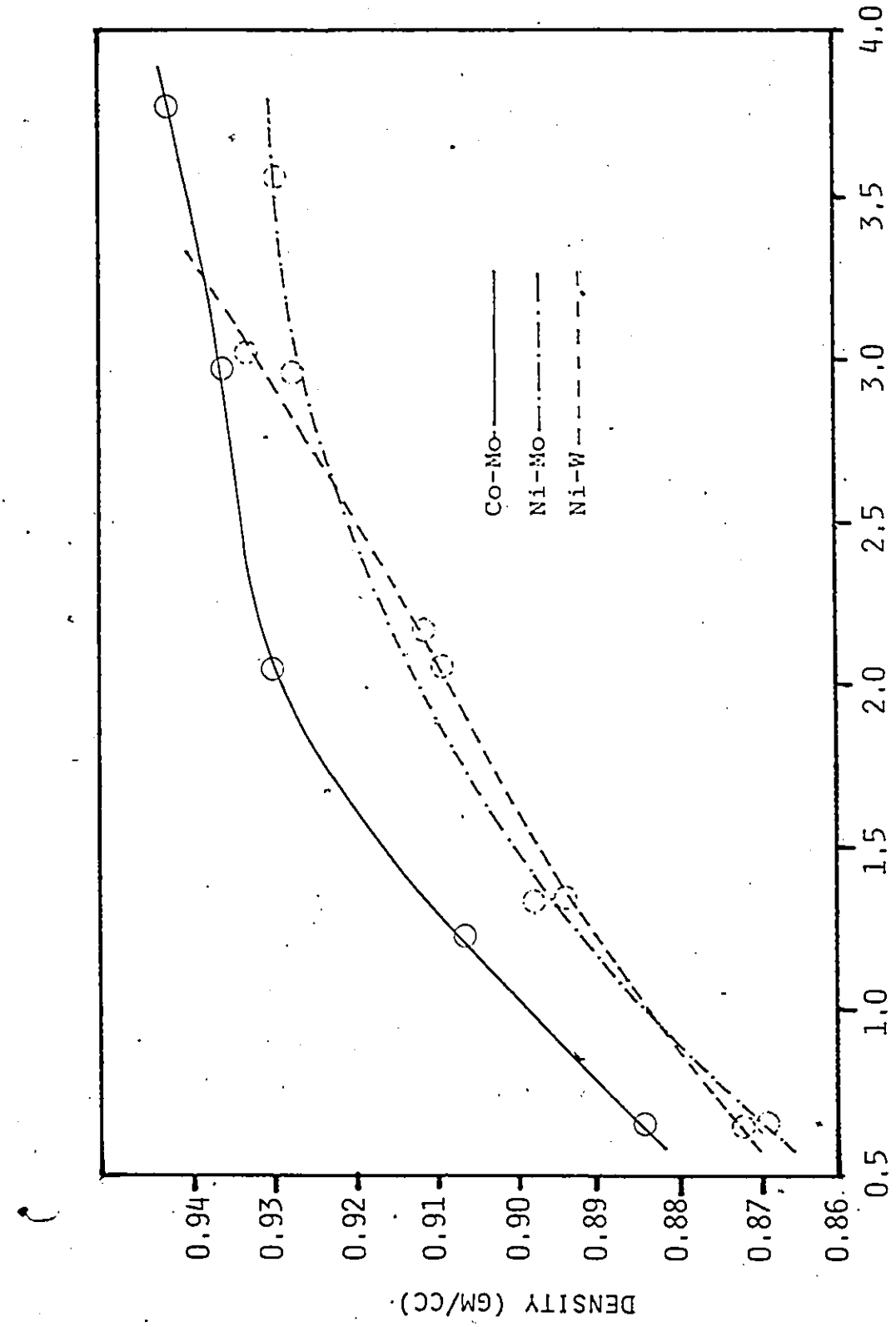


FIG.17 LIQUID FLOW RATE EFFECT ON DENSITY.

160 ml./hr. (i.e., L.H.S.V. from 0.5 to 4.0). Effect of liquid feed rates on physical properties is shown in Figures 17 and 18. Density of the product oil decreased with decrease in L.H.S.V. for all catalysts. Co-Mo gave rise to higher densities at all flow rates where as Ni-W and Ni-Mo gave rise to lighter oils. Values of densities obtained with Ni-W catalyst and Ni-Mo catalyst were compareable in most of the range . However, at higher flow rates the increase in density with flow rates was higher in case of Ni-W as compared to Ni-Mo. The densities of both Ni-Mo and Co-Mo decreased faster with decrease in flow rates below a value of L.H.S.V. of 2.0. It can be concluded from the above that Ni-W catalyst can not give good results at higher feed rates where as Ni-Mo can give light products even at higher flow rates.

Figure 18 shows how viscosities change with increase in flow rates for all the three catalysts. Decrease in viscosities of product oils with decreasing flow rates was quite uniform in case of Co-Mo catalyst where as in case of Ni-Mo and Ni-W catalysts the decrease was faster with feed rates up to L.H.S.V. of 2.0. For feed rates below this , viscosities obtained with Ni-W and Ni-Mo catalysts did not decrease so fast. Since in this range lighter products were obtained (Figure 17) , it can be said that more ring structures were formed instead of long chain paraffins and olefins. This conclusion is further confirmed from the aniline point analysis.

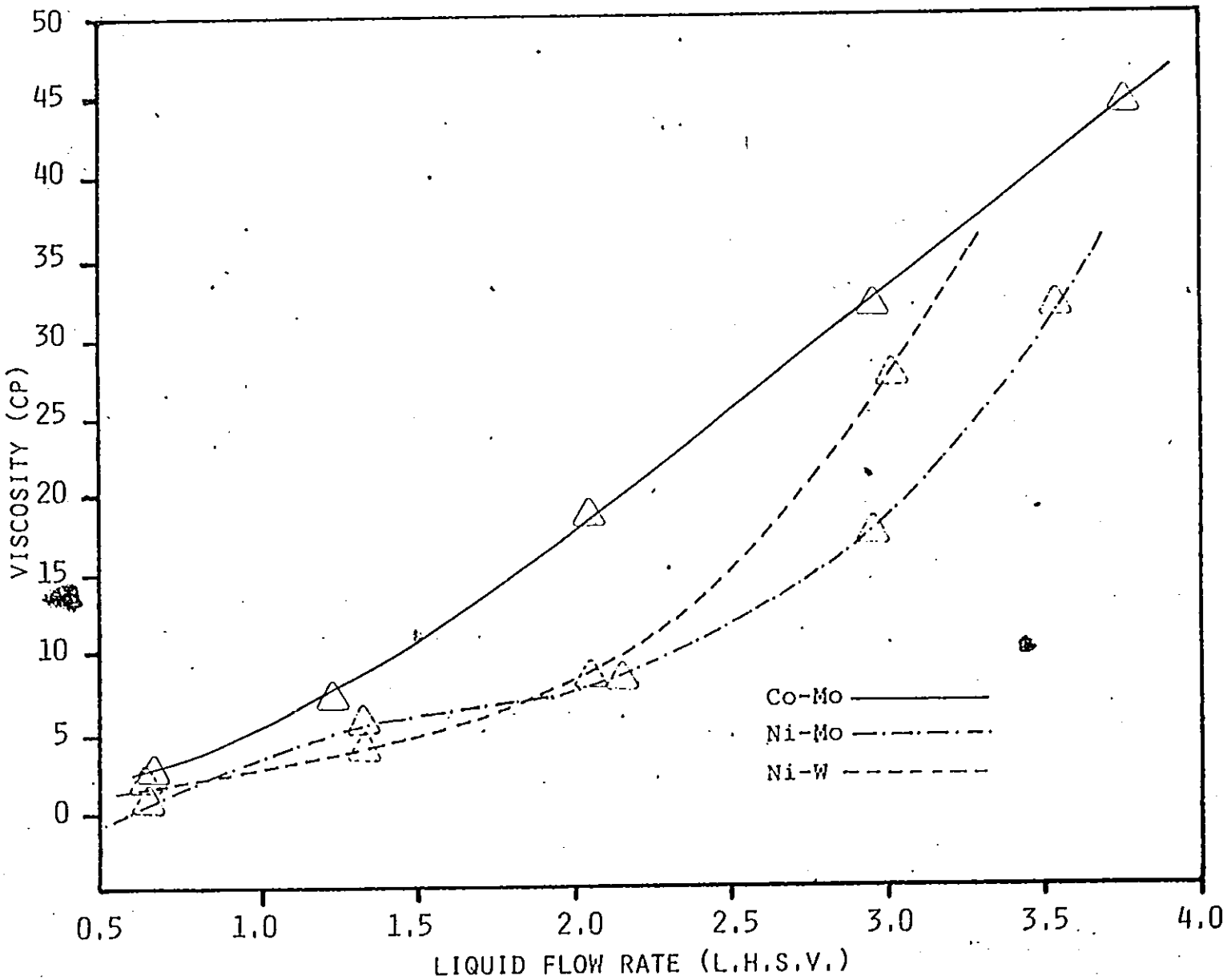


FIG.18 LIQUID FLOW RATE EFFECT ON VISCOSITY.

Changes in cetane index values of product oils are shown in Figure 19. Cetane index values did not vary much with feed flow rates for L.H.S.V. of 1.5 or more. But below L.H.S.V. of 1.5 cetane index values increase a little (in case of Ni-W and Co-Mo catalysts) and then there was a sudden decrease in cetane index values for all the catalysts. For Ni-Mo catalyst, cetane index did not show an increase even below L.H.S.V. of 1.5, however, the value decreased suddenly at lower L.H.S.V. . Cetane index values did not increase in this case because of more aromatics and this confirms the conclusion drawn earlier.

C/H ratio variation with feed rates (Fig.20) indicated a constant value for Ni-W catalyst below L.H.S.V of 2.0. While Co-Mo and Ni-Mo showed a fairly constant values at L.H.S.V greater than 1.5, an opposit trend was observed below L.H.S.V. of 1.5 .Combining this observation with cetane index values and physical properties, one can conclude that Co-Mo catalyst had the least tendency to give rise to aromatics and ring structures even at lower feed rates. This conclusion is further confirmed by Figure 21. Aniline points did fall with decrease in feed rates, though this was minimum for Co-Mo catalyst. In case of Ni-Mo and Ni-W catalysts, the aniline point values fall substantially when feed rates were decreased. The reason for this decrease was the same as mentioned earlier.

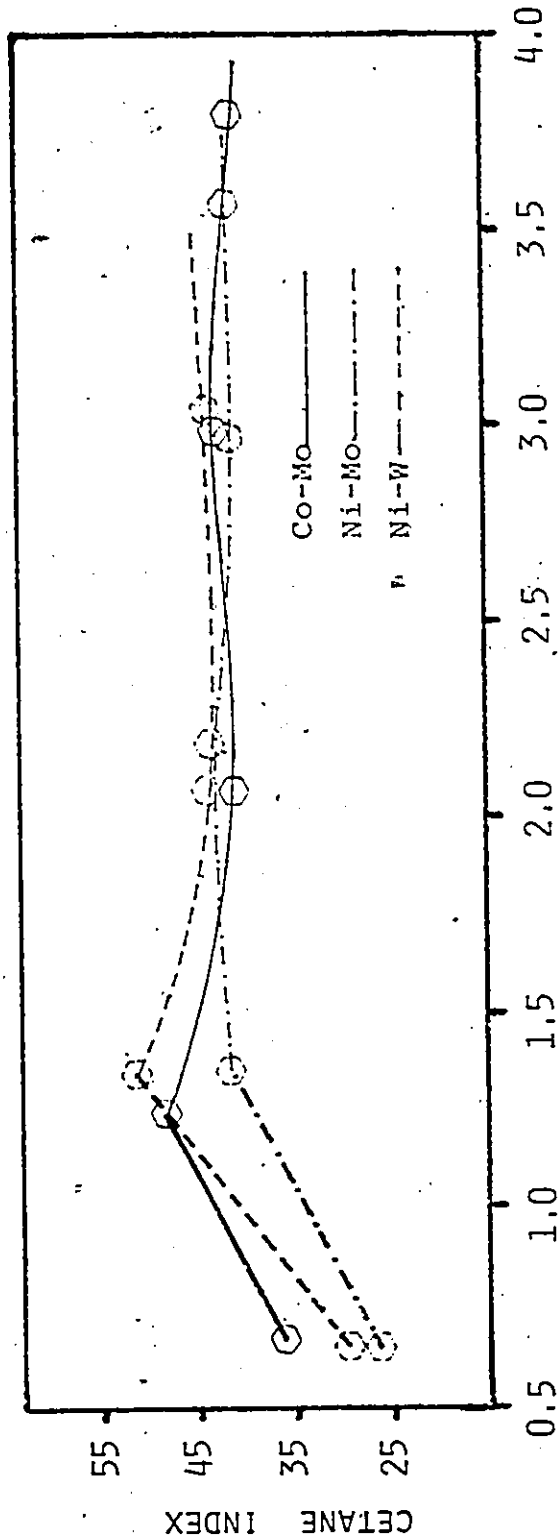
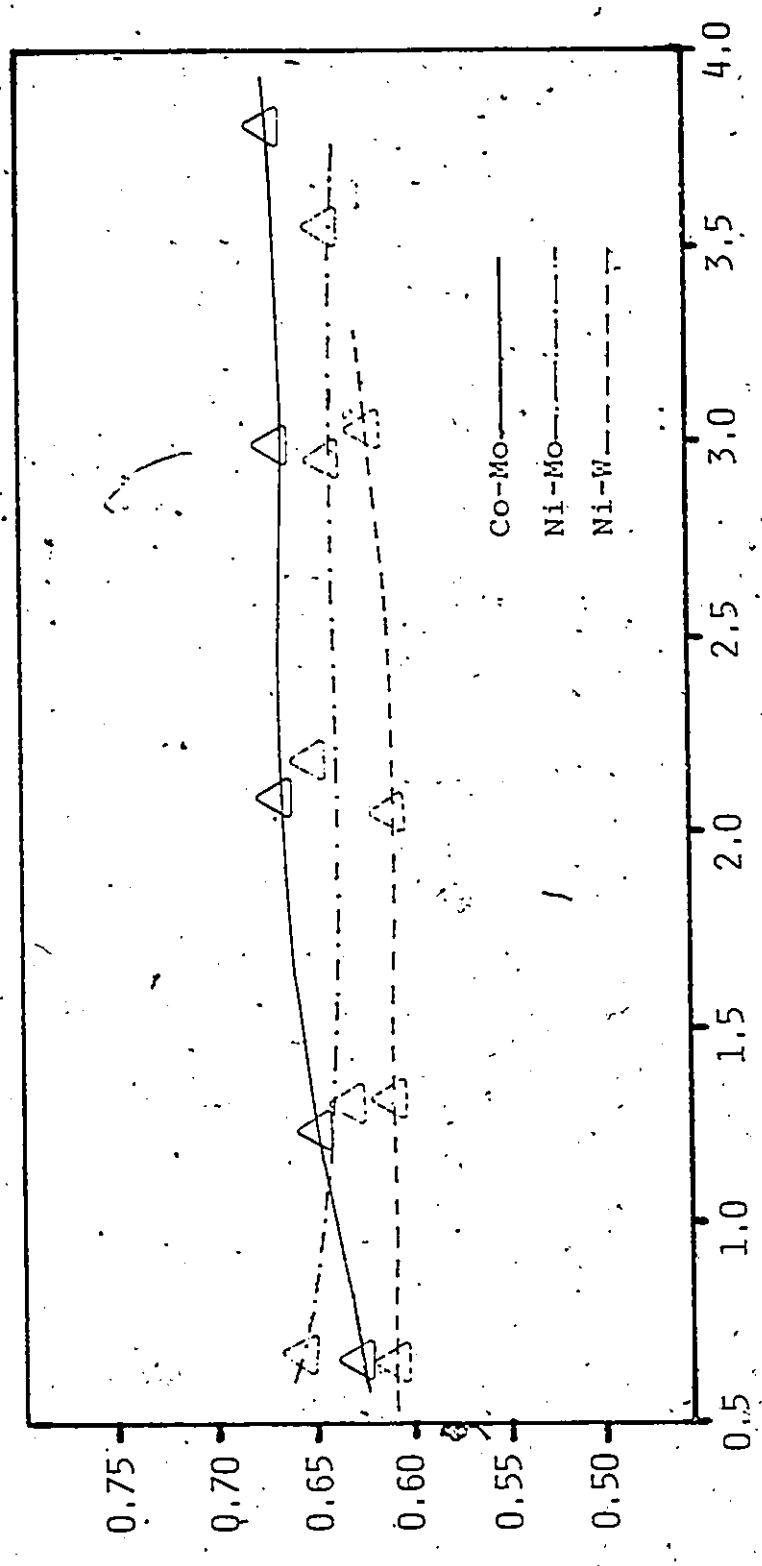


