THE EFFECT OF ACID WASHING ON THE HYDROTREATMENT OF SOLVENT REFINED COAL LIQUIDS

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PREFACE

The major objective of this study was to investigate the effect of a decrease in nitrogen concentration on the catalytic hydrotreatment of Solvent Refined Coal (SRC) liquids. Two coal liquids were used: SRC Process Solvent and SRC II Heavy Distillate. Nitrogen compounds were extracted using dilute acidic solutions. The effects of temperature, acid concentration and acid solution/oil volume ratio on the removal of nitrogen from the liquids were investigated. The raw SRC liquids, as well as liquids subjected to acid extraction, were hydrotreated in a trickle bed reactor at temperatures of 399 C and 413 C at 10.34 MPa. Two catalysts were used: HDN-30 (American Cyanimid Co.) and Shell 324. The products were analyzed for nitrogen, sulfur, hydrogen, and carbon. Selected samples, as well as the feedstocks, were subjected to ASTM distillation. Representative samples were also analyzed for basic nitrogen. The results of the above analysis were used to compare the hydrotreatment runs made with acid washed feed with that of the raw feed. The effect on catalyst deactivation was then assessed.

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INTRODUCTION

Energy for consumption in the United States is presently derived from five major domestic sources: crude oil, natural gas, coal, hydroelectric and nuclear. Presently, high prices for crude oil and natural gas, as well as economic recession have temporarily reduced the demand for energy from all sources. However, demand is expected to increase at approximately one percent over the next ten years.

Foreign supplies of crude oil have recently declined from the peak import levels of 1978. However, the U. S. is nowhere near energy independence at present and will not be in the immediate future. If present trends continue, imported oil will account for nearly fifty percent of the domestic oil consumption by 1990. Production of domestic crude oil and natural gas has not increased significantly in spite of dramatic increases in exploration and development efforts during the latter part of the last decade. Those efforts have presently decreased to one third of the peak level of 1981.

Nonconventional sources of energy such as coal derived liquids represent a domestic source of liquid fuels and petrochemical feedstocks that will inevitably be needed to supplement declining production of domestic crude oil. However, the high aromatic content and heterocompound concentration found in coal derived liquids makes it necessary to upgrade the liquids before processing as a petroleum substitute or use as a boiler feedstock.

Upgrading processes developed at present are typically based on catalytic hydrotreatement. Rapid catalyst deactivation during hydrotreatment has limited the success of the process and efforts are presently being undertaken to develop multifunctional catalysts required for the extreme conditions of coal derived liquid hydrotreatment. However, a basic understanding of the mechanisms of catalyst deactivation is necessary. This study is part of a larger ongoing investigation at Oklahoma State University with the objective of providing necessary information for catalyst development. The objective of this study was to investigate the role of basic nitrogen compounds in catalyst deactivation and was undertaken in two stages:

1. Investigation of the feasibility of removing basic nitrogen compounds by acidic extraction.

2. Hydrotreatment of raw and acid washed coal derived liquids with a commercial catalyst to investigate the effects of basic nitrogen removal on catalyst deactivation measured by the rate of hydrogenation, hydrodenitrogenation, and hydrodesulfurization.

Available literature pertaining to the characterization of coal derived liquids, solubility of aromatic hydrocarbons, and extractive procedures for coal derived liquids and other synfuels was reviewed to provide a basis for the

investigation. Acid extractions were conducted on two Solvent Refined Coal (SRC) liquids to assess the feasiblilty of extracting basic nitrogen compounds. The same liquids were hydrotreated in a fixed bed reactor using two commercial catalysts to assess the effect of nitrogen removal on catalyst deactivation. Up to 38% of the total nitrogen was removed by acidic extraction. Removal varied with changes in temperature, acid concentration and acid/oil volume ratio. Significant differences were observed in hydrotreated products of the raw and acid washed SRC liquids. A reduction in the nitrogen concentration was observed in the hydrotreatment products of both acid washed liquids over the raw liquids. However, acid washing appeared to decrease the rate of deactivation with one liquid but not the other. In general, acid washing improved the quality of the hydrotreated products. However, poisoning by basic nitrogen compounds does not appear to be the primary deactivation mechanism in this study.

CHAPTER II

THEORETICAL DISCUSSION

The first part of this investigation deals with removal of basic nitrogen compounds from Solvent Refined Coal (SRC) liquids by extraction. Literature will be reviewed pertaining to characterization of coal derived liquids in general and of SRC liquids specifically where possible. To gain insight into the feasibilty of extraction of nitrogen compounds the literature pertaining to solubility polycyclic aromatic compounds will be reviewed as well as previous studies dealing with extraction of coal derived liquids.

The second part of the investigation concerns catalyst deactivation during hydrotreatment. Relevant literature on hydrogenation kinetics will be reviewed. A trickle bed reactor was used in this study and has been used successfully by previous investigators at Oklahoma State University (Chang, 1982; Ahmed, 1979; Bhan 1981; Chan 1982). The effectiveness of the trickle bed reactor as well as literature pertaining to mechanisms of deactivation will be reviewed.

Characterization of Solvent Refined Coal Liquids

Composition

Coal derived liquids are complex mixtures containing several thousand compounds. Solvent Refined Coal (SRC) liquids typically contain 1-2% nitrogen, about 1% sulfur, 2-8% oxygen and 5-8% hydrogen. The composition of all coal derived liquids will vary due to the heterogeneous nature of the parent coals, the type of liquefaction processes, and the severity of the processes.

SRC liquids are highly aromatic. Later and co-workers (1981) separated an SRC II liquid into seven fractions to facilitate a detailed analysis. Only 5.5% of the total liquid was aliphatic hydrocarbons. The remainder of the liquid was separated into neutral, nitrogen and hydroxyl polycyclic aromatic compounds with concentrations of 56.6, 20.0 and 14.0 percent respectively. Non-heterocyclic aromatic hydrocarbons comprised the largest group in the neutral fraction and in the liquid as a whole.

Shultz et al. (1977) also found a low concentration of saturates (4.1%) in a Synthoil liquid. Cogswell and Lathem (1978) investigated a Synthoil liquid which had been processed at the same conditions (27.5 MPa, 400 C) as that in the Shultz study and found 10 -13 % saturates.

Coal derived liquids are highly polar. Shultz and coworkers, in the study mentioned above, found 10.2% bases and 6.3% acids in the Synthoil. Cogswell and Lathem found

20% bases and 30% acids. Approximately 75% of the bases were nitrogen compounds and 85% of the acids were phenolic compounds.

The ratio of acids to bases may be important if the liquid is to be contacted with water. Papirer et al. (1982) investigated the asphaltene fractions of several crude oils for emulsion forming abilities in water. They found that the asphaltenic fraction with the highest emulsion forming capability was the liquid with the highest acid/base imbalance and low hydrogen bonding ability.

Nitrogen compounds comprise a significant portion of SRC liquids. Acidic, basic and neutral nitrogen compounds have been reported in various coal derived liquids. Shultz and co-workers (1977) found basic and pyrolic nitrogen in the ratio of 3:1 in the Synthoil liquid and identified 185 molecular formulas of nitrogen compounds. Most of those formulas represent more than one isomer. Bodzek et al. (1978) investigated the asphaltene fraction of two hydrogenated coal extracts and a hydrogenated coal tar and found the basic fraction to contain 60% of the total nitrogen present.

Novotny et al. (1980) analyzed an SRC recycle solvent and identified 41 basic nitrogen compounds. Two compound types were reported to be predominant: a) alkylated quinolines, and b) cyclopentaquinolines. Schiller (1977) found 67.7 - 88.8% of the total nitrogen compounds in four SRC solvents to be two and three ring compounds with quinolines and tetrahydroquinolines predominating.

A recent study by Later et al.(1981) has provided a detailed characterization of SRC II Heavy Distillate. Nitrogen compounds identified were mostly two, three and four ring compounds and are listed in Table I. Alkylated quinolines, benzoquinolines and carbozoles were predominant.

Sulfur compounds generally comprise a smaller fraction of the total liquid than nitrogen compounds. Later and co-workers (1981) determined that less than one percent of the total SRC Heavy Distillate was sulfur compounds. A knowledge of the sulfur compound types is essential, however, for development of multifunctional catalysts for coal liquids. Willey and co-workers (1981) analyzed the sulfur compounds in SRC I and SRC II liquids and found primarily benzothiophenes, dibenzothiophenes, phenanthro [4,5-bcd]thiophenes. Four ring sulfur compounds predominated with several five ring compounds identified. The results of that study are listed in Table II.

Very few studies have been directed toward characterization of oxygen compounds in SRC liquids. Fruchter et al. (1977) found phenols, cresols, xylenols and several akylated derivitives in an SRC liquid. Later and co-workers reported a strong presence of hydroxyl functional groups and very little carbonyl oxygen in the SRC II liquid mentioned above. Parent compounds identified were indanols, hydroxybiphenyls, hydroxyfluorenes and naphthylphenols.