FIG.19 LIQUID FLOW RATE EFFECT ON CETANE INDEX.



FIG,20 LIQUID FLOW-RATE EFFECT ON C/H RATIO.

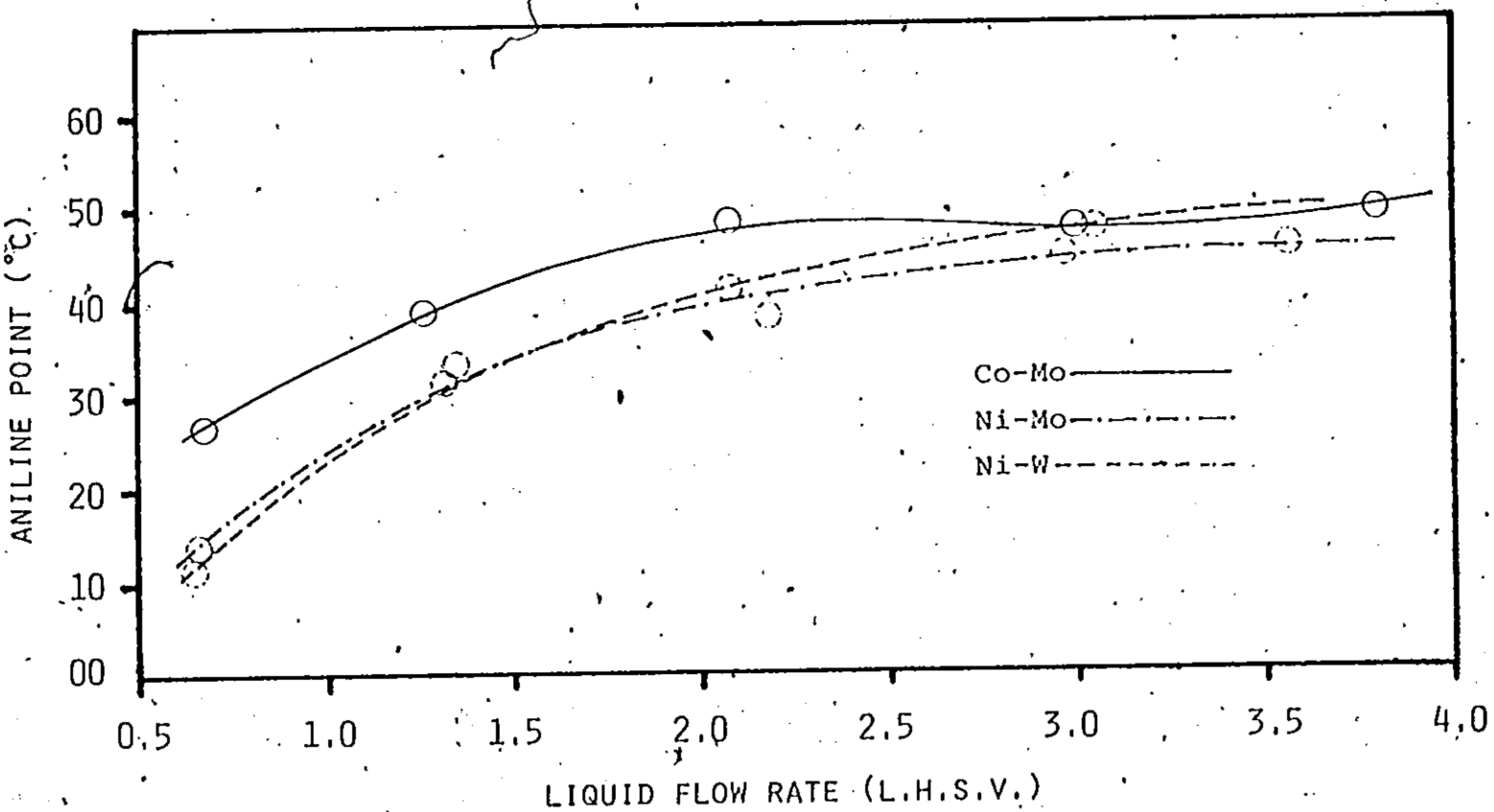


FIG.21 LIQUID FLOW RATE EFFECT ON ANILINE POINT.

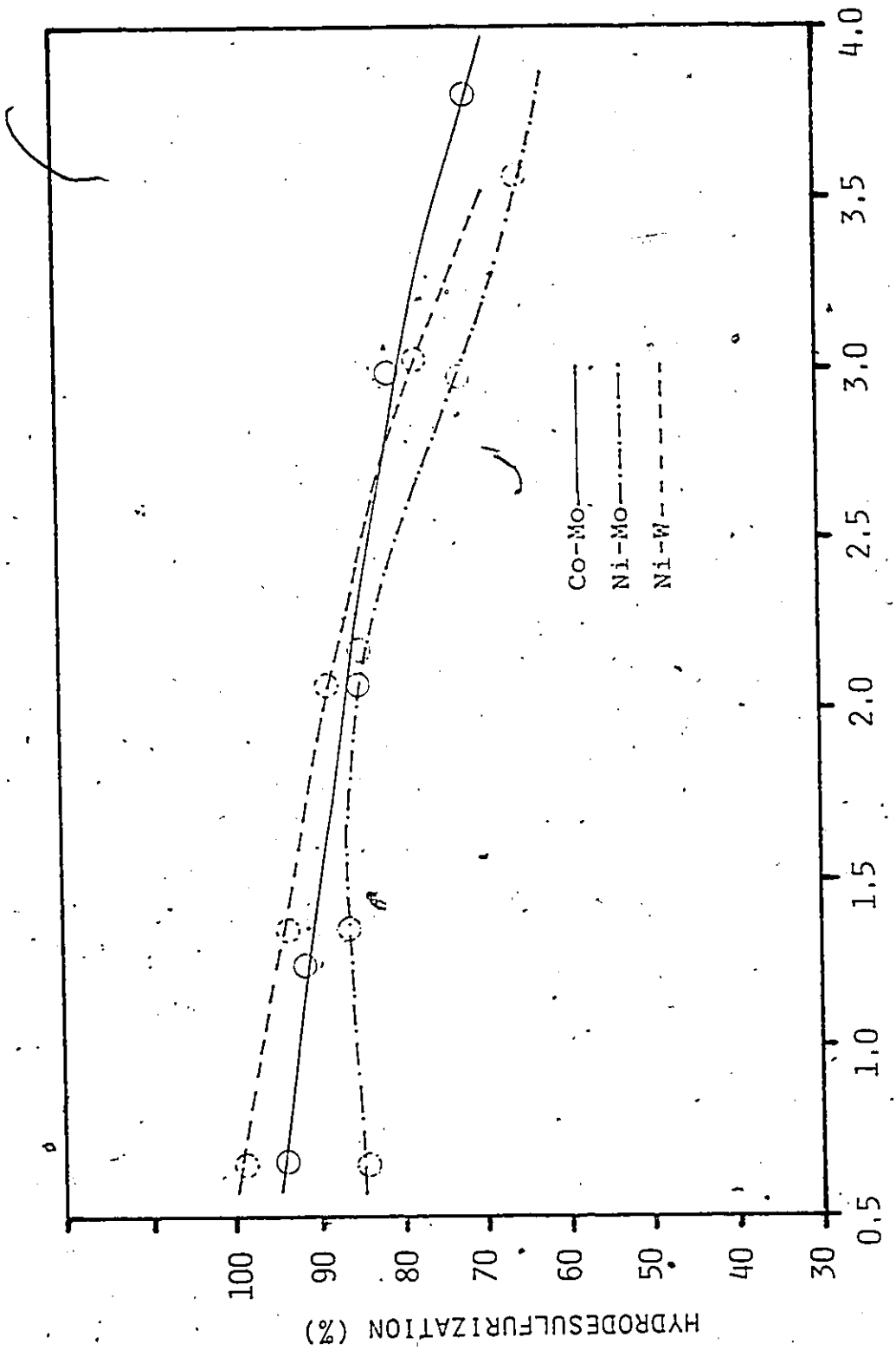


FIG.22 LIQUID FEED RATE EFFECT ON HYDRODESULFURIZATION.

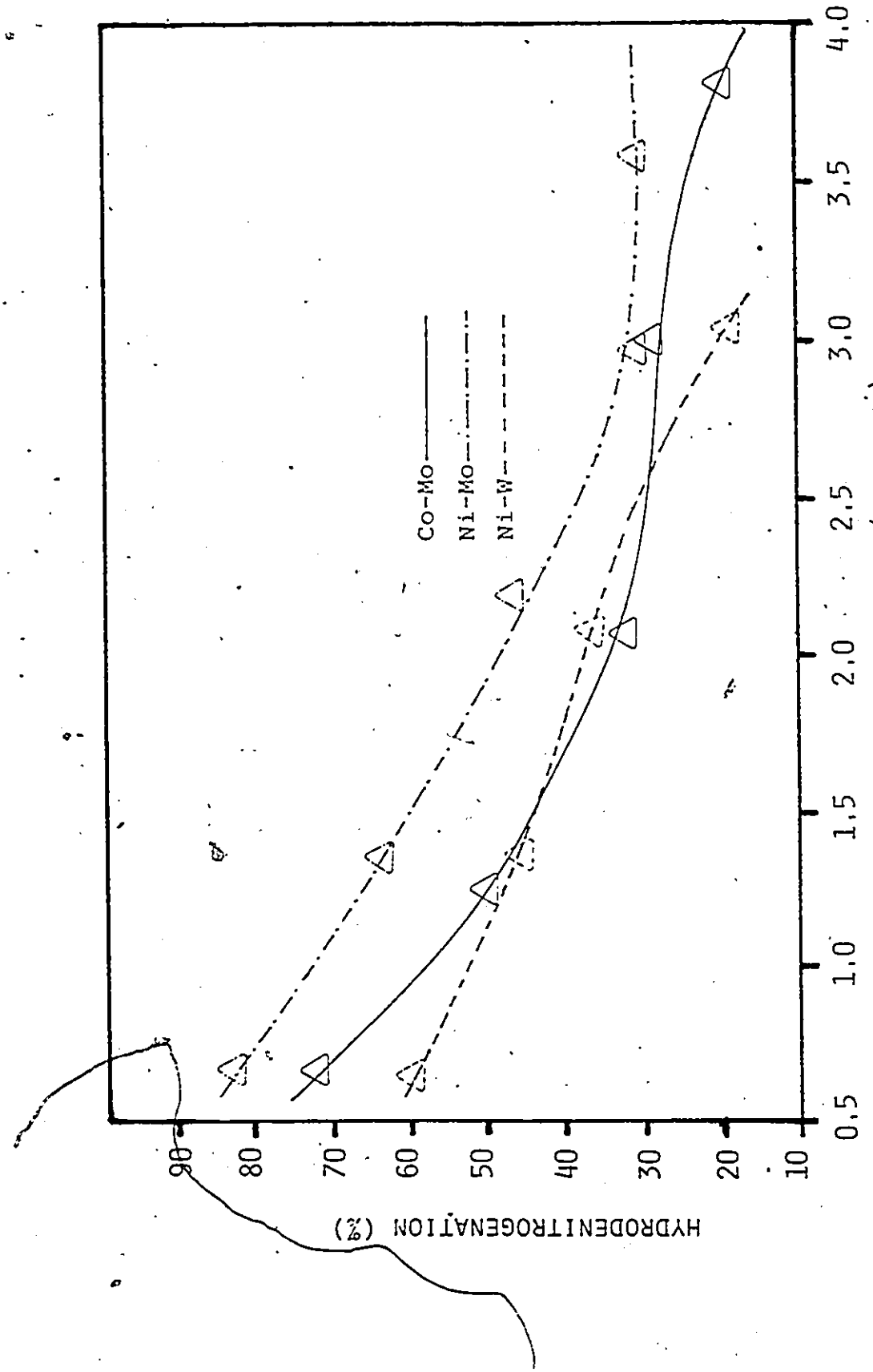


FIG.23 LIQUID FEED RATE EFFECT ON HYDRODENITROGENATION.

While Ni-W catalyst gave best hydrodesulfurization (HDS) activity (Figure 22) in lower range of feed rates the performance of Co-Mo catalyst was better at higher feed rates. Ni-Mo was found to be least active over the whole range. There was a sudden drop in HDS performance of Ni-Mo catalyst at very low flow rates (L.H.S.V. less than 1.0). C/H ratio in this case also increased in this range (Figure 20). It appears as if , at the lower feed rates,this catalyst was unable to break free the sulfur radicals from the ring aromatics. On the other hand this catalyst had the best HDN activity over the entire range (Figure 23). Though a marked increase in HDN activity was observed with decrease in L.H.S.V below 3.0, Ni-W showed the least HDN activity over the entire range except at around L.H.S.V. of 2.0 where it performed little better than Co-Mo catalyst.

ASTM DISTILLATION :

ASTM D-86 distillation results are shown in Figures 24, 25 and 26. For ease of comparison , effect of temperature variation for all catalysts are given in Figure 24, while Figure 25 shows the effect of pressure variations and Figure 26 shows effect of feed rate variation. It can be seen that percentage volume boiling at lower temperatures increased with increase in hydrotreatment temperature and pressure and with decrease in liquid feed rates. The individual cases follow same explaination as discussed earlier.

ASTM D-86 DISTILLATION RESULTS

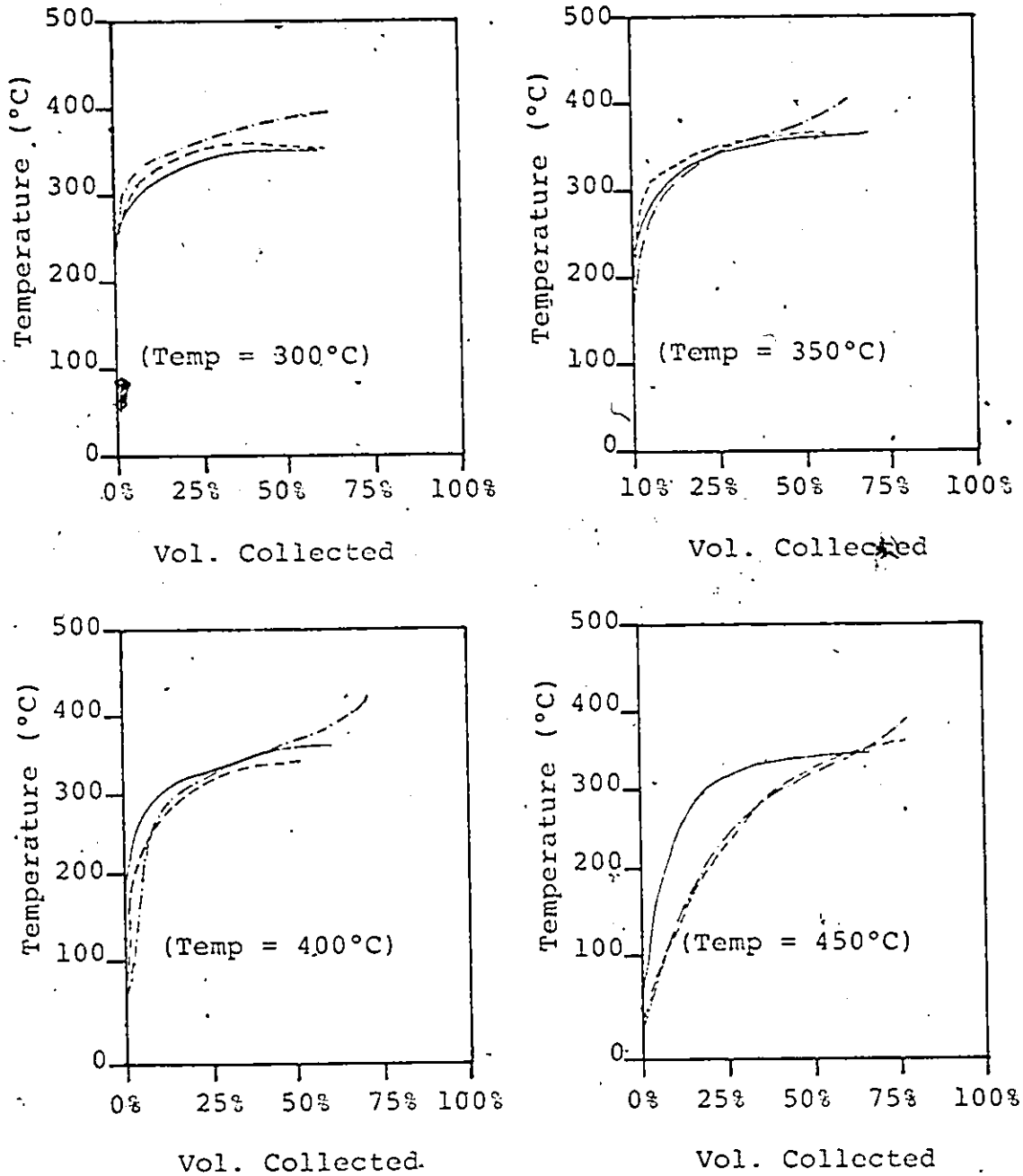


FIG.24 EFFECT OF TEMPERATURE

ASTM D-86 DISTILLATION RESULTS

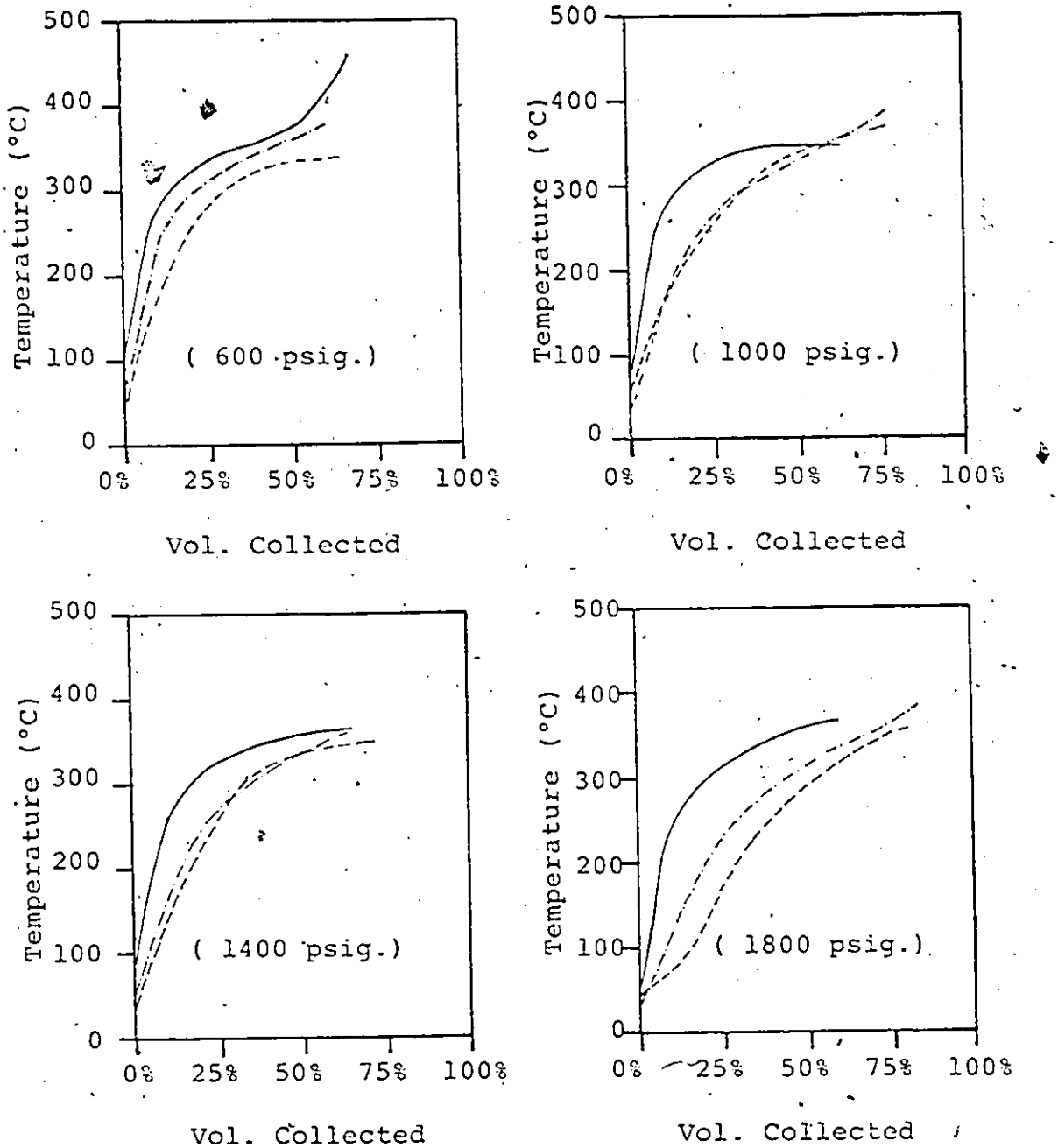


FIG.25 EFFECT OF PRESSURE

ASTM D-86 DISTILLATION RESULTS

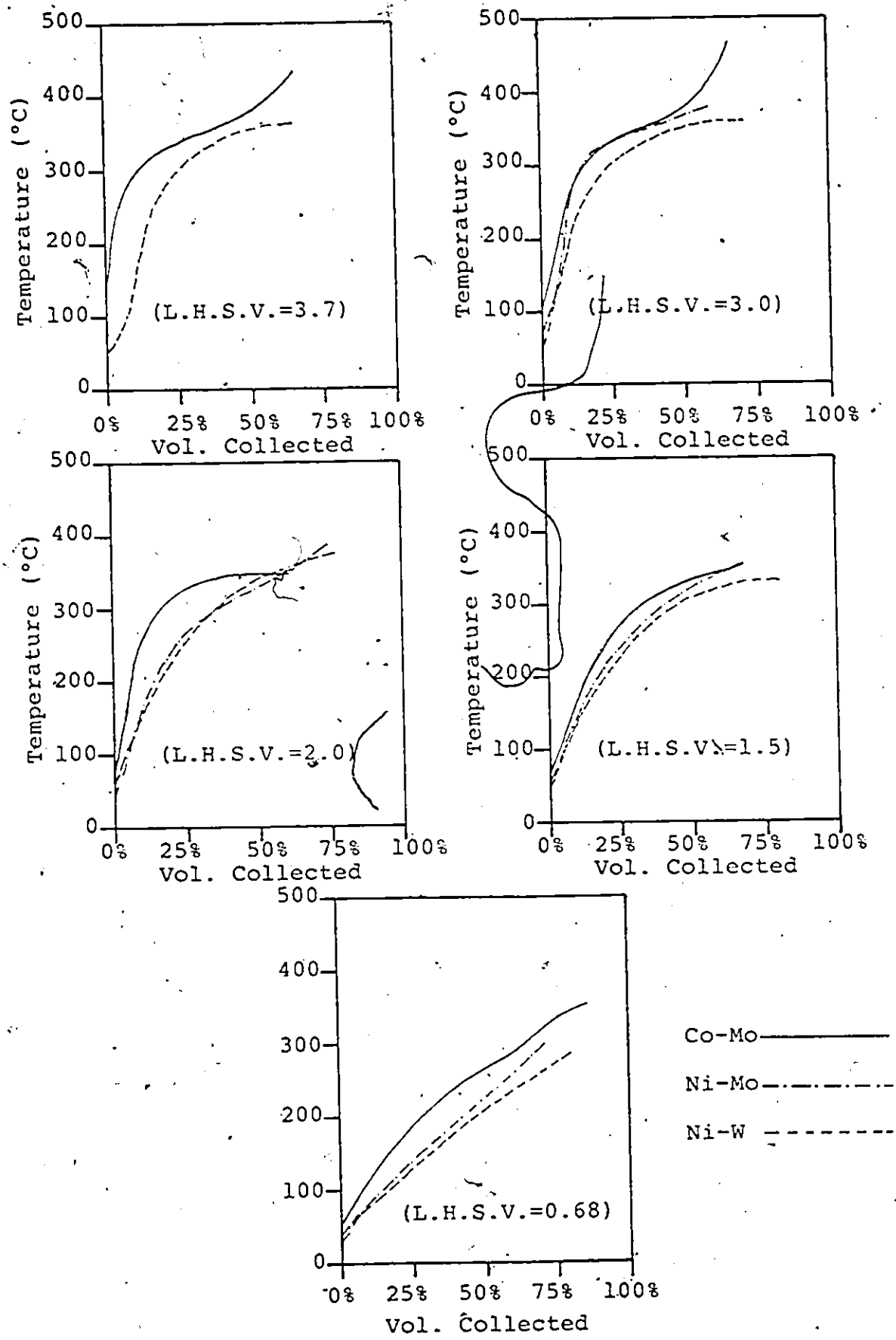


FIG.26 EFFECT OF LIQUID FLOW RATE

EFFLUENT GAS ANALYSIS :

Effluent gases were sampled in a gas bag and analyzed The composition of the gas was found to be as follow;

Gas		%by wt.
H_2	-	96.8
H_2S	-	2.3
CH_4	-	0.4
C_2H_6	-	0.2
C_3H_8	-	0.08

Somehow NH_3 could not be traced in the above analysis. The gas sample was collected from reaction in which hydrotreatment was being studied with the Co-Mo catalyst and the operating conditions were 400°c temperature, 1000 psig pressure and L.H.S.V. of 2 . This analysis confirmed that H_2 gas was always in excess in side the reactor.