In summary, SRC liquids are highly aromatic mixtures

TABLE I

NITROGEN COMPOUNDS IN SRC HEAVY DISTILLATE
(Later et al., 1981)

MOLECULAR WEIGHT	COMPOUND
145	*C_2 INDOLE
159	C_3 INDOLE
173	C_4 INDOLE
171	TETRAHYDRACARBAZOLE
167	CARBAZOLE AND ISOMERS
181	C_1 CARBAZOLE
195	C_2 CARBAZOLE
209	C_3 CARBAZOLE
223	C_4 CARBAZOLE
237	C_5 CARBAZOLE
217	BENZACARBAZOLE
231	C_1 BENAZCARBAZOLE
245	C_2 BENZACARBAZOLE
143	NAPTHYLAMINE
169	AMINOBYPHENYL
183	C_1 AMINOBIPHENYL
197	C_2 AMINOBIPHENYL
181	AMINOFLOURENE
179	BENZOQUINOLINE
193	C_1 BENZOQUINOLINE
193	AMINOPHENANTHRENE
207	C_2 BENZOQUINOLINE
207	C_1 AMINOPHENANTHRENE
221	C_3 BENZOQUINOLINE
235	C_4 BENZOQUINOLINE
233	TETRAHYDRONAPTHOQUINOLINE
217	AMINOPYRENE
217	AMINOFLOURANTHENE
229	NAPHTHOQUINOLIN
231	C_1 AMINOPYRENE
231	C_1 AMINOFLUORANTHENE
157	C_2 QUINOLINE
171	C_3 QUINOLINE
185	C_4 QUINOLINE
199	C_5 QUINOLINE
183	TETRAHYDRODQUINOLINE
179	ACRIDINE
197	C_1 TETRAHYDROQUINOLINE

TABLE I (Continued)

MOLECULAR WEIGHT	COMPOUND
193	C_1 BENZQUINOLINE
203	AZAFLUORANTHENE
207	C_2 BENZQUINOLINE
221	C_2 BENZQUINOLINE
203	AZAPYRENE
217	C_1 AZAPYRENE
217	C_1 AZAFLUORANTHENE
229	NAPHTHOQUINOLINE

*C_1, C_2...= METHYL, ETHYL... ETC.

TABLE II

SULFUR COMPOUNDS IN SRC I AND SRC II LIQUIDS
(Willey et al., 1981)

COMPOUND
BENZOTHIOPHENE
2,3-DIHYDROBENZOTHIOPHENE
C_1-DIHYDROBENZOTHIOPHENE
C_1-BENZOTHIOPHENE
3-METHYLBENZOTHIOPHENE
C_2-DIHYDROBENZOTHIOPHENE
5-EHTYLBENZOTHIOPHENE
C_2-BENZOTHIOPHENE
DIBENZOTHIOPHENE
NAPHTHO[2,1-b]THIOPHENE
C_1-DIBENZOTHIOPHENE
C_2-DIBENZOTHIOPHENE
PHENANTHRO[4,5-bcd]THIOPHENE
C_3-DIBENZOTHIOPHENE
C_1-PHENANTHRO[4,5-bcd]THIOPHENE
BENZO[b]NAPHTHO[2,1-d]THIOPHENE
PHENANTHRO[1,2-b]THIOPHENE
C_1-BENZO[b]NAPTHO[2,1-d]THIOPHENE

containing several thousand individual compounds and isomers. Nitrogen, sulfur and oxygen compounds comprise a significant portion of the liquids with nitrogen and sulfur usually present in heterocyclic compounds. Acidic, basic and neutral nitrogen compounds have been identified in various coal derived liquids with basic nitrogen compounds predominating.

Solubility Behavior of Aromatic Hydrocarbons

A knowledge of solubility behavior of polycyclic aromatic hydrocarbons is essential for the development of extractive procedures upgrading of coal derived liquids. The available information is, however, generally insufficient. Most of the available solubility data concerns lower molecular weight aromatics and very few data are reported for heterocyclic aromatics. Multicomponent aromatic solubility data are rare. Recent interest in the effect of oceanic oil spills has sparked a more vigorous investigation of the subject.

Nearly all polycyclic aromatic hydrocarbons investigated are soluble in water although most are soluble only to a small extent. Several investigators at have modeled solubility behavior as a function of variables such as temperature, carbon number, molar volume, normal boiling points, and molecular lengths. These correlations are based on binary and ternary systems and are of little value when dealing with multifarious mixtures such as coal derived liquids. The solubility data for 32 polycyclic aromatic hydrocarbons (non-heterocyclic) determined by Mackay and

Shiu (1977) are presented in Table III. The data indicate a general decrease in solubility with increasing molecular weight. Compounds with a carbon number greater than fourteen have solubilities less than one mg/l. Many nitrogen compounds are soluble in water due to the effect of hydrogen bonding. Heterocyclic amines are generally less soluble than other amines and also appear less soluble with increasing molecular weight. Mahaffee (1981) reviewed aqueous solubility data for nitrogen compounds and the data for some the parent compounds are listed in Table IV. The data indicate that solubility of aromatic amines follow no specific trends and prediction of solubilities difficult where the data is absent. However, basic nitrogen compounds form acid salts readily and are generally quite water soluble (Solomons, 1978).

Several general trends have been observed in non-heterocyclic aromatic solubility which are noteworthy. The solubility of aromatic hydrocarbons tend to decrease with decreasing temperature. May (1981) measured solubility of 11 polycyclic aromatic hydrocarbons and found a logarithmic decrease in solubility with decreasing temperature. This trend has been confirmed by other observers (Eganhouse and Calder, 1976). Paraffinic hydrocarbons have shown a decrease in solubility with increasing temperature over certain temperature ranges (Polak et al., 1973). Aromatic hydrocarbons show a general trend of a decrease in solubility with increasing carbon number, molar volume, and molecular length (Klevins,

TABLE III

POLYNUCLEAR AROMATIC HYDROCARBON SOLUABILITIES IN WATER
(Mackay and Shiu, 1977)

COMPOUND	SOLUABILITY (mg/l @ 25 C)
Indan	109.1
Naphthalene	31.7
1-methylnaphthalene	28.5
2-methylnaphthelene	25.4
1,3-dimethylnaphthalene	8.0
1,4-dimethylnaphthalene	11.4
1,5-dimethylnaphthalene	3.4
2,3-dimethylnaphthalene	3.0
2,6-dimethylnaphthalene	2.0
1-ethylnaphthalene	10.7
1,4,5-triethylnaphthalene	2.1
Biphenyl	7.0
Acenaphthlene	3.9
Fluorene	2.0
Phenanthrene	1.3
Anthracene	0.073
2-methylanthracene	0.039
9-methylanthracene	0.261
9,10-dimethylanthracene	0.056
Pyrene	0.135
Fluoranthene	0.260
1,2-benzofluorene	0.045
2,3-benzofluorene	0.0020
Chrysene	0.0020
Triphenylene	0.043
Naphthacene	0.00057
1,2-benzanthracene	0.014
7,12-Dimethyl-1,2-benzathracene	0.061
Perylene	0.0004
3,4-benzopyrene	0.0038
3-methylcholanthrene	0.0029
Benzo[g,h,i]perylene	0.00026
Coronene	0.00014

TABLE IV

SOLUBILITY OF NITROGEN COMPOUNDS IN WATER
(Mahaffee, 1981)

COMPOUND	SOLUABILITY (25 C)
Acridine	50 ppm
Analine	36600 ppm
Carbazole	1.67 ppm
Indole	1850 ppm
Isoquinoline	4545 ppm
Pyridine	Miscible
Pyrrole	80000 ppm
Quinoline	6666 ppm

1950).

Multicomponent solubility behavior deviates unpredictably from single component solubility. Eganhouse and Calder (1976) found that naphthalene enhanced the solubility of biphenyl but had no effect on phenanthrene. Biphenyl and phenanthrene exhibited mutual solubility reduction. When all three were combined, even larger solubility reductions occurred. This would indicate that the solubility of any individual component from a multicomponent mixture would be highly dependent upon the composition of the mixture. Solutions of electrolytes can either enhance or inhibit the solubility of aromatic compounds. This phenomenon is termed salting in or salting out. Strachan et al. (1980) observed the salting out effect at low concentrations of aqueous sulfuric acid. The salting out effect has also been observed in solutions of sea water.

In summary, the aqueous solubilities of aromatic nitrogen compounds range from completely miscible to insoluble. Basic nitrogen compounds form acid salts, however, and are generally quite soluble. Most non-heterocyclic aromatic compounds are slightly soluble in water and show decreasing solubility with decreasing temperature, increasing molecular weight, molar volume and molecular length.

Extractive Processes for Coal Derived Liquids

The use of extractive processes to improve liquid quality has been studied on coal tars and shale oils as well as coal derived liquids. Reductions of acids, bases, and metals concentrations have been reported. Experiments with coal tars have dealt primarily with the removal of tar acids. Cloke (1978) reported mixing ten percent hot caustic soda with the naphthalene fraction of a coal tar to reduce the tar acid concentration from 7-8% to 0.5%. Similarily, the carbolic fraction was washed with cold caustic soda followed by washing with sulfuric acid. A similar process reported using two normal caustic soda-sodium sulfate to extract tar acids from a wider boiling range of tars than that of caustic soda alone (Holdsworth and Holmes, 1978).