COLUMN SEPARATION STUDY :

One of the samples (with Co-Mo catalyst at 450°C, 1000 psig and L.H.S.V. of 2) and the original heavy oil were used in liquid column chromatographic separation . Asphaltene was removed from both samples. It was found that product oil contained no asphaltene at all. This showed that all the asphaltene present in the original oil got converted to oil and other useful products on hydrotreatment. Weight percents of various fractions separated are given in Table-12.

TABLE-12

Column separation results of heavy oil and product oil

Fraction designation	Colour	Heavy oil (wt.%)	Product oil (WT.%)
White oil	Like wax	1.1	2.7
Yellow oil	Light yellow	84.6	90.5
$CHCl_3$ resin	Reddish brown	11.6	3.8
THF resin	Dark brown	2.0	1.5
Residue in column (by difference)	Blackish	0.7	Nil
Others (low boiling components lost during evaporation) (by difference)	——	Not expected	1.5

It can be seen from the above Table that the resin originally present in heavy oil got converted to oil and other light products during hydrotreatment process.

GAS CHROMATOGRAPHIC ANALYSIS :

All oil samples were injected in to the gas chromatograph with V-101 packed column and later with OPN/Porasil-C column. Figure 27 shows the chromatograph of original heavy oil with V-101 column. The lightest oil produced with Co-Mo catalyst (at L.H.S.V. of 0.5, 450°C and 1000 psig) gave the

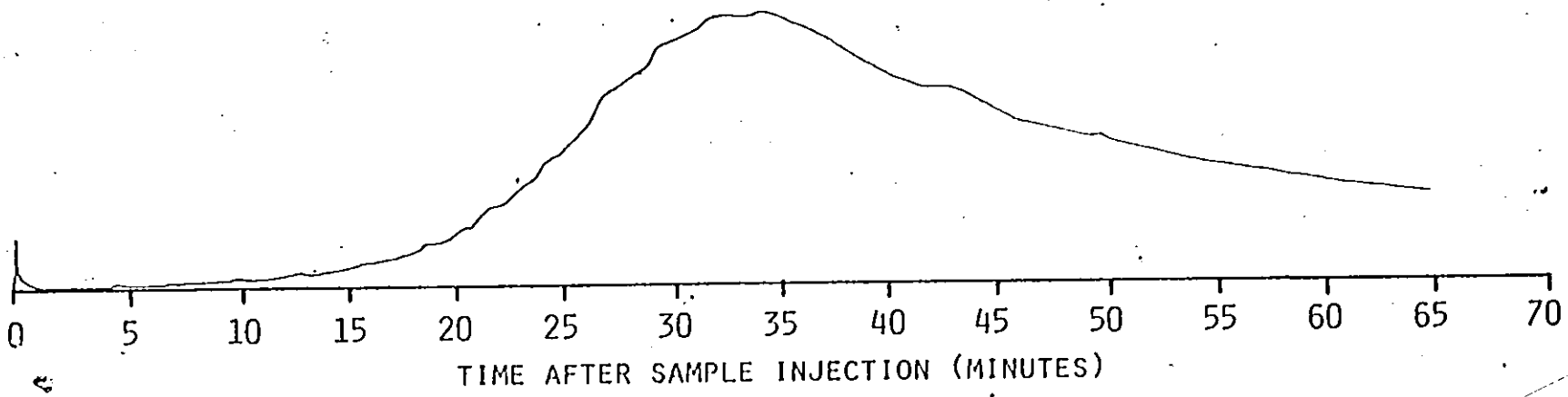


FIG.27 GAS CHROMATOGRAM OF HEAVY OIL (COLUMN - FOR HIGH BOILING COMPONENTS)

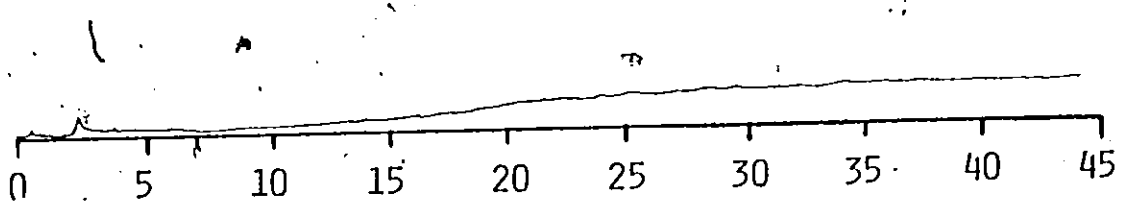


FIG.29 GAS CHROMATOGRAM OF HEAVY OIL
(COLUMN - FOR LOW BOILING COMPONENTS)

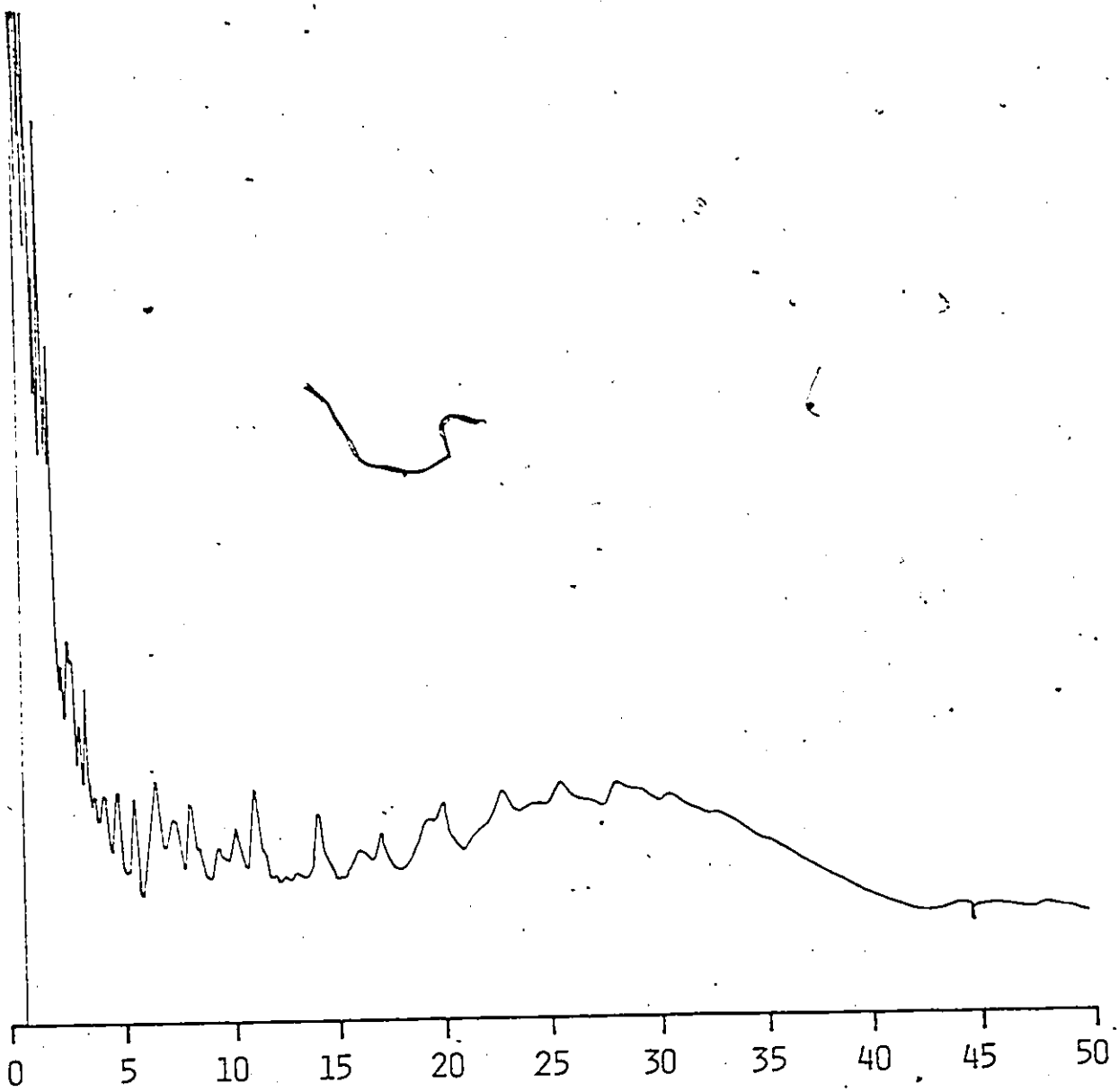


FIG.28 GAS CHROMATOGRAM OF PRODUCT OIL SAMPLE
(COLUMN - FOR HIGH BOILING COMPONENTS)

response which is shown in Figure 28. Chromatographs of all other samples fell between these two chromatographs. Area under different peaks varried indicating different amounts of the particular compound in all samples. The conclusions drawn from this analysis are similar to the ones already discussed.

In the same way, gas chromatographic response with OPN/Poracil-C column can be seen from the chromatograph of original oil and a particular sample indicated above (Figures 29 and 30). This column was used particularly for resolving low boiling components. All the low boiling components in Figure 30 were formed during the hydrotreatment as none of these were present originally as indicated by Figure 29. Chromatographs for other samples with Co-Mo and other catalysts were similar with variation in area under various peaks.

In case of a few oil samples derived with Ni-Mo and Ni-W catalysts, a different behaviour was observed in variation of heights of some of the peaks. In case of Ni-W this peak ocurred at 24 minutes and area under this peak increased with increase in pressure , decrease in temperature and increase in flow rates. The same peak, in case of Ni-Mo catalyst was more pronounced at high pressure and feed rates. However, in this case at lower temperature, another peak at retention time of 10 minutes appeared and was more pronounced.

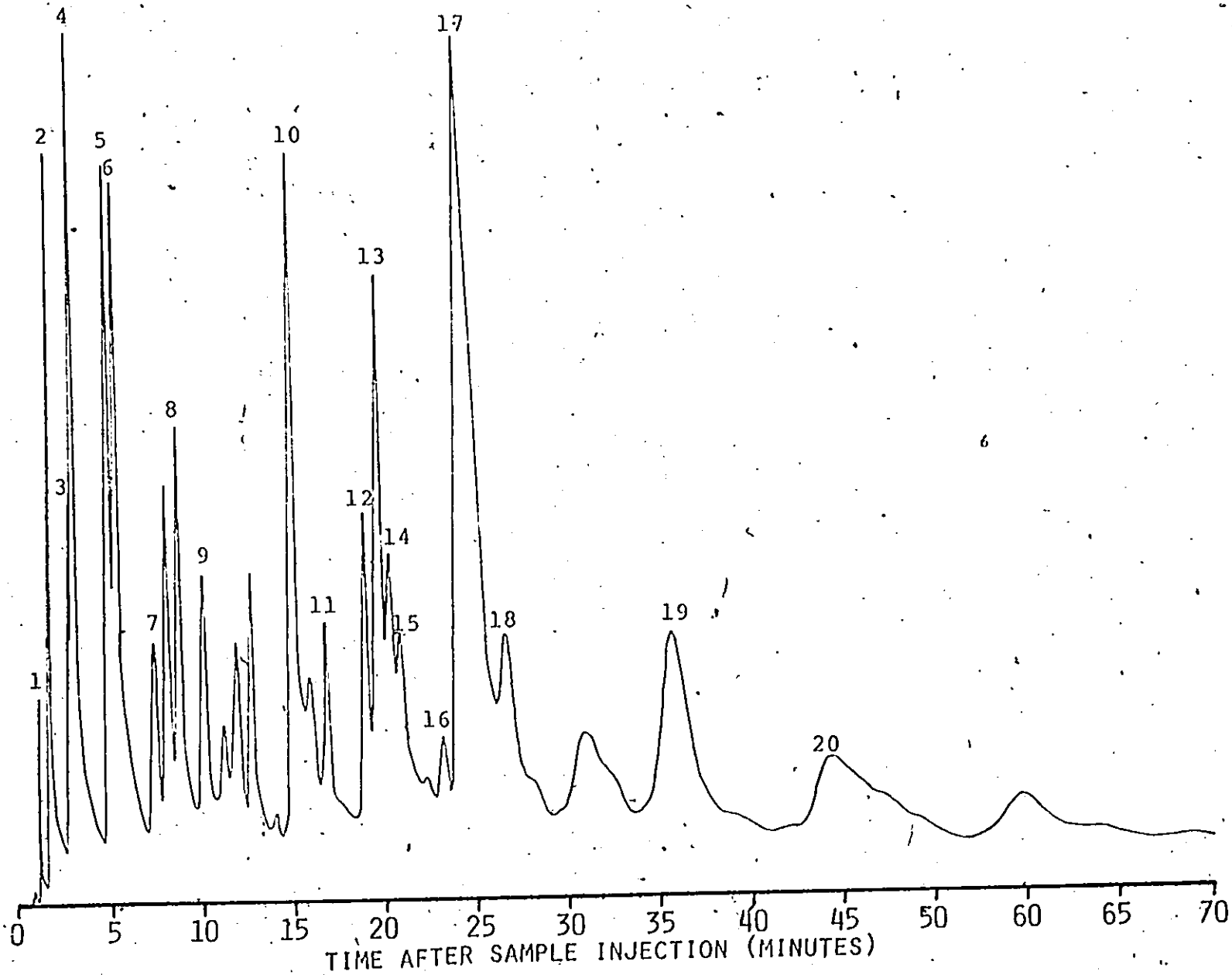


FIG.30 GAS CHROMATOGRAM OF PRODUCT OIL SAMPLE (COLUMN - FOR LOW BOILING COMPONENTS).