Mirza and co-workers (1965) washed a low temperature coal tar (boiling range - 250 to 300 C) with ten percent sodium hydroxide followed by a wash with sulfuric acid. The sulfur concentration was reduced by 13% to 0.36 weight percent and the nitrogen concentration was reduced by 55% to 0.37 weight percent. Following the extractions the liquids were hydrotreated at several temperatures and pressures using a cobalt molybdenum catalysts and a nickle tungsten sulfide catalyst. A significant improvement in hydrodesulfurization was reported with both catalysts. However, a slight decrease in denitrogenation was reported with the washed liquid relative to the unwashed with the cobalt molybdenum catalyst and a 20% increase in denitrogenation activity was reported with the nickle-tungsten sulfide catalyst.

Extractive procedures have been used on shale oil both prior to hydrotreatment and following hydrotreatment upgrading. Curtin et al. (1978) used a caustic wash to remove arsenic prior to hydrotreatment. Up to 50% of the arsenic was removed using a continuous process. Moore and co-workers (1982) used batch and continuous acidic extractions as part of a shale oil upgrading process. After hydrotreatment, the product was sent to an extractor with a portion of the stream routed through a catalytic cracker. Samples from the extractor were analyzed following three feed conditions: a) no portion of the feed had passed through the catalytic cracker, b) a mixture of cracked and uncracked feed, and c) all the feed had passed through the cracker. Very little difference in the nitrogen concentrations was observed between the three feed conditions even though the concentration in the cracked feed was reduced by 14%. A maximum nitrogen removal of 65% was observed using an acid concentration of 41%. Robinson (1979) used sulfuric acid and clay to reduce the level of nitrogen in hydrotreated shale oil in order to meet military fuel requirements. A reduction of 99% to 0.0032% was reported using the acid-clay treatment.

Attempts to upgrade coal liquefaction products by extraction are similar to experiments with shale oil. Lin and Holy (1978) used sulfuric acid in concentrations of 5, 50 and 90 percent to extract basic nitrogen from four coal derived liquids. A maximum of 93% total nitrogen removal was observed using the 90% sulfuric acid. An increase in removal occurred with increasing acid concentration and increasing acid solution/oil ratio.

Dry hydrogen chloride was used by Schneider et al. (1979) as part of a catalytic hydroliquefaction process. Removal of 87% of the total nitrogen was achieved yeilding a product with less than 0.1% nitrogen.

Removal of phenolics has been reported using four weight percent ammonia (Tiwari et al., 1978) in a continuous counter-current operation. 100% of the phenol, 86% of the cresols and 35% of the xylenols were removed in three stages. Practically no higher phenols were removed.

Hydrotreatment of Coal Derived Liquids

Trickle Bed Reactors

Trickle bed reactor systems have been used successfully in previous studies at Oklahoma State University for hydrotreatment of coal derived liquids (Chang, 1982; Chan, 1982; Bhan, 1981; Ahmed, 1979; Sivasubramanium, 1977). Ideal plug flow is generally assumed in trickle bed operations, however, deviation from ideal behavior can occur due to liquid maldistribution, incomplete catalyst wetting, axial backmixing and diffusion resistance. These deviations have been discussed in the studies listed above.

Satterfield (1975), in a review of trickle bed reactors, reported that a significant fraction of the liquid migrates toward the wall and effectively bypasses the catalyst in narrow reactors typically encountered in a laboratory. The fraction may be as much a 60% with a ratio of the reactor diameter/particle diameter of ten. Satterfield and Ozel (1973) observed a tendency of the liquid to flow in rivulets down through the catalyst bed.

Liquid holdup, defined as the volume of liquid present per volume of empty reactor, is used to express the effectiveness of liquid catalyst contact. Henry and Gilbert (1973) proposed that the reaction rate is proportional to the liquid holdup and proposed the following relationship:

$$\ln C_o/C_i \propto -h^{1/3} (LSHV)^{-2/3} D_p^{-2/3} (v^{1/3})$$

where

C_o, C_i = outlet and inlet concentrations

h = bed height

LSHV = liquid hourly space volume.

D_p = particle diameter

v = kinematic viscostiy of the liquid

Mears (1974) suggested that the reaction rate is proportional to the outside surface of the catalyst which is effectively wetted by the liquid and proposed the following relationship:

$$\ln (C_i/C_o) \propto h^{-2/3} (LSHV)^{-.68} D_p^{.18} v^{-.05} (\sigma_c/\sigma)^{.21}$$

where σ = surface tension

σ_c = critical surface tension

Montagne, Shaw and Paraskos (1977) applied the above correlations to hydrodesulfurization data for Kuwait Crude oil. The liquid flow rate used in the study was 0.05 kg/m^{2}s which, according to Satterfield (1975), would not be high enough to completely wet the catalyst. They observed that the correlation of Mears more accurately represented the data while the correlation of Henry and Gilbert did not fit the data.

Axial backmixing is thought to be a factor only when the catalyst bed length falls below a minimum and very high conversions are obtained. Mears (1971) proposed the following relationship for minimum bed length:

$$h/D_p \geq (20n/Pe_l)(\ln(C_i/C_o))$$

where

n = order of the reaction

Pe_l = liquid Peclet Number

Resistance to mass transfer can occur either in the gas phase or in the liquid phase. If an excess of hydrogen is used, the resistance of gas to liquid mass transfer is small. Resistance in the liquid phase can occur in the liquid film surrounding the catalyst or in the pores of the catalyst. Satterfield (1968) observed that under typical hydrodesulfurization conditions, resistance to mass transfer in the liquid film around the catalyst is small. The resistance to mass transfer in the pores may be significant, however, and is dependent upon the feedstock and reaction conditions (Satterfield, 1975).

Hydrotreatment

As discussed previously, SRC liquids are highly aromatic with a large concentration of heterocompounds. Severe reaction conditions are required to bring about desired levels of hydrodenitrogenation and hydrodesulfurization. In hydrotreatment of coal derived liquids, HDN is much more difficult than HDS. This is partially explained by the reaction mechanism. Shih et al, (1977) studied quinoline HDN and found that saturation of the ring is necessary before carbon-nitrogen bond scission occurs. The reaction network is shown in Figure 1. Shih reported both hydrogenation and hydrogenolysis to be first order with respect to the nitrogen substrate. Steric hinderence was reported to be a significant factor in many of the reaction steps.

Katzer and Sivasubramanium (1979) have reported that HDN becomes more difficult as the boiling point of the feedstock increases. They suggested the following reasons in accounting for the phenomenon:

1. Formation of secondary products during hydrodenitrogenation which are more resistant to nitrogen removal than the original compound.
2. Competitive adsorption by the higher molecular weight highly aromatic molecules in the feed.
3. Self inhibition by the high concentration of nitrogen containing compounds.
4. More severe catalyst deactivation caused by the higher molecular weight aromatic compounds in the feed.

Nitrogen compounds also inhibit other reactions such as HDS. Satterfield, Model and Mayer (1975) observed severe inhibition of HDS of thiophene by pyridine over a sulfided Co-Mo/alumina catalyst.

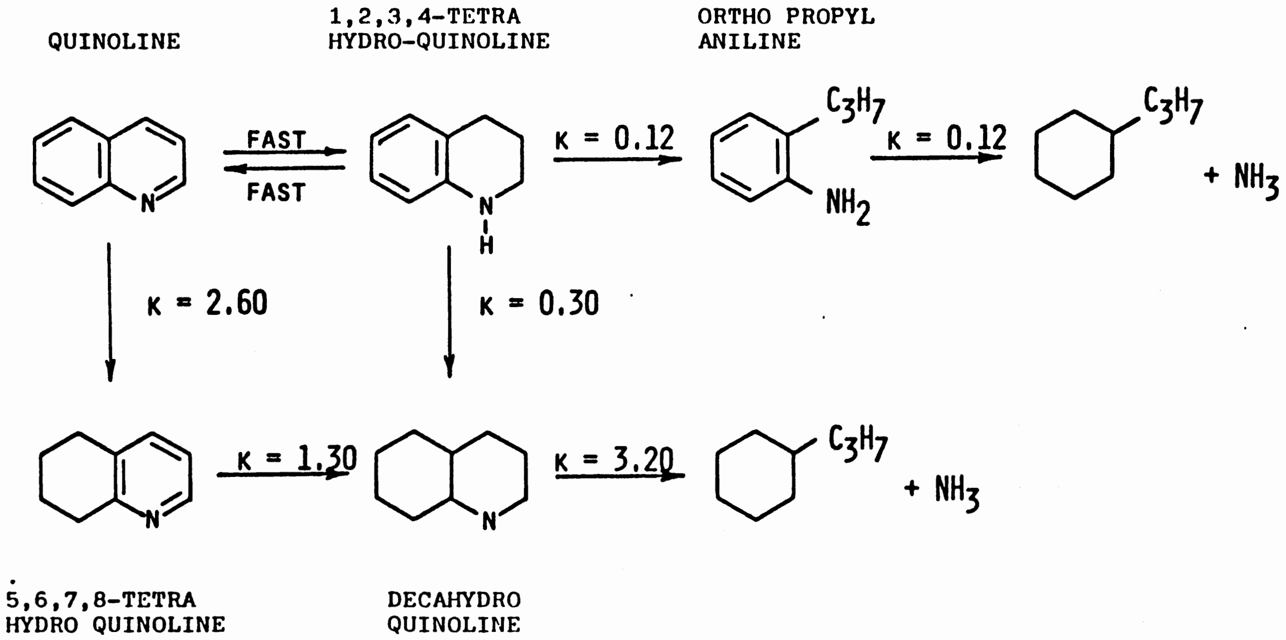

Figure 1. Reaction Network for Hydrodenitrogenation of Quinoline at 342 C, 136 atm, Ni-Mo/Al_2O_3 Catalyst (Shih et al. 1977)