TABLE-13

COMPOUNDS IDENTIFIED BY GAS CHROMATOGRAPHY

Peak No.	Compounds
1	AIR
2	CARBON DISULFIDE and BUTANE
3	ISOPENTENE and 3-METHYL PENTANE
4	PENTANE and CYCLOPENTANE
5	2,3-DIMETHYL PENTANE and METHYL CYCLOPENTANE
6	HEXANE and CYCLOHEXANE
7	CYCLOHEXENE
8	HEPTANE
9	ISO-OCTANE, BENZENE and THIOPHENE
10	CYCLO-OCTANE and TOLUENE
11	n-NONANE
12	ETHYL BENZENE
13	p-XYLENE, m-XYLENE and STYRENE
14	o-XYLENE
15	DECANE
16	PROPYL BENZENE
17	MESITYLENE
18	PYRROLE
19	PEPRIDIENE and TETRALINE
20	NAPHTHALINE

Efforts were made to identify these peaks , but unfortunately, even after trying about 75 pure chemicals which were expected to be present, only twenty peaks could be identified. The identified compounds are shown in Table-13. The two peaks whose behaviour was different , as mentioned above, could not be identified from the known compounds tested and further investigations are in progress to identify these peaks.

INFRA-RED STUDY :

Infra-red spectra of heavy oil and the product oils was obtained as described in analytical part. Many samples were tested but here only the spectra obtained with heavy oil and one of the light oils produced with Co-Mo catalyst will be discussed. Figures 31 and 32 show the spectra obtained with heavy oil and the sample respectively. Spectra obtained with other samples was similar except changes in peak heights. These spectra are similar to that obtained for Athabasca bitumen by Moschpedis et al.(15). Changes noticed in various bands are discussed as follow :

(a) Band at 3490 cm^{-1} : A small peak at 3490 cm^{-1} appeared for the heavy oil (Figure 31). This peak was passibly due to pyrrole or its derivatives. It disappeared on hydrotreatment when heavy oil was hydrodenitrogenated (Figure 32).

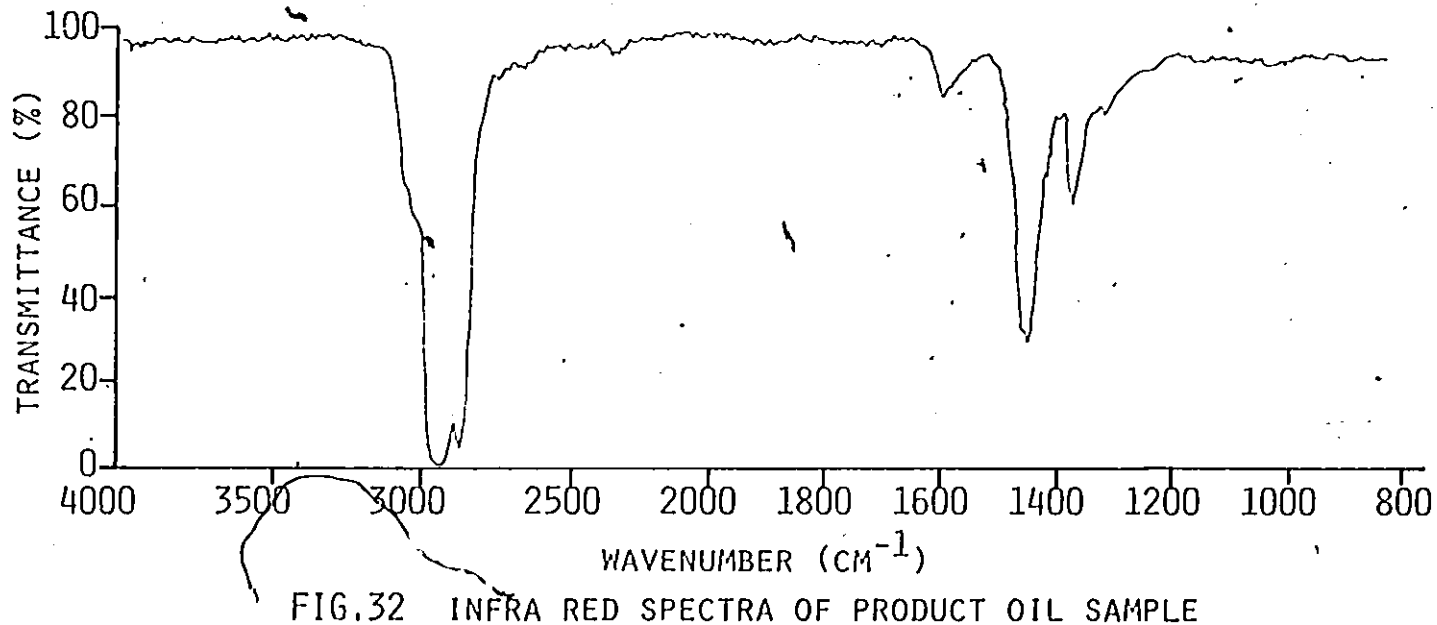


FIG.32 INFRA RED SPECTRA OF PRODUCT OIL SAMPLE

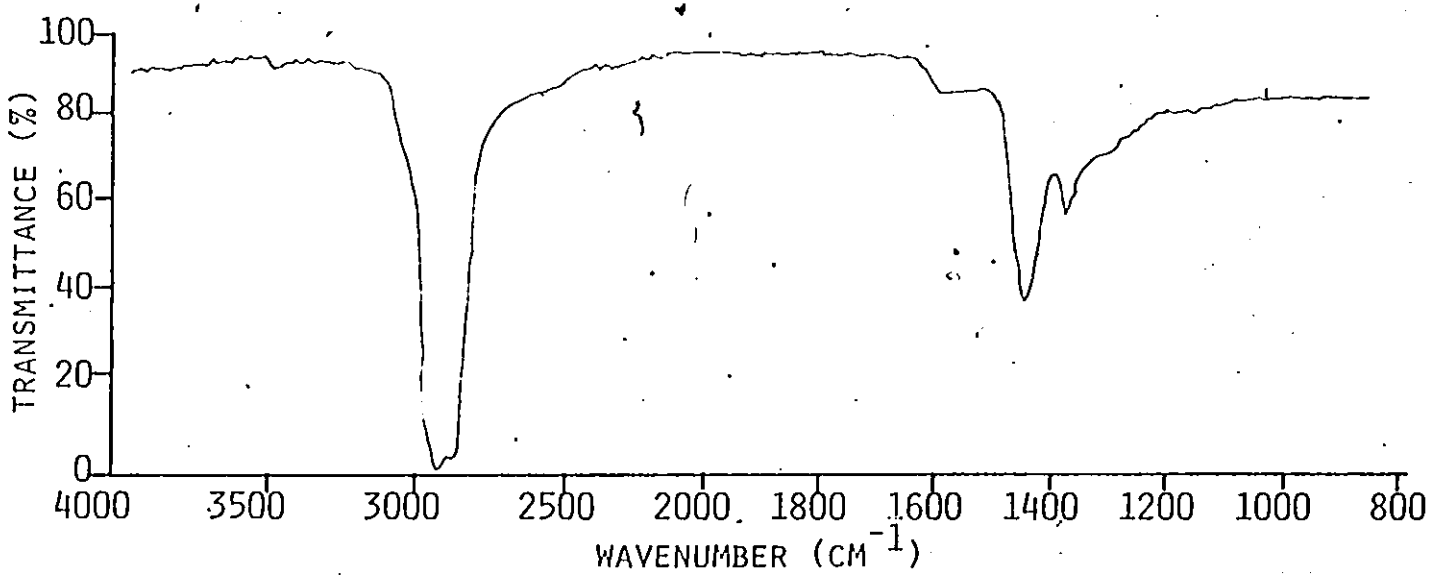


FIG.31 INFRA RED SPECTRA OF HEAVY OIL

(b) Band at 3000-2850 cm^{-1}: The broad shoulder at 3000 cm^{-1} for the heavy oil (Figure 31) increased with hydrotreating (Figure 32). This is due to an increase in the compounds containing C-H bonds. This band is due to C-H stretch (C≡C-H). The other sharp peak (3000-2850 cm^{-1}) is also due to C-H stretch.

(c) Broad band at 2600-2550 cm^{-1} : This broad band may be due to S-H (Rao (16)). A comparison of the bands in Figures 31 and 32 indicates that S-H band was reduced on hydroprocessing and that heavy oil was hydrodesulfurized.

(d) Band at 2350 cm^{-1}: Band appearing at 2350 in Figure 32 is due to H_2S . This was confirmed by gas chromatography and also by taking the infra-red spectra of H_2S in CCl_4 (0.5 wt.% in CCl_4). The absence of this band in the heavy oil (Figure 31) suggests that H_2S was not present originally but was formed only during hydrotreatment.

(e) Band at 1600-1350 cm^{-1}: The presence of aromatic ring is indicated by appearance of four bands for six numbered rings, or three, four or five numbered rings in the region (1600-1350 cm^{-1}). The increase in the intensities of the bands in this region in Figure 32 suggests an increase in the concentration of benzene or benzene derivatives due to hydrotreatment of heavy oil.

(f) Band at 1200-1100 cm^{-1} : These are due to heterocyclic compounds (Katritzky (17),Rao (16)) present in heavy oil . It is clear from comparison of Figures 31 and 32 that the intensity of this particular band was reduced to a good extent on hydrotreatment . Heterocyclic compounds present originally in the heavy oil were reduced during hydrotreating on account of hydrocracking or thermal cracking.

REMARKS :

Coke formation was observed in case of all catalysts. It was most severe in case of Ni-W catalyst. Ni-Mo and Co-Mo catalysts gave almost similar performance as far as coking was concerned. The coking occurred mainly in the upper 2 to 3 cms of catalyst zone.

5. DISCUSSIONS

This study confirms the well known fact that nitrogen is more difficult to be removed than sulfur. In this study Ni-W catalyst was found to be the best for HDS activity and Ni-Mo catalyst gave best HDN results. Co-Mo catalyst did not fare badly for both HDS and HDN . However, these results did not exactly follow the previously known trends. Speight (6) indicated that Co-Mo on alumina was best for HDS reactions and Ni-Mo best for HDN activity. Ni-W catalyst was generally known to be good for hydrogenation.

The above difference may be due to the fact that the catalysts used in this study did not have the same pore sizes. As shown in Table-11, average pore sizes of Co-Mo, Ni-Mo and Ni-W catalysts were 91, 114 and 142°A respectively. Catalyst activities did increase with increase in average pore size as indicated by many researchers (e.g., Green et al.(5), Beuther et al(18) and Minaev et al.(19)). This fact gets further confirmation from our work, as indicated by the pressure effect on various catalyst activies.

Lower average pore size of Co-Mo catalyst may be one of the reasons for its not showing best HDS activity which was otherwise expected, while high pore size in Ni-W was responsible for its giving best HDS activity. Therefore, it can be said that pore diffusion had a substantial effect

on activities of these catalysts.

Aniline point and cetane index studies have not been reported frequently. Mirza et al.(11) have reported aniline point variations with operating parameters on hydrotreatment of Tar oil fractions with Co-Mo catalyst . Our study does indicate a similar trend in aniline point changes but the difference lies in the quantums of these changes. This was expected to occur because of different origins of heavy oils used in the two studies.

Data from both HDS and HDN studies fitted quite closely to a first order reaction model :

$$\ln \frac{S_f}{S_p} = \frac{k_s}{L.H.S.V.} \qquad \text{for HDS}$$

and

$$\ln \frac{N_f}{N_p} = \frac{k_n}{L.H.S.V.} \qquad \text{for HDN}$$

where k_s and k_n are rate constants for first order HDS and HDN rate equations respectively and S_f, N_f and S_p, N_p are sulfur and nitrogen concentrations in feed and product samples respectively.

Data for the three catalysts are plotted in Figures 33 and 34. The individual k-values from the slope of lines were evaluated and are shown in Table-14.