Catalyst Deactivation

Catalyst deactivation during hydrotreatment is a significant problem. Satterfield (1980) has reported four mechanisms by which deactivation may occur:

1. Coke Formation
2. Metal deposition on active sites
3. Active site poisoning by basic nitrogen compounds.
4. Sintering

Coke can deactivate the catalyst by covering active sites and blocking pore mouths. The mechanism of coke formation is not well understood. Chang (1982) listed two main types of coke formation: filimentous and amorphous. The filimentous carbon is formed by catalytic decomposition of carbon gasses on small metal particles. Amorphous carbon deposits are formed by condensation and polymerization reactions.

Heterocompounds may have a greater coking tendency than other aromatic compounds. Madison and Roberts (1958) reported nitrogen containing compounds have a higher coking tendency than their hydrocarbon analogs. Forimsky (1978) reported a higher concentration of nitrogen and oxygen in the coke than in the feedstock. Lipovich et al. (1978) has observed strong coking tendencies for indole and thiophene. They also observed a decrease in coking tendency of styrene, n-heptane and methyl naphthalene with an increase in temperature above 420 C. Uchida (1975) observed coke depositing preferentially at Lewis acid sites instead Bronsted acid sites in N-butene hydrogenation over a silica-alumina catalyst.

Deposition of metallic compounds can cause permanent deactivation, whereas, deactivation due to coking is reversible by burning off the carbon deposit. Metal deposition in liquefaction catalysts is reportedly significant. Stanulonis et al. (1976) studied a sulfided Co-Mo/silical/alumina catalyst used in the synthoil process. They observed 50-70% of the catalyst peripheral surface covered with ferrous sulfate in the upstream portion of the reactor. The substance showed a penetration of 100 μm. In the downstream portion of the bed, aluminum and silicon covered 20% of the surface area and caused 40% loss of pore volume. Titanium was also found in the downstream portion of the reactor. Holloway and Nelson (1977) investigated a cobalt-molybdate catalyst used in the Synthoil process and found iron and titanium penetration in the catalyst to a depth of 200 μm. A high concentration of titanium was also found in the surface residue. Chan (1982) doctored an SRC light oil with titanocene dichloride. He found that the titanocene dichloride was easily hydrodemetalized by the Ni-Mo/alumina catalyst and is deposited on the catalyst. The titanocene dichloride also suppressed coke formation in the middle and lower zones of the catalyst bed but the top zone did not show this effect.

Basic nitrogen compounds are known to be reversibly and irreversibly adsorbed on active catalysts sites causing temporary or permanent deactivation. Lipsch and Schuit (1969) observed irreversible pyridine poisoning of a Co-Mo/-alumina catalyst. The catalyst was reduced at 500 C in H_2 then the thiophene conversion was measured afer successive pulses of pyridine. Cowley and Massoth (1978) observed permanent poisoning during hydrodesulfurization of benzothiophene with a sulfided Mo/alumina catalyst. Introduction of pyridine caused an increase in catalyst weight and a corresponding decrease in the HDS activity. Holloway and Nelson (1977) observed a high concentration of nitrogen in a toluene extracted catalyst from the Synthoil process which indicated adsorption of the nitrogen compounds on the catalyst. They reported coking to be the primary deactivation mechanism with nitrogen compound poisoning and metal deposition as secondary deactivating mechanisms.

In summary, ideal plug flow behavior has been generally assumed for evaluating hydrtreatment of coal derived liquids in trickle bed reactors. However, liquid maldistribution, incomplete catalyst wetting, axial backmixing and diffusion resistance can cause deviation from ideal behavior. Denitrogenation during hydrotreatment is difficult due to the reaction mechanism whereby complete saturation of the ring is required before carbon-nitrogen bond scission. Catalyst deactivation during hydrotreatment can be caused by coke formation, poisoning, metal deposition or sintering. Coke formation, however, is generally thought to be the primary deactivation mechanism.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The objectives of this study were twofold: First, the ability of dilute aqueous solutions to extract basic nitrogen compounds from Solvent Refined Coal liquids was assessed and second, the effects of aqueous extraction on catalytic hydrotreatment of the liquids was determined. A discussion of the extraction equipment and extraction procedure will follow. The hydrotreatment equipment was a modification of reactor systems used by Chang (1982) and Bhan (1981). The systems and the modifications will be discussed.

Extraction

Equipment

Two types of extraction equipment were used in this study. The first type consisted of separatory funnels ranging in size from 125 milliliter to three liter. All agitation of the solution was done manually at ambient conditions.

A 500 milliliter cylindrical pyrex separatory funnel was used for assessing the effects of temperature on extractions. Heat was provided to the funnel by heating tape connected to a variac for a power source. The temperature was monitored with a thermocouple placed in the solution and connected to a digital readout. The solution was stirred mechanically by a pyrex stirring rod. A six liter funnel of the same type was constructed to make possible treatment of large volumes of liquid necessary for hydrotreatment.

Procedure

The procedure for mechanical and manual agitation was essentially the same. For both cases, the aqueous solution was prepared using Fisher ACS certified reagents and distilled water. One, two or ten normal reagents were diluted to the proper strength.

For the manually agitated extraction, the aqueous solution and the oil were mixed in a separatory funnel (125 ml - 3 liter) and manually shaken for 15 minutes. The mixture was then left to settle for 12 hours. The liquids were then drained from the funnel into glass jars. Any remaining oil was filtered from the aqueous sample and the solution was centrifuged at 2500 RPM before analysis. The oil sample was also centrifuged.

Use of the cylindrical funnel with the mechanical stirring apparatus varied only slightly from the above procedure. The aqueous solution was prepared as before by diluting the nearest normality Fisher Reagent to the proper strength. The aqueous solution was then placed in the funnel and heated to approximately five degrees centigrade above the desired extraction temperature. The oil sample was then added to the funnel and the mixture brought up to the desired temperature.

Reactor systems

Two trickle bed reactor systems were used in this study. The EN1 reactor system is located in the laboratory facilities of Engineering North. The Catalyst Life Test Unit (CLTU) is located in the Hazardous Reaction Laboratory at Oklahoma State University. Both reactor systems were were designed to automatically control temperature, pressure and flow rates. The CLTU system is designed to operate unattended. The EN1 reactor system, however, requires constant monitoring.

Reactor System EN1

The operation of the EN1 system is manual, therefore, the system must be constantly monitored during a hydrotreatment run. Only minor modifications were made in the system from that originally constructed by Bhan. The system is shown in Figure 2.

The reactor consists of a 1.27cm (0.50 inch) O.D., 1.09 cm (0.43 inch) I.D. 316 stainless steel tube with 50.8 cm (20 inches) of effective reactor length. The tube, packing and heating arrangement are shown in Figure 3. Liquid and gas were fed to the top of the reactor and flowed cocurrently down through the reactor. A stainless steel