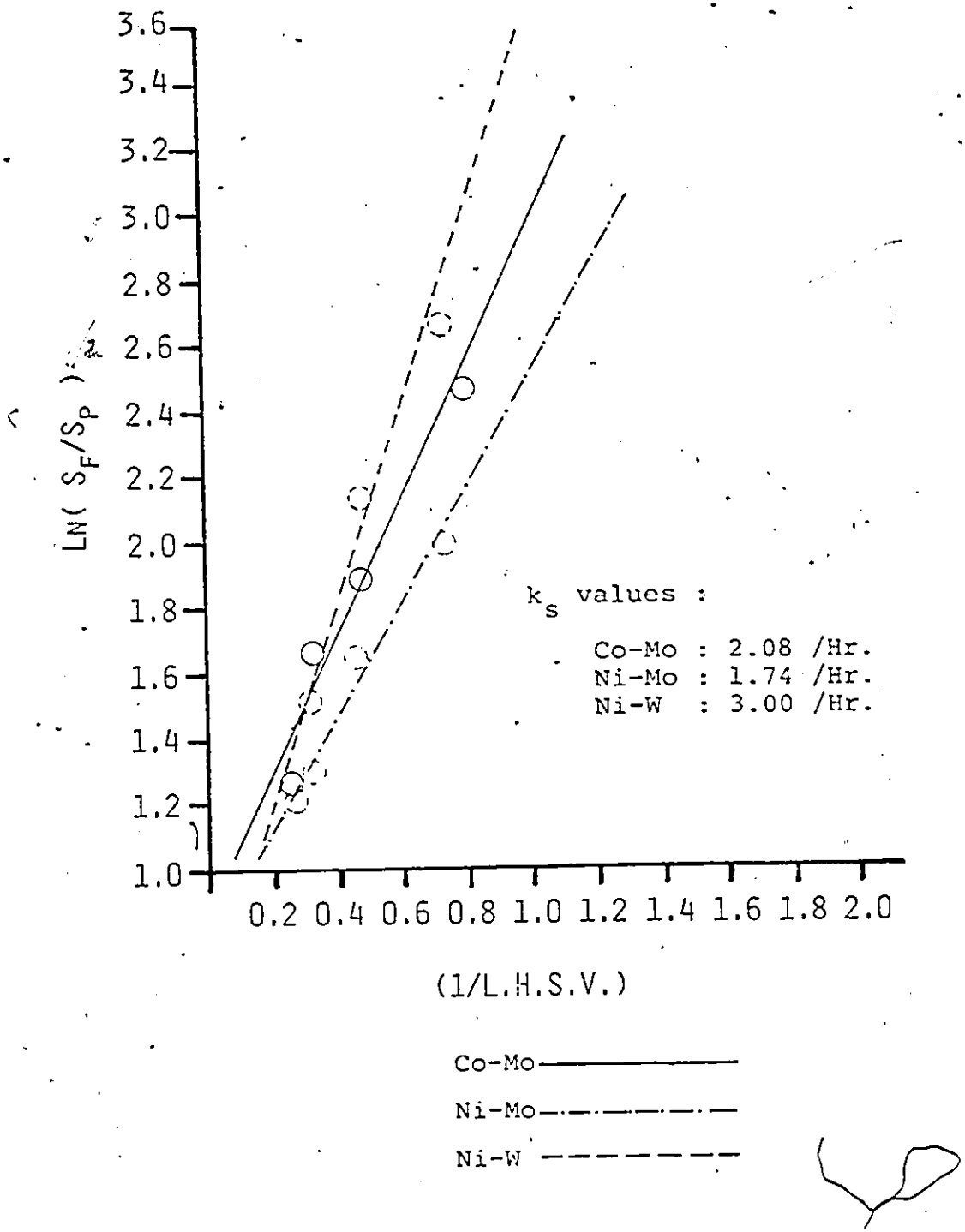


FIG.33 LN S_F/S_P VS. 1/L.H.S.V.

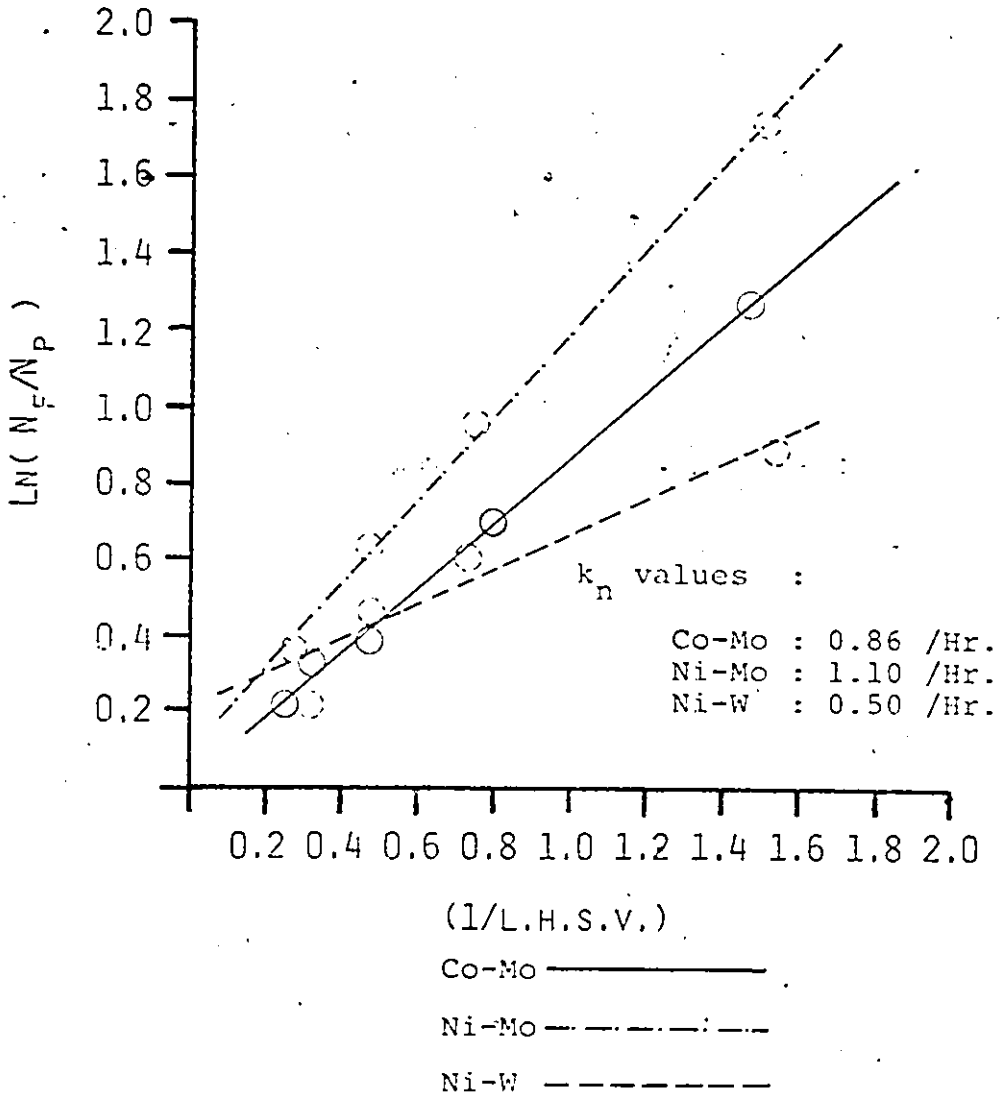


FIG.34 Ln N_F/N_P vs. 1/L.H.S.V.

TABLE-14

Evaluated rate constants for HDS and HDN activities.

Catalyst	k_s ($Hr.^{-1}$)	k_n ($Hr.^{-1}$)
Co-Mo	2.08	0.86
Ni-Mo	1.74	1.10
Ni-W	3.00	0.50

Frost et al.(9) showed the hydrodesulfurization (HDS) of Venezuelan residual fuels. They found that their HDS data with commercial cobalt molybdate on alumina catalyst, fitted the best in first order rate equations and they obtained rate constant value of 2.0 which is close to the one obtained in this study. Similar results are also reported by Speight (6).

Experimental determination of effectiveness factors involve use of very fine size particles and measurements of the reaction rates. This was not possible in this case as the feed oil involved was very viscous and would have presented operational difficulties. Other alternative was to use another size of particles and use trial and error method to calculate the effectiveness factors. This method also proved to be no good for this investigation since values

of Thiele type modulus Φ, were large. Thiele type modulus is defined as :

$$\Phi = 2 \frac{V_p}{S_x} \sqrt{\frac{k\, C^{n-1}}{\bar{r}\, D_{eff}}}$$

Expression for D_{eff} in such cases is given by Satterfield et. al.(20) as follow :

$$D_{eff} = \frac{D_b\, \theta\, e^{-4.6\lambda}}{\tau\, K_p}$$

and for bulk diffusivity D_b Wilke and Chang's equation can be used.

From these expressions it can be seen that a direct evaluation of different terms , involves a great degree of simplifying assumptions because the exact data for the heavy oil used is not available. Therefore, The outcome of such an analysis can not be expected to come close to real values. However, it is worth mentioning that the effectiveness factor values reported in literature (e.g. Ahmed (21)) for HDN and HDS reactions with catalysts similar to those used in this study, are of the order of 0.12 to 0.39 . Such low effectiveness factors reveal pore diffusional effects to dominate in all HDS and HDN activities.

The analysis of data obtained with chemically reacting flow systems requires the consideration of the interactions between momentum, heat and mass transfer processes. Isothermal operations reduce the complexity of the system to a great extent and results in the simplification of analysis. Fluid dynamic aspects to be considered in trickle bed reactors include the flow distribution, fluid hold up and back mixing effects. This particular investigation was not designed to look in to the effects of fluid dynamic parameters on the performance of trickle bed reactor. However, analysis of influence of these parameters on results are discussed in the following text.

In case of fixed bed reactors, operating in trickle bed flow mode , the gas flows more or less as a continuous phase. This particular flow pattern can result in efficient contacting of gas and liquid phases with negligible mass transfer resistance across the gas liquid interface. Transition from gas continuous to pulsing flow is also possible. In any hydrotreating operation, catalyst particles are covered with a thin layer of liquid and the reaction mechanism involves the diffusion of hydrogen through this film to the catalyst surface. Maximum diffusion area is available when all catalyst particles are wet and there are no possibilities of liquid channeling or pulsing flow (slug flow).

Consideration of the tube diameter (D_t) to particle diameter (D_p) ratio, liquid flux and the gas flux can give an insight to the flow distribution effects . In this study D_t/D_p was between 3.5 to 6 for coarse size (5 to 8 mesh) and 6 to 14.3 for smaller size (8 to 16 mesh). Higher D_t/D_p ratio (greater than 10) promotes better distribution (Porter et al. (14)). Sooter (22) and Satchell (23) in their hydro-treatment studies with raw anthracene oil in trickle bed reactor used D_t/D_p of 3.45 and varied liquid flux from 0.09 to 0.83 Kg oil/m^2 sec and observed no significant effects on heteroatom removal. The liquid flux used in this study was in the range of 0.034 to 0.24 Kg oil/m^2.sec. This suggests that the effect of flow distribution in the present study was of little importance.

The liquid flow in trickle bed reactors has been found to be well approximated with plug flow (Paraskos et al. (24)). Koros (25) also found that the flow pattern in trickle bed reactors corressponds to plug flow pattern with high degree of radial mixing. This further helps the heat and mass transfer operations occurring at the catalyst surface. To check for back mixing in trickle bed reactors, Mears (26) suggested the following criteria for assessing the back mixing effects :

$$\frac{h}{D_p} > \frac{20\ n}{B_o}\ \ln\ (C_i/C_o)$$

This criterion requires the calculation of liquid Peclet number and the assumptions required in making this calculation can be seriously questionable. Hochman and Effron (27) in their studies with nitrogen-methane system in co-current gas liquid operation in a packed bed correlated the liquid Renolds number and Peclet number. Mears (26) using this correlation suggested h/D_p value of greater than 350 in first order hydrotreating of gas oil, to have any significant axial dispersions(back mixing). In the present study h/D_p of maximum 335 was used. Therefore, it can be safely concluded that any significant back mixing was absent in the trickle bed operation in this study and the operation was very nearly a plug flow . The data obtained in this study therefore, can be simply used for reactor design in the experession:

$$\frac{1}{\text{L.H.S.V.}} = \int \frac{dC_A}{-r_A}$$

where the terms have their usual definitions.

Regarding catalyst deactivation, it was observed that activities of these catalysts did not deteriorate much during the course of the experimental runs. Activity was monitored by drawing samples with same operating conditions at different intervals (i.e., Sample Nos:1,001,101; 5,005,105; 9,009,109 and 14,014,114) and analysing them.

6. CONCLUSIONS

The following are some of the few conclusions drawn on the basis of the present work :

1. Heavy gas oil derived from Athabasca bitumen can be successfully catalytically hydrotreated to more useful lighter products in a continuous trickle bed reactor.

2. Higher temperatures (400 to 450°C) gave rise to more hydrogenolysis of heavy oil and also, it improved HDS as well as HDN activities of the three catalysts used.

3. Lower feed rates produce more of low boiling products, as also both HDS and HDN activities of the catalysts were enhanced, but higher cracking rates gave rise to more catalyst deactivation by coking.

4. Ni-W on alumina catalyst gave the best performance as far as cracking and hydrogenation activities were concerned. This catalyst was also best for HDS except that coke formation was more on this catalyst.

5. Ni-Mo on alumina catalyst gave best HDN performance but its performance in HDS was poor. Also this catalyst gave rise to more of aromatics than the other two catalysts.

6. Co-Mo on alumina catalyst gave rise to maximum amount of paraffins in product oils. It did not prove as effective as other two catalysts in cracking and hydrogenation but its performance in both HDS and HDN was average.

7. RECOMMENDATIONS

The following recommendations are made on the basis of present study for further investigations :

1. Prepare the catalysts with different percentage of active metals (i.e., Mo, W, Ni and Co) and supports of different pore sizes, to study the effect of variation of active metal concentration and pore size variation on catalyst activity.

2. To carry on the study on deactivation and coke deposition on these catalyst.

3 Efforts to identify some of the un-identified peaks on gas-chromatographs should be made which may provide a useful information to postulate the mechanistic models for hydro-desulfurization and hydrodenitrogenation reactions.