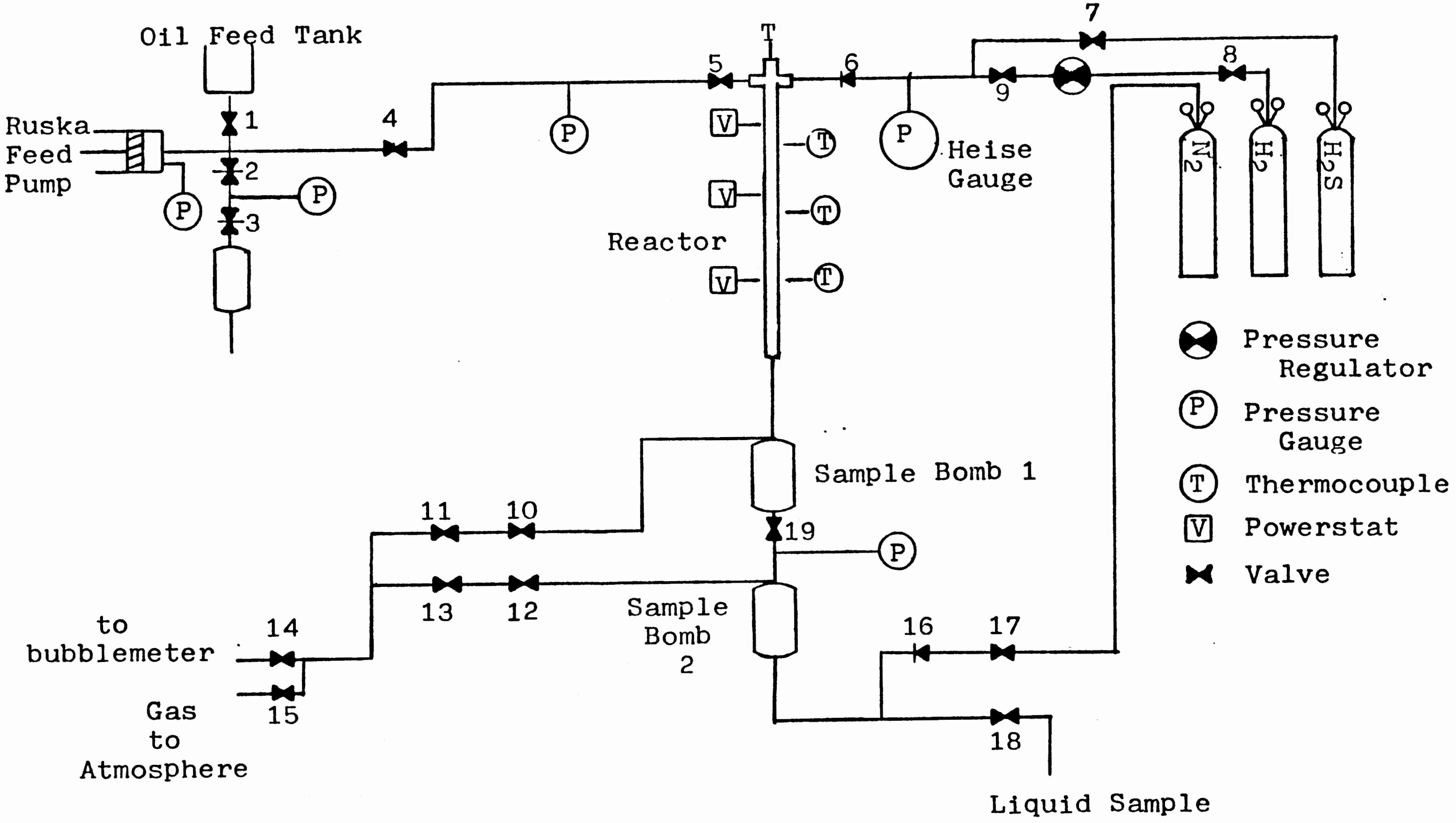

Figure 2. Reactor System EN1.

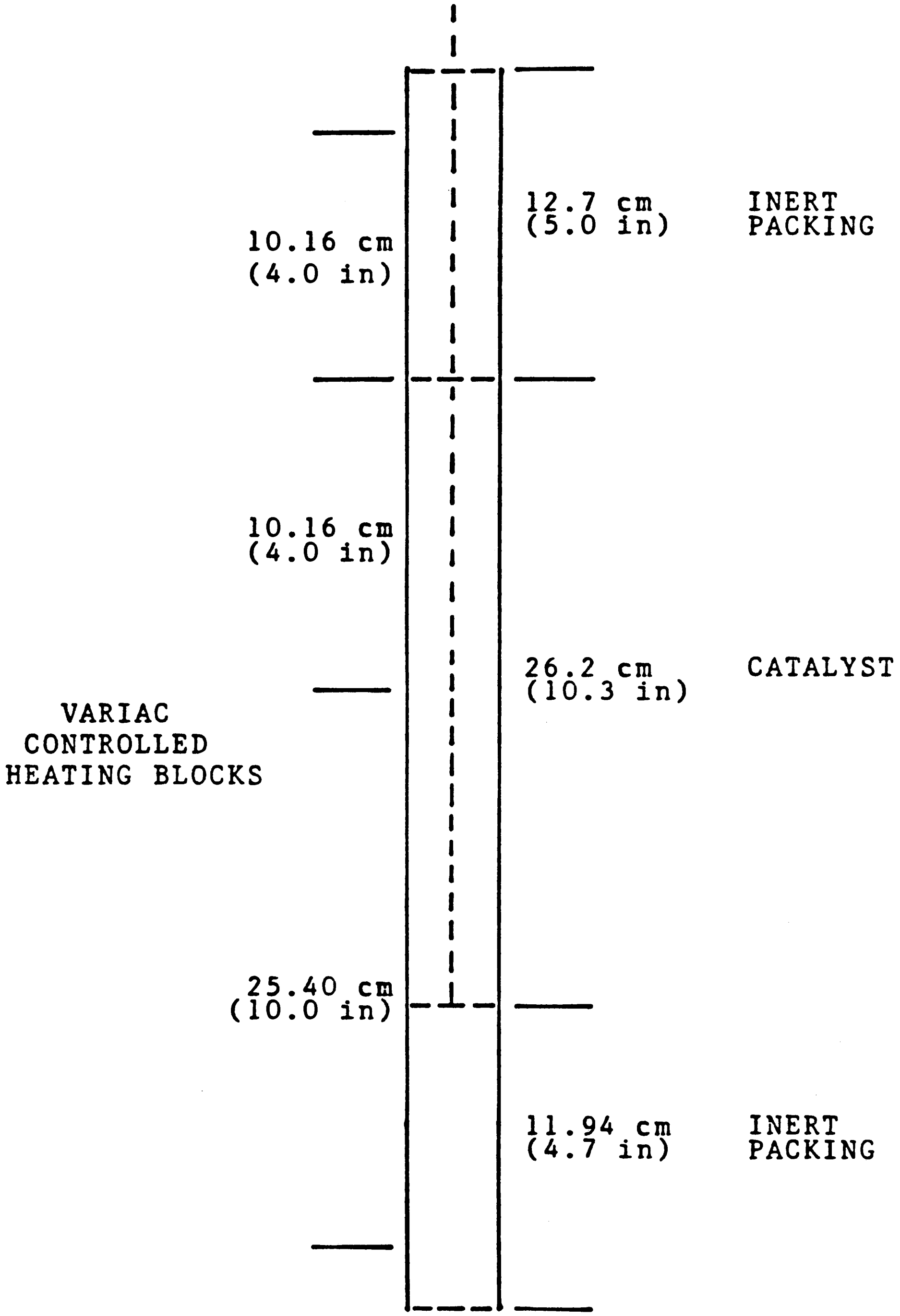

Figure 3. Heating and Packing Arrangement for Reactor EN1.

wire screen was wedged between fittings at the bottom of the reactor to provide support for the catalyst and inert particles. 12.7 cm (5.0 inches) of one millimeter diameter glass beads were located at the top of the reactor to provide a preheating zone for the liquid. Glass beads were also placed at the bottom of the reactor to a height of ~~26.2~~ cm (10.3 inches) for catalyst support.

The reactor was heated by ceramic beaded wire wrapped around three aluminum blocks. Power to the beaded wire was supplied by manually controlled variacs. The smaller blocks were placed at the top of the reactor to allow greater control of any hot spots which might occur at the top of the catalyst zone.

The oil was fed to the Reactor from a one liter Ruska positive displacement pump. Oil flow from the pump to the reactor was through 0.635 cm (1/4 inch) stainless steel tubing. Two rupture disks (12.40 and 15.85 MPa, 1800 and 2300 psig) were located in series on the oil feed line as a safety precaution. A pressure gauge was located between the rupture disks and was monitored on a regular basis. Pressure gauges were located on the pump and in two locations on the feed line to allow isolation of any plug which might occur. A valve was located immediatly prior to the reactor entrance made possible filling and pressurizing the oil feed lines prior to the start of each run.

Hydrogen gas was fed to the system from a three bottle manifold system. Only one bottle was on line at any one time. The manifold system allowed rapid bottle change, when necessary, without disturbing the system pressure. A mity-mite regulator located on the hydrogen feed line regulated the reactor pressure to 10.34 MPa (1500 psig). The reactor pressure was monitored using a Heisse gauge located between the regulator and the reactor.

The temperatures throughout the system were monitored using iron-constantan thermocouples connected to an Omega digital readout. One thermocouple was placed in each of the aluminum blocks surrounding the reactor tube. A 0.16 cm (1/16 inch) thermocouple inside a 0.32 cm (1/8 inch) thermowell axially tranversed the catalyst bed and the movement of the thermocouple through the thermowell allowed temperature measurements throughout the inert and catalyst zones. Thermocouples were also located on the feed and effluent lines.

The reactor effluent flowed through 0.64 cm (1/4 inch) tubing to gas-liquid separation bomb 1. A diagram of the bomb is shown in Figure 4. The gas flows through the top of the bomb and through a micrometering valve to a bubble-meter for gas flow measurement. The gas is then vented to the atmosphere. During the sampling procedure the oil from bomb 1 was passed to bomb 2. Bomb 2 was then isolated from the system and depressurized. A nitrogen line was connected to the effluent line of bomb 2 to purge the oil for removal of H_2S and NH_3. The oil was then passed through the remaining valves to the sample jars.

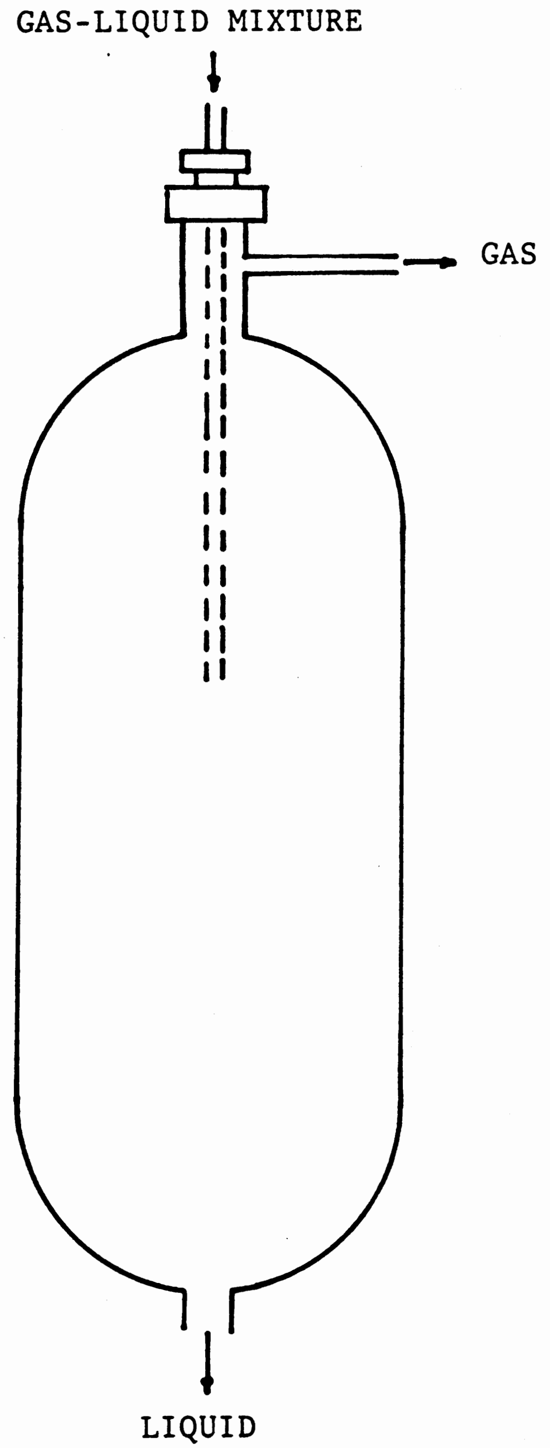

Figure 4. Gas-Liquid Separation Bomb.

Catalyst Life Test Unit

The Catalyst Life Test Unit was originally designed to automatically control temperature, pressure, and flow rates. Chang (1982) made several modifications in the system including extensive modifications to the oil feed system to enable the system to handle highly viscous fluids.

Several modifications were made in the system for this study. The original system consisted of three reactors in parallel. Only one reactor was required in this study which allowed replacement of the pressurized feed system with a single Ruska positive displacement pump.

A simplified diagram of the CLTU Reactor system is shown in Figure 4. The oil feed was fed to the top of the reactor through 0.64 cm (1/4 inch) stainless steel tubing. An overpressure switch was located on the feed line and was set at 13.09 MPa (1900 psig). A rupture disk was also located on the oil feed line as a secondary safety factor.

Hydrogen gas was fed to the system from one of two 41.34 MPa (6000 psig) cylinders allowing undisturbed gas flow. Hydrogen gas was compressed to 31.00 MPa (4500 psig) in the cylinders from lower pressure bottles. The hydrogen feed pressure was regulated to 12.40 Mpa (1800 psig) by a Mity-Mite pressure regulator and controlled prior to the reactor by a micrometering valve. A pressure transducer was located immediatly following the micrometering valve and was connected to a Dialatrol automatic controller which

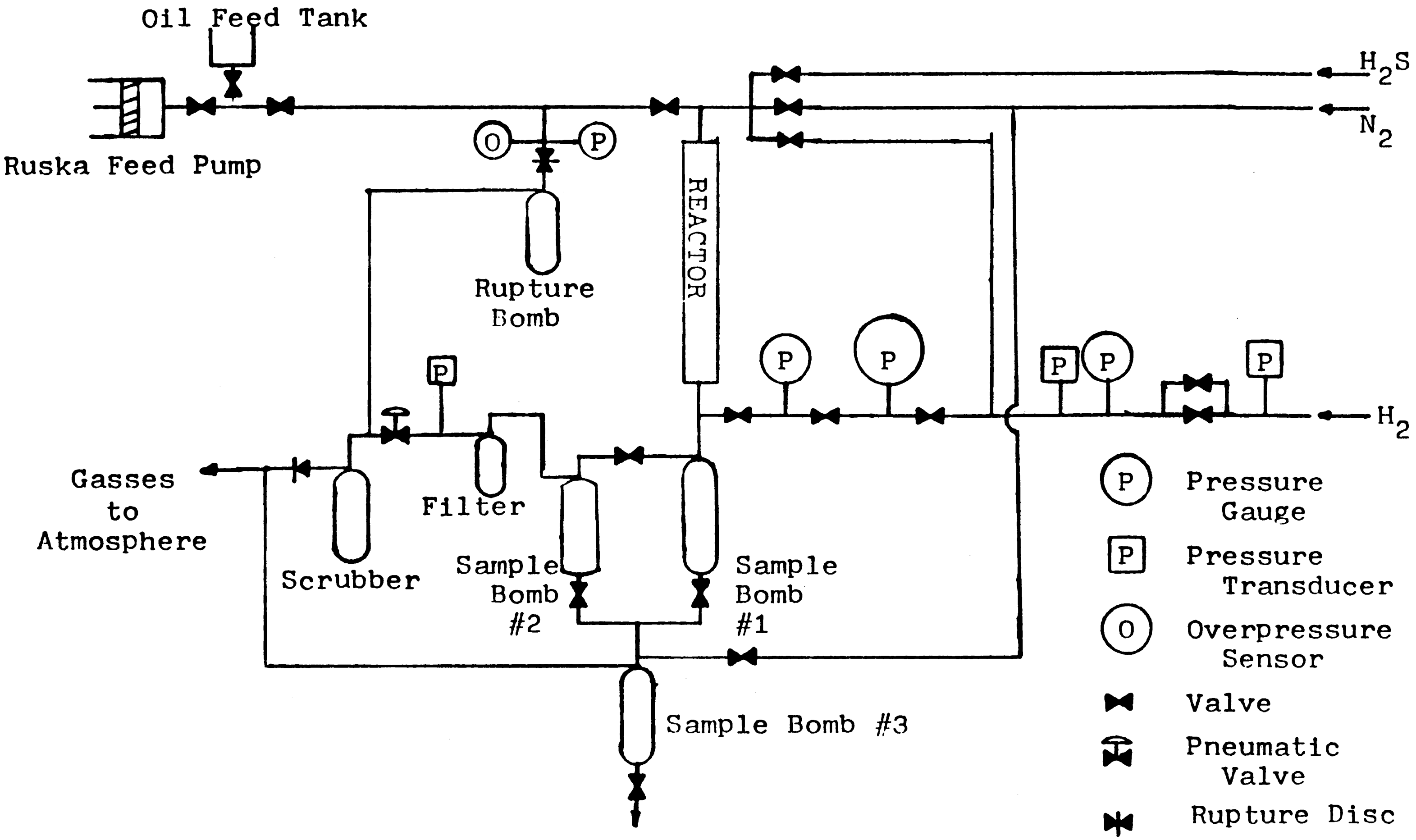

Figure 4. CLTU Reactor System

in turn controled a pneumatic valve on the gas exit stream. The system was designed so that high upstream pressures would result in opening of the valve downstream to the reactor resulting in increased gas flow from the reactor.

The reactor tubing, packing and heating system are shown in Figure 6. The reactor tube is 316 stainless steel, 1.31 cm (.515 inch) I.D., and 86.36 cm (34 inches) in length. A solid copper cylinder 1.91 cm (0.75 inch) I.D., 8.89 cm (3.50 inch) O.D. is used to maintain constant temperature. Heat is supplied to the system by circular heating bands wrapped around the copper cylinder and is controlled by a Honeywell Dialatrol and two variacs.

The outer wall temperature of the reactor is monitored in seven positions using iron-constantan thermocouples. The thermocouple located at the wall position corresponding to the center of the catalyst bed is connected to the Honeywell dialatrol which controls the heating bands corresponding to the catalyst bed. A 0.32 cm (1/8 inch) thermowell axially traverses the length of the catalyst bed allowing movement of a 0.16 cm (1/16 inch) thermocouple through the catalyst zone.