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9. APPENDIX-A

(Experimantal data)

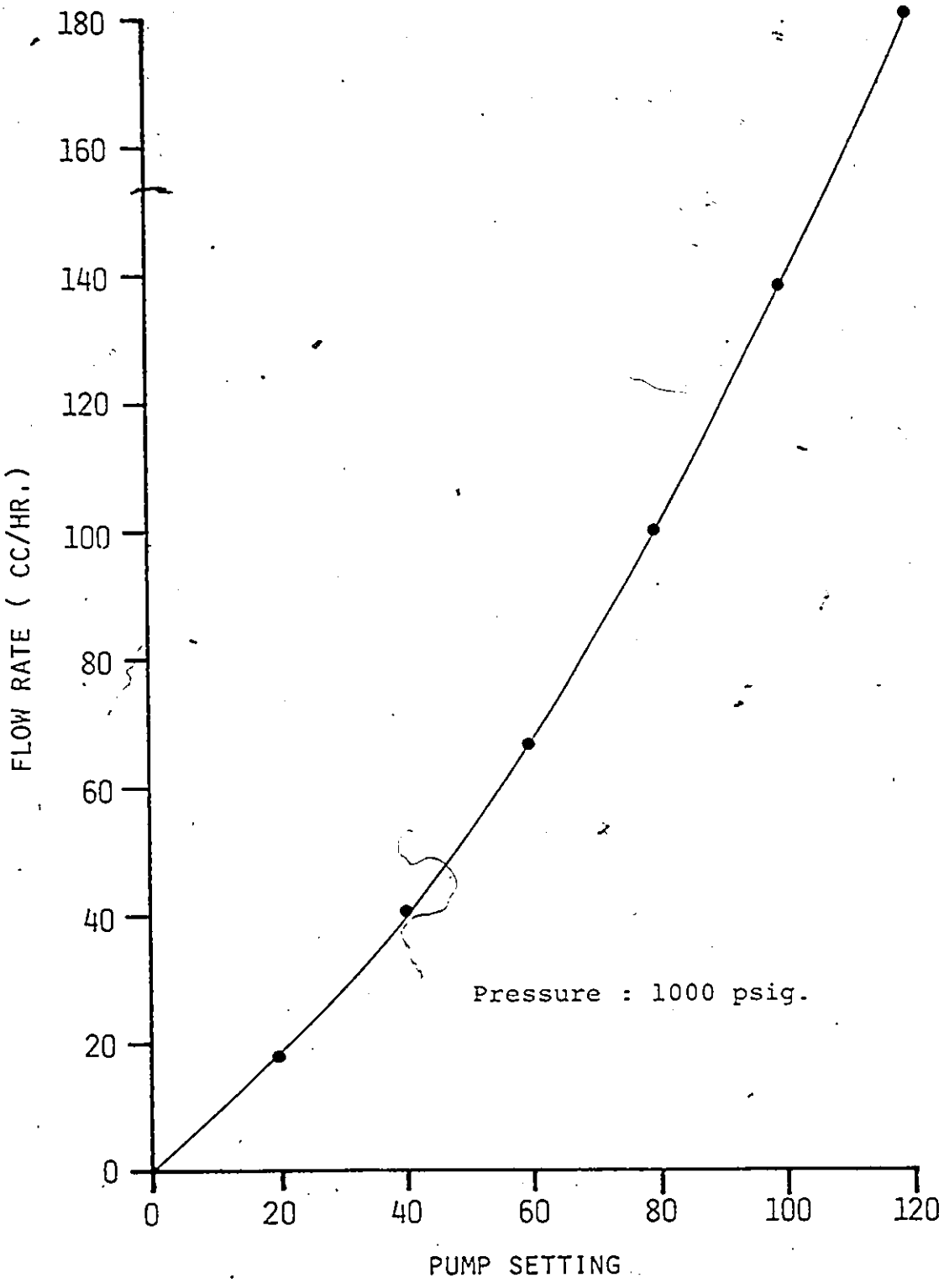


FIG.35 PUMP CALIBRATION

TABLE-15

Sample identifications and operating conditions

Temperature (°C)	Pressure (psig)	Co-Mo catalyst		Ni-Mo catalyst		Ni-W catalyst	
		Flow rate cc/Hr	Sample No.	Flow rate cc/Hr.	Sample No.	Flow rate cc/Hr.	Sample No.
300	1000	86	1	87	001	85	101
350	1000	86	2	88	002	86	102
400	1000	86	3	88	003	86	103
450	1000	86	4	87	004	86	104
300	1000	86	5	87	005	85	105
450	600	80	6	78	006	80	106
450	1400	81	7	79	007	81	107
450	1800	80	8	79	008	82	108
300	1000	86	9	87	009	85	109
450	1000	152	10	143	010	--	--
450	1000	120	11	119	011	122	111
450	1000	50	12	54	012	54	112
450	1000	27	13	26	013	26	113
300	1000	86	14	87	014	85	114

TABLE-16

Data for Co-Mo catalyst (I)

Sample No.	Density (gm/cc)	°API	Viscosity (cp)	Saybolt Universal viscosity (SUS-100°F)	Aniline point (°C)	Cetane index	Diesel index
1	0.971	14.2	143	681	48	27.6	16.8
2	0.959	16.0	122	588	45	34.4	18.1
3	0.947	18.0	85	415	50	34.0	22.0
4	0.941	19.0	47	223	48.5	38.0	22.7
5	0.972	14.1	143	681	48	27.4	16.9
6	0.937	19.6	32.4	161.8	46.8	40	22.8
7	0.926	21.3	24.2	119.8	50.4	42.8	26.1
8	0.920	22.4	22.7	117.7	51.6	45.0	28.0
9	0.972	14.1	144	691	47.7	27.3	16.6
10	0.941	18.9	48	236.6	49.2	41.3	22.8
11	0.935	19.8	31.5	157.9	47.2	42.0	23.2
12	0.906	24.7	7.1	51.4	39.0	48.6	25.2
13	0.885	28.5	2.8	36.5	26.8	36.4	29.9
14	0.973	14.1	144	691	47.5	27.3	16.6

TABLE-17

Data for Co-Mo catalyst (II)

Sample	% by wt. sulfur	%HDS	% by wt. nitrogen	%HDN	% by wt. carbon	% by wt. hydrogen	C/H ratio
1	2.53	22.6	0.53	7.0	86.31	10.46	0.69
2	1.83	44.0	0.53	7.0	86.82	10.99	0.66
3	1.0	69.4	0.46	19.3	87.28	11.25	0.65
4	0.53	83.8	0.39	31.6	87.32	11.30	0.65
5	2.55	22.0	0.54	5.3	86.32	10.47	0.69
6	0.63	80.7	0.4	29.8	87.8	11.0	0.67
7	0.57	82.6	0.28	50.8	87.53	11.29	0.65
8	0.37	88.7	0.25	56.1	87.85	11.81	0.62
9	2.56	21.7	0.55	3.5	86.34	10.47	0.69
10	0.93	71.6	0.46	19.3	87.37	10.92	0.67
11	0.62	81.0	0.41	28.1	87.54	10.95	0.67
12	0.28	91.4	0.29	50.0	87.99	11.27	0.65
13	0.2	94.0	0.16	72.0	88.06	11.75	0.63
14	2.56	21.7	0.55	3.5	86.33	10.43	0.69

TABLE-18

ASTM D-86 Distillation data for the Co-Mo catalyst.

Sample NO.	Boiling point (°C) for the % volume of distillate collected								
	IBP	5%	10%	20%	30%	40%	50%	60%	70%
1	246	290	311	332	344	346	347.5	348	-
2	230	285	305	342	346	355	363	364	364
3	200	280	301	332	343	357	364	365	365
4	53	180	263	313	333	341	342	342	343
5	248	291	312	333	344	347	348	348	-
6	69	213	280	320	340	356	370	418	460
7	55	174	259	311	332	346	356	360	360
8	53	172	245	300	325	344	357	363	-
9	247	290	311	332	345	348	348	349	-
10	72	245	295	326	347	363	373	405	-
11	65	177	246	319	341	358	373	429	-
12	55	123	170	235	290	312	329	341	344
13	45	85	115	165	200	242	260	281	320
14	247	293	312	332	345	347	348	349	-

TABLE-19

Data for Ni-Mo catalyst (I)

Sample No.	Density (gm/cc)	°API	Viscosity (cp)	Saybolt Universal viscosity (SUS-100°F)	Aniline point (°C)	Cetane index	Diesel index
001	0.964	15.3	155	743.8	50.0	31.6	18.8
002	0.953	16.8	117	567.7	52.0	35.8	21.2
003	0.939	19.2	45	222.7	50.4	35.1	23.6
004	0.911	23.8	7.8	53.8	38.1	43.6	23.9
005	0.964	15.2	157	752.3	50.4	32.0	18.7
006	0.924	21.6	12.4	71.0	41.4	38.7	23.0
007	0.903	25.2	5.04	44.2	38.0	45.2	25.3
008	0.885	28.2	3.16	37.8	37.0	46.4	27.8
009	0.964	15.2	159	761.8	50.4	32.2	18.65
010	0.929	20.8	31.5	158.9	45.6	41.4	23.7
011	0.927	21.2	17.0	90.7	44.8	41.2	23.9
012	0.898	26.0	5.04	44.2	33.9	41.2	24.2
013	0.870	31.2	1.5	32	13.5	26.2	17.6
014	0.966	15.0	163	780.8	50.5	32.5	18.4

TABLE-20

Data for Ni-Mo catalyst (II)

Sample No.	% by wt. sulfur	%HDS	% by wt. nitrogen	%HDN	% by wt. carbon	% by wt. hydrogen	C/H ratio
001	2.06	37	0.52	8.8	88.64	10.63	0.68
002	1.66	49.2	0.51	10.5	87.57	10.96	0.67
003	1.30	60.2	0.38	33.3	87.84	11.38	0.64
004	0.50	84.2	0.31	45.6	88.55	11.43	0.65
005	2.10	35.8	0.53	7.0	86.63	10.62	0.68
006	0.65	80.1	0.38	33.3	88.07	11.38	0.64
007	0.36	89.0	0.19	66.7	88.16	11.90	0.62
008	0.26	92.1	0.17	70.2	86.82	11.55	0.63
009	2.12	35.2	0.53	7.0	86.65	10.32	0.70
010	1.12	65.75	0.40	29.8	86.72	11.36	0.64
011	0.90	72.5	0.40	29.8	87.83	11.50	0.64
012	0.45	86.2	0.23	61.4	88.25	11.70	0.63
013	0.50	84.7	0.10	82.5	87.74	11.15	0.66
014	2.15	34.3	0.54	5.3	86.66	10.32	0.70

TABLE-21

ASTM D-86 Distillation data for the Ni-Mo catalyst.

Sample No.	Boiling point (°C) for the % volume of distillation collected								
	IBP	5%	10%	20%	30%	40%	50%	60%	70%
001	205	309	320	341	353	357	354	354	-
002	202	304	320	343	357	364	364	364	-
003	75	242	279	319	338	246	248	248	-
004	45	112	149	222	276	315	337	351	359
005	206	310	320	342	354	355	355	355	-
006	50	106	166	254	300	323	334	343	343
007	38	93	156	222	286	314	332	341	348
008	40	55	75	147	210	254	293	321	341
009	208	311	321	342	353	354	355	356	-
010	50	70	147	274	319	342	355	362	-
011	50	134	207	283	316	339	350	356	356
012	50	98	140	203	250	284	307	322	330
013	40	65	80	112	147	182	212	238	263
014	207	312	322	343	354	354	355	355	-

TABLE-22

Data for Ni-W catalyst, (I)

Sample No.	Density (gm/cc)	°API	Viscosity (cp)	Saybolt Universal viscosity (SUS-100°F)	Aniline point (°C)	Cetane index	Diesel index
101	0.963	15.4	165	792.7	49.3	36.8	18.6
102	0.947	18.0	64.7	316.5	51.1	39.9	22.32
103	0.934	20.0	31.5	158.1	50.0	43.4	24.4
104	0.907	24.6	8.05	54.9	40.8	44.1	25.9
105	0.963	15.4	166	797.7	49.0	36.9	18.5
106	0.929	20.8	17.7	93.65	44.2	41.4	23.2
107	0.903	25.2	7.01	51.2	43.5	45.7	27.8
108	0.891	27.4	5.56	144.7	43.1	46.03	30.02
109	0.964	15.3	168	805.7	48.8	37.0	18.34
111	0.932	20.4	26.8	135.7	47.6	43.61	24.01
112	0.894	26.8	3.98	40.5	31.8	51.03	23.92
113	0.873	30.6	1.82	32.85	11.5	29.64	16.13
114	0.964	15.3	171	822	48.7	37.1	18.31

TABLE-23

Data for Ni-W catalyst (II)

Sample No.	% by wt. sulfur	%HDS	% by wt. nitrogen	%HDN	% by wt. carbon	% by wt. hydrogen	C/H ratio
101	2.60	20.5	0.56	1.8	87.35	11.55	0.63
102	1.47	55	0.48	15.8	87.25	11.73	0.62
103	0.78	76.1	0.41	28	88.02	11.83	0.62
104	0.39	88	0.36	36.8	88.22	12.05	0.61
105	2.65	19.0	0.57	00	87.7	11.74	0.62
106	0.59	82.0	0.40	29.8	88.54	11.90	0.62
107	0.26	92.0	0.25	56.1	88.41	12.28	0.60
108	0.2	93.9	0.21	63.2	87.91	12.42	0.59
109	2.66	18.7	0.57	00	87.37	11.94	0.61
111	0.72	78	0.46	19.3	86.51	11.63	0.62
112	0.23	93.0	0.31	45.6	88.18	12.05	0.61
113	0.1	97.0	0.23	89.6	88.51	12.09	0.61
114	2.66	18.6	0.57	00	87.36	11.56	0.63

TABLE-24

ASTM D-86 Distillation data for the Ni-W catalyst.

Sample No.	Boiling point (°C) for the % volume of distillate collected								
	IBP	5%	10%	20%	30%	40%	50%	60%	70%
101	230	325	335	355	369	378	385	389	-
102	150	265	304	335	353	366	375	382	-
103	73	208	284	325	344	359	373	388	420
104	40	100	153	235	280	310	332	348	365
105	231	326	336	354	368	375	385	389	-
106	55	150	234	297	319	342	355	365	-
107	50	113	167	245	285	312	334	351	-
108	35	76	125	205	258	290	316	335	355
109	230	327	337	355	369	379	386	389	-
111	50	120	262	319	340	357	370	-	-
112	45	100	150	220	260	298	320	340	-
113	35	62	82	125	162	193	228	261	294
114	232	327	337	356	369	380	385	388	-

10. APPENDIX-B

(Sample calculations)

Density calculations :

Sample number : 008
Temperature : 22°C

Weight of empty specific gravity bottle : 8.4503 gms.
Weight of specific gravity bottle with mercury : 35.5943 gms.