The system contains two bombs for gas-liquid separation which were generally not heated. A third bomb, prior to the pressure transducer, was filled with glass beads to facilitate removal of any condensibles from the gas stream which might affect the performance of the pneumatic valve. After passing through the pneumatic valve, the gas flowed

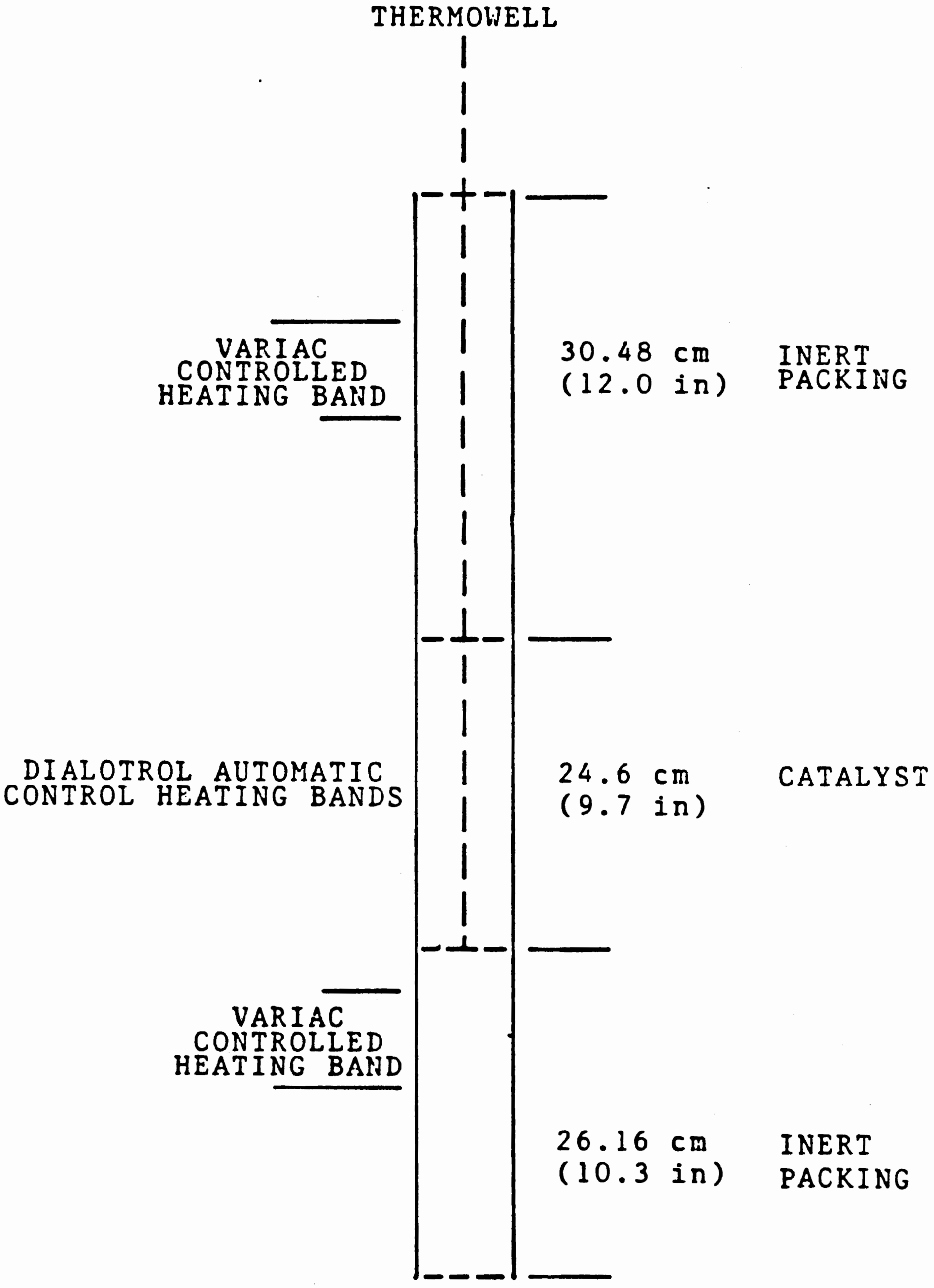

Figure 6. Heating and Packing Arrangement for the CLTU Reactor

through a scrubber containing 20% sodium hydroxide. A wet-test flow meter was located after the scrubber. Following the scrubber, the gasses were vented to the atmosphere.

The liquids which collect in sample bombs 1 and 2 are passed to sample bomb 3 during the sampling procedure. This results in a slight depressurization of the system (0.34 Mpa, 50 psig). Repressurization of the bombs and the system as a whole takes place through the bombs and not through the reactor tube. As a result, the flow rate through the catalyst bed during repressurization does not exceed the normal operating flowrate.

CHAPTER IV

EXPERIMENTAL RESULTS

One of the objectives of this study is to assess the feasibility of extracting nitrogen compounds from SRC liquids. Two sets of extraction experiments were conducted to achieve this goal: the first with SRC Process Solvent as a preliminary study, and the second with SRC Heavy Distillate assessing the effects of temperature, acid concentration and acid solution/oil volume ratio. The properties of the feedstocks are given in Table V.

Ten hydrotreatment runs were conducted to assess the effect of acid washing on catalyst deactivation during hydrotreament. Again, the runs are separated into those with Process Solvent as the feed and those with Heavy Distillate as the feedstock.

All experimental results are tabulated in Appendix A.

Extraction Results

Preliminary Extraction Results

The first set of extractions was conducted to investigate the effect of water, acid and basic washes on creosote oil or Process Solvent and to establish a procedural basis for future extraction work. Results from this series are

TABLE V

PROPERTIES OF SRC PROCESS SOLVENT AND HEAVY DISTILLATE

	COMPOSITION (WGT. %)	
	PROCESS SOLVENT	HEAVY DISTILLATE
CARBON	87.05	89.03
HYDROGEN	7.47	7.26
NITROGEN	0.95	1.09
SULFUR	0.54	0.54
OXYGEN	4.20*	1.75*
ASH	NIL	0.12
SPECIFIC GRAVITY	1.069	1.073

*BY DIFFERENCE

shown in Figure 7. All extractions, except two, were conducted using an aqueous solution/oil volume ratio of 5:1. Washes with distilled water removed very little nitrogen from either creosote oil or Process Solvent. A 6.4% hydrochloric acid removed 37.2% and 31% from creosote oil and Process Solvent respectively. Caustic washes removed nearly 6% of the nitrogen from creosote oil, however, no additional removal was observed using the same caustic wash behind an acid wash in experiment 6. In experiment 7, a Process Solvent sample was subjected to a series of four washes in the sequence: acid, water, acid, water. Little additional nitrogen was removed by the last three extractions.

XPST Extraction Series

The objective of this series was to determine the effect of agitation time during extraction on nitrogen removal. Process Solvent and a 1% HCL solution in a 1:5 ratio were agitated vigourously at 40 C (104 F) for 2.5 hour. The sample size relative to the volume of the oil phase was 1:100.

The results shown in Figure 8 indicate a majority of the nitrogen is removed within the first five minutes and very little additional removal is observed up to 2.5 hours of mixing.