Density of mercury at 22°C : 13.5409 gm/cc
Therefore volume of specific gravity bottle :

$$= \frac{35.5943-8.4503}{13.5409} = 2.0046 \text{ cc}$$

Weight of specific gravity bottle with sample : 10.2245 gms .

$$\text{Sample density} = \frac{10.2245-8.4503}{2.0046} = \underline{0.8852 \text{ gm/cc}}$$

Saybolt Universal Viscosity :

Sample number : 008
Sample density : 0.8852 gm/cc
Sample viscosity : 3.16 cp
Therefore, sample kinematic viscosity : 3.57 cst

From Table-1 of ASTM D-2161 Saybolt Universal viscosity at 100°F is read against kinematic viscosity of 3.57 cst. This value is 37.8 SUS at 100°F. For temperature correction to temperature of 22°C, correction factor is read from Table-2 which comes to be 0.9987.

Therefore Saybolt Universal Viscosity of this sample =

37.8 X 0.9987 = 37.75 Secs.

Diesel index calculation :

Sample number : 008
Sample density : 0.8852 gm/cc

This density value is converted to °API using Table B-1 of Gary (3). And the value obtained for this sample is

°API : 28.2
Aniline point of sample : 37.0°C

Therefore, Diesel index can be calculated as:

$$\text{Diesel index} = \frac{(28.2)(37.0 \times 1.8 + 32)}{100} = 27.8$$

Cetane index calculation :

Sample number : 104
°API : 24.6
Mid range boiling point from ASTM distillation : 332°C
=629.6°F

ASTM D976 method for cetane index calculation has already been described earlier. Using those equations :

$$x = 97.83(\ln 629.6)^2 + 2.2088(24.6)(\ln 629.6) + 0.01247(24.6)^2 - 423.51(\ln 629.6) - 4.7808(24.6) + 419.59$$
$$= 42.686488$$

Therefore cetane index $= 0.49083 + 1.06577(42.686488) - 0.0010552(42.686488)^2$

$= 44.06$

Evaluation of rate constants :

Follwoing is a example of calculation of rate constant for Ni-W catalyst in case of hydrodesulfurization reaction :

In figure 33 ln (S_f/S_p) has been plotted against 1/L.H.S.V. The slope of this line is determined by reading the co-ordinates of two points on this line and for this line slope is :

$$= \frac{2.85 - 1.11}{1.2 - 0.2} = 1.74$$

Therefore, the rate constant for this catalyst is : 1.74 $hr.^{-1}$

DETAILS OF BACK PRESSURE REGULATOR

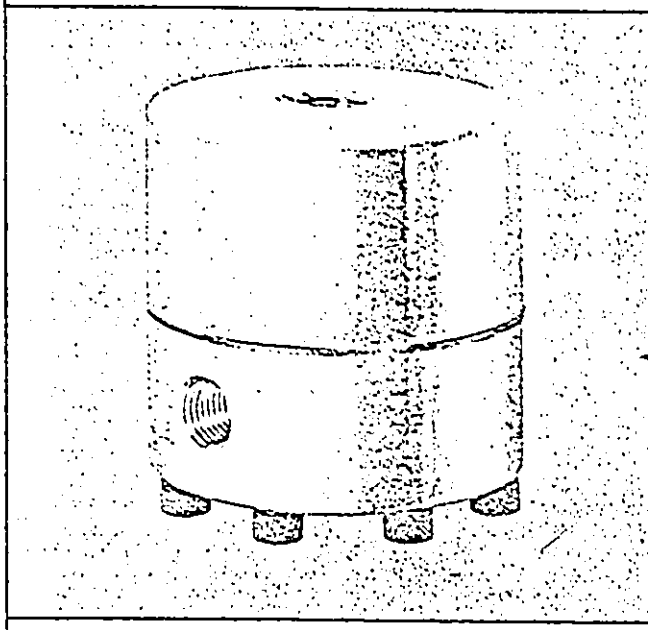
The Mity-Mite for back pressure regulating service is an extremely simple, angle pattern, regulator having only one moving part. The diaphragm senses upstream pressure on its underside and is balanced by dome pressure on the upper side. In addition the diaphragm serves as the valve, closing on a nozzle which is an integral part of the body. This regulator acts to limit upstream pressure and has no control over outlet pressure. Unlike relief valves, this unit is designed for continuous throttling service, operating between two pressure levels to maintain the upstream system pressure.

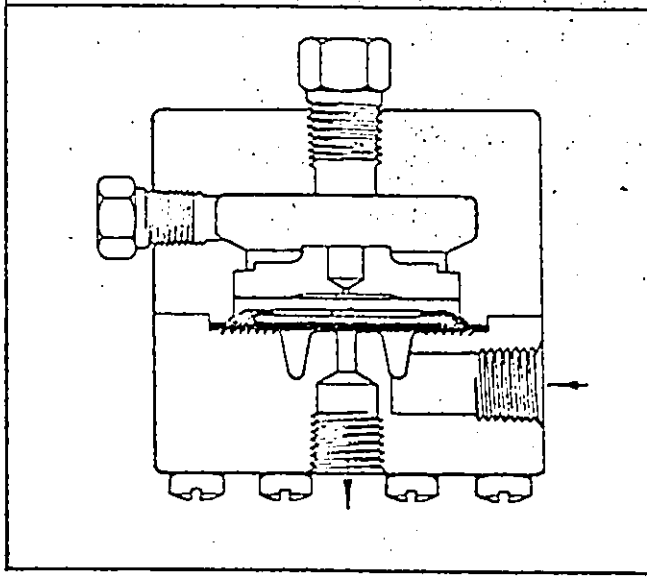
All Mity-Mite back pressure regulators are of the externally dome loaded type and may be used to control either gases or liquids providing such fluids do not react chemically on the regulator parts which contact the flow stream. The dome must be charged with a compressible gas to a pressure approximating the desired back pressure setting. Two connections are provided in the dome. One is intended for the attachment of a gauge and the other is for dome charging purposes. An assortment of double needle valve loading assemblies are available for this purpose.

OPERATION

The back pressure Mity-Mite operates on the principle of balanced pressures. Since the effective diaphragm area exposed to upstream pressure is slightly less than that exposed to the dome pressure, to achieve balance, the actual back pressure setting will always be slightly *higher* than the dome pressure. Therefore, the dome must be loaded to a pressure slightly *lower* than the pressure to be maintained in the upstream line.

When the inlet line pressure tends to exceed the back pressure setting the diaphragm is lifted off the nozzle permitting flow thru the outlet of the valve body. In actual service, the regulator will assume a throttling condition to maintain the set pressure regardless of the flow rate within the capacity limitations of the regulator.



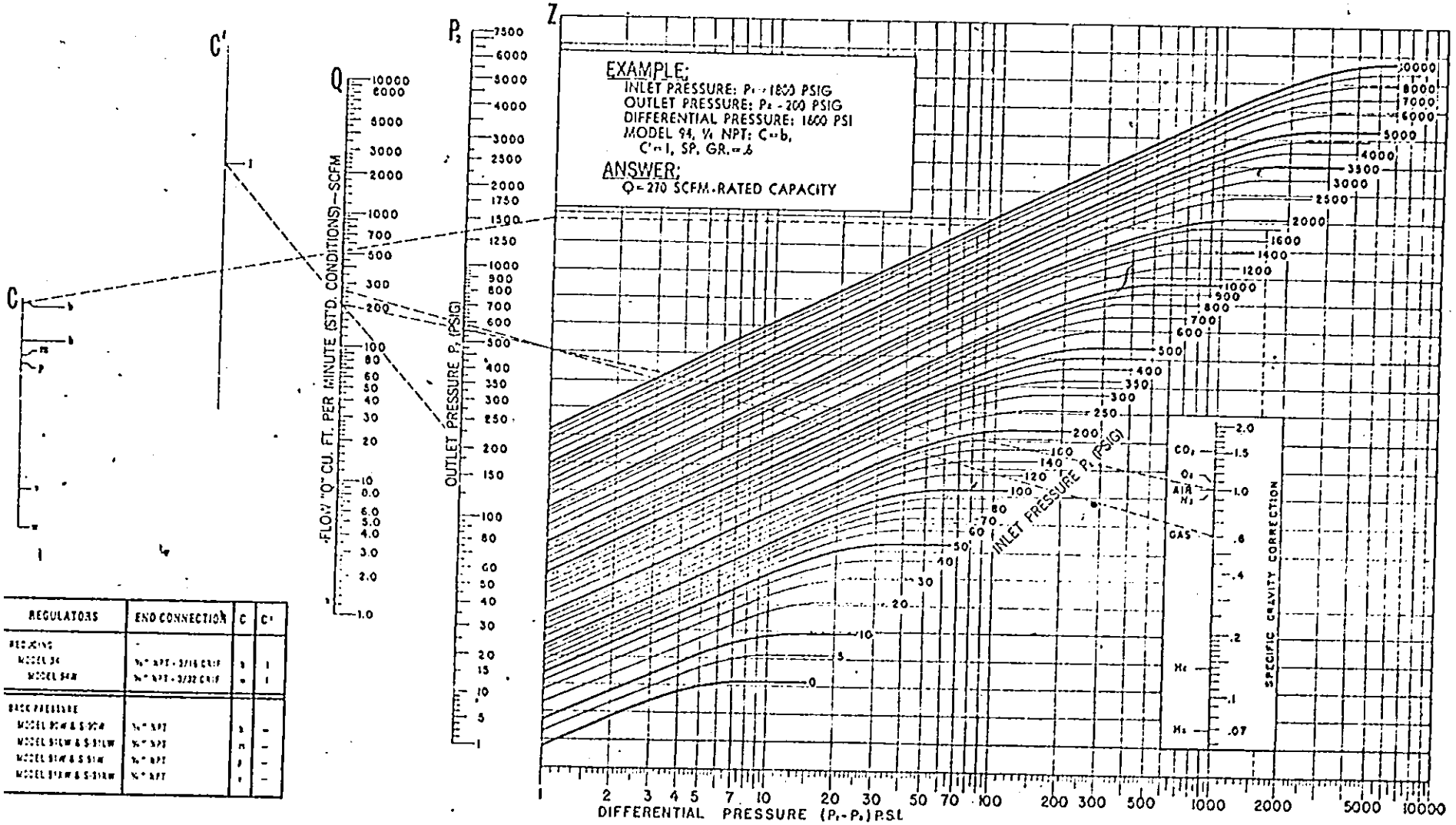


Pressures: Ranging to 3000 psi

Size: ¼" FNPT

Materials: Body and dome: Aluminum alloy or T-316 stainless
Diaphragm: Nitrile rubber or Teflon

Temperature ratings: Model 90 series −0°F to +165°F
Model 91 series −65°F to +200°F



REGULATORS	END CONNECTION	C	C'
REDUCING			
MODEL 94	¼" NPT - 3/16 CNIF	b	1
MODEL 94W	¼" NPT - 3/32 CNIF	a	1
BACK PRESSURE			
MODEL 90W & S-90W	¼" NPT	b	—
MODEL 91W & S-91W	¼" NPT	a	—
MODEL 91W & S-91W	¼" NPT	b	—
MODEL 91W & S-91WW	¼" NPT	a	—

HOW TO USE CAPACITY CHART

1. Determine the following quantities:*
   - (a) Minimum expected inlet pressure P_1 at the Regulator (or desired inlet pressure—if a Back Pressure Regulator) in pounds per square inch gage, taking into account pipe line drop if appreciable.
   - (b) Desired outlet control pressure P_2 in pounds per square inch gage (or maximum expected discharge pressure—if a Back Pressure Regulator).
   - (c) Minimum anticipated differential pressure ($P_1 - P_2$). That is, the differences in pressure as determined in (a) and (b). If the minimum differential pressure is known to exceed one half the absolute inlet pressure, the exact value of the differential pressure need not be known.
   - (d) End connection size and type for the regulator model under consideration.
2. On the chart locate the pressure curve corresponding to the minimum inlet pressure, and on the differential pressure scale locate the point corresponding to the minimum differential pressure. From this point on the differential pressure scale, follow a vertical line to the point of intersection with the previously located inlet pressure curve. From this intersection follow a horizontal line to an intersection with line Z.
3. From the table find the value of C corresponding to the basic model number of the regulator selected and the desired end connection size and type. Locate this value on line C. Using a straight edge, draw a line connecting this point on line C with the point on line Z previously located. Note the intersection of this line on scale Q.
4. From the table find the value of C' for the same model—and connection size—and type as in 3 above. Locate this value on line C'. Draw a line connecting this point on line C' with a point on line P_2 corresponding to the outlet pressure as determined in 1 (b) above. Note the intersection of this line on scale Q.
5. The *lesser* of the two values of Q, as determined above in steps 3 and 4, is the maximum capacity of the regulator, under the above conditions, in cubic feet of free air per minute at standard conditions of 60°F and 14.7 psia.
6. If the fluid is a gas other than air, the flow rate must be corrected for specific gravity. To accomplish this, draw a straight line from the point on scale Q determined in step 5, to 1.0 on the specific gravity correction scale. Using the intersection of this line with vertical line Z as a turning point, draw a straight line connecting the value of specific gravity of the gas being considered to a new intersection with scale Q. This intersection gives the maximum capacity of the regulator in cubic feet of free gas per minute at standard conditions.

*In determining the capacity of *Back Pressure Regulators* omit step 4 in the above procedure.