XSHD Extraction Series

SRC Heavy Distillate was used as the feed in all experi-

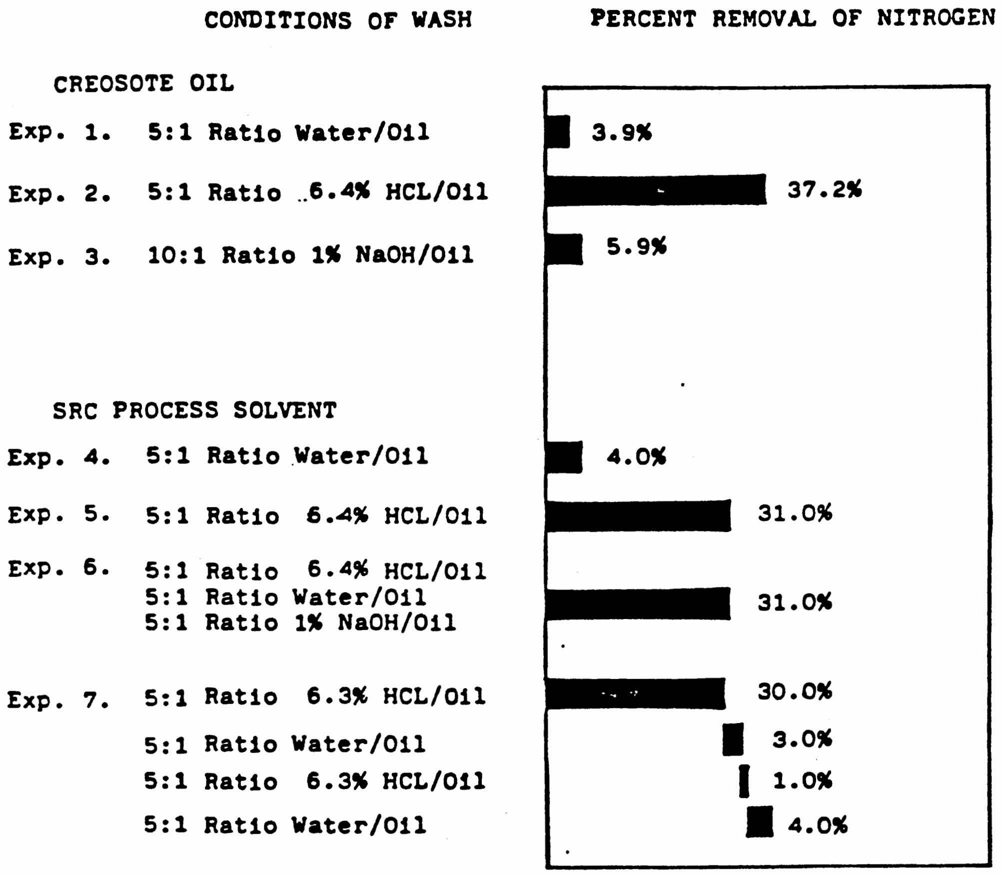

Figure 7. Preliminary Extraction Results

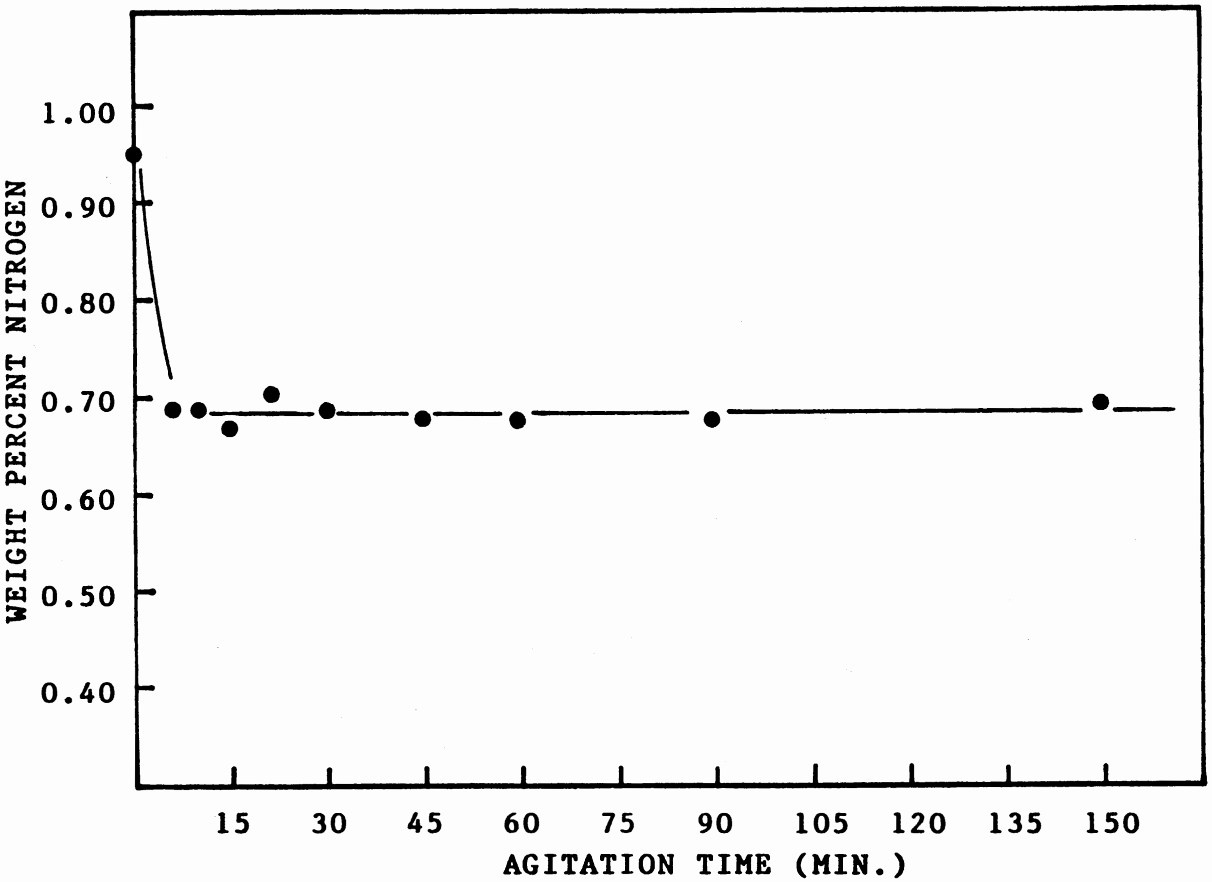

Figure 8. The Effect of Agitation Time on the Removal of Nitrogen from SRC Process Solvent

ments in this series. Both Hydrochloric acid and sulfuric acid solutions were used as solvents. The objective of this series was to determine the effect of increasing temperature, acid concentration and acidic solution/ oil ratio on nitrogen removal.

Temperature. The results from this series (XSHDT), shown in Figure 9, indicate an increase in removal of nitrogen with increasing temperature with for sulfuric acid and hydrochloric acid solutions. A slightly better removal is observed with hydrochloric acid than with sulfuric acid. In both cases, the effect is greater at near room temperature and increasing the extraction temperature beyond 60 C (140 F) yeilds little increase in removal.

Acid Concentration. Extractions were conducted with concentrations of the acids varying from zero to twenty percent. The results are shown in Figure 10. In that range the largest relative increase in nitrogen removal occurred when the concentration was increased from zero to one percent. Again, the hydrochloric acid wash removed slightly more nitrogen than sulfuric acid in lower and intermediate concentrations. However, at 20% acid concentration the nitrogen remaining was approximately the same for both acids. Very little dditional removal was observed by increasing the concentration beyond one percent for the sulfuric acid wash and a slight decrease in removal was observed with the hydrochloric acid. The concentration of carbon in

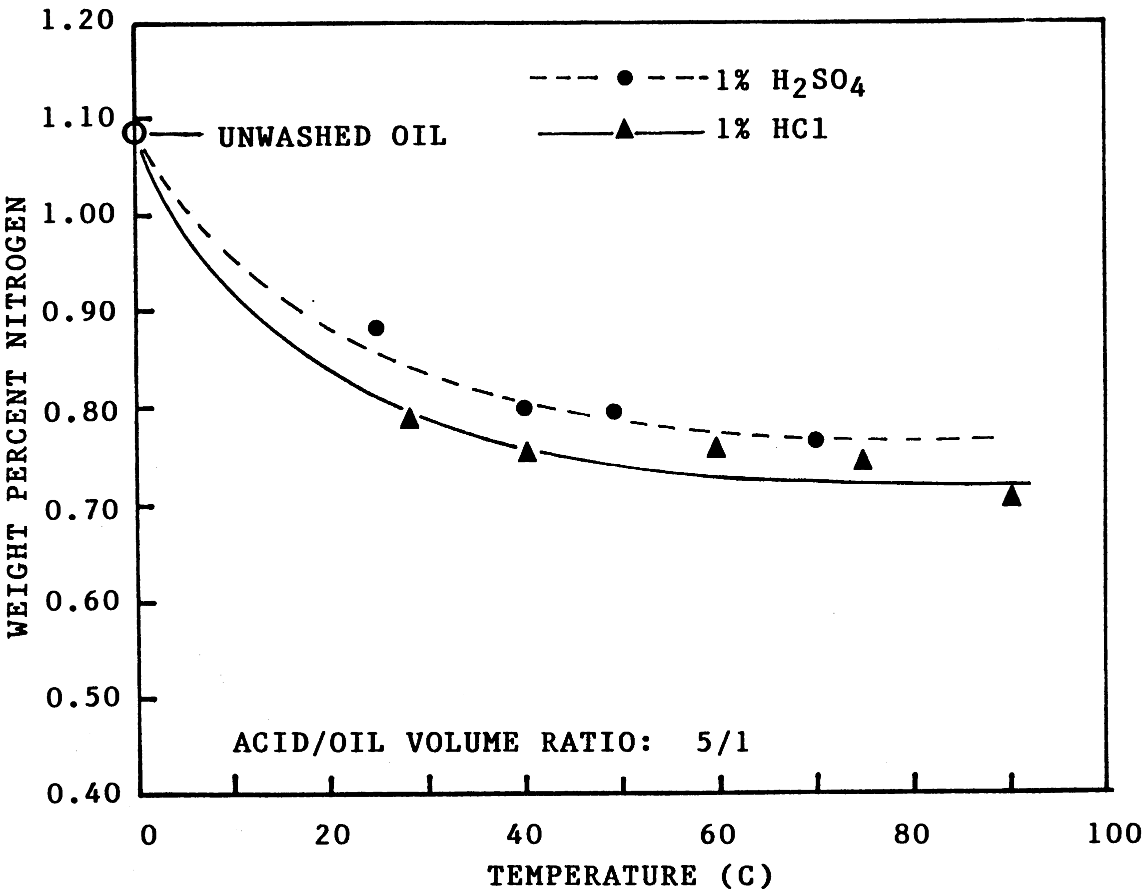

Figure 9. The Effect of Temperature on the Removal of Nitrogen from SRC Heavy Distillate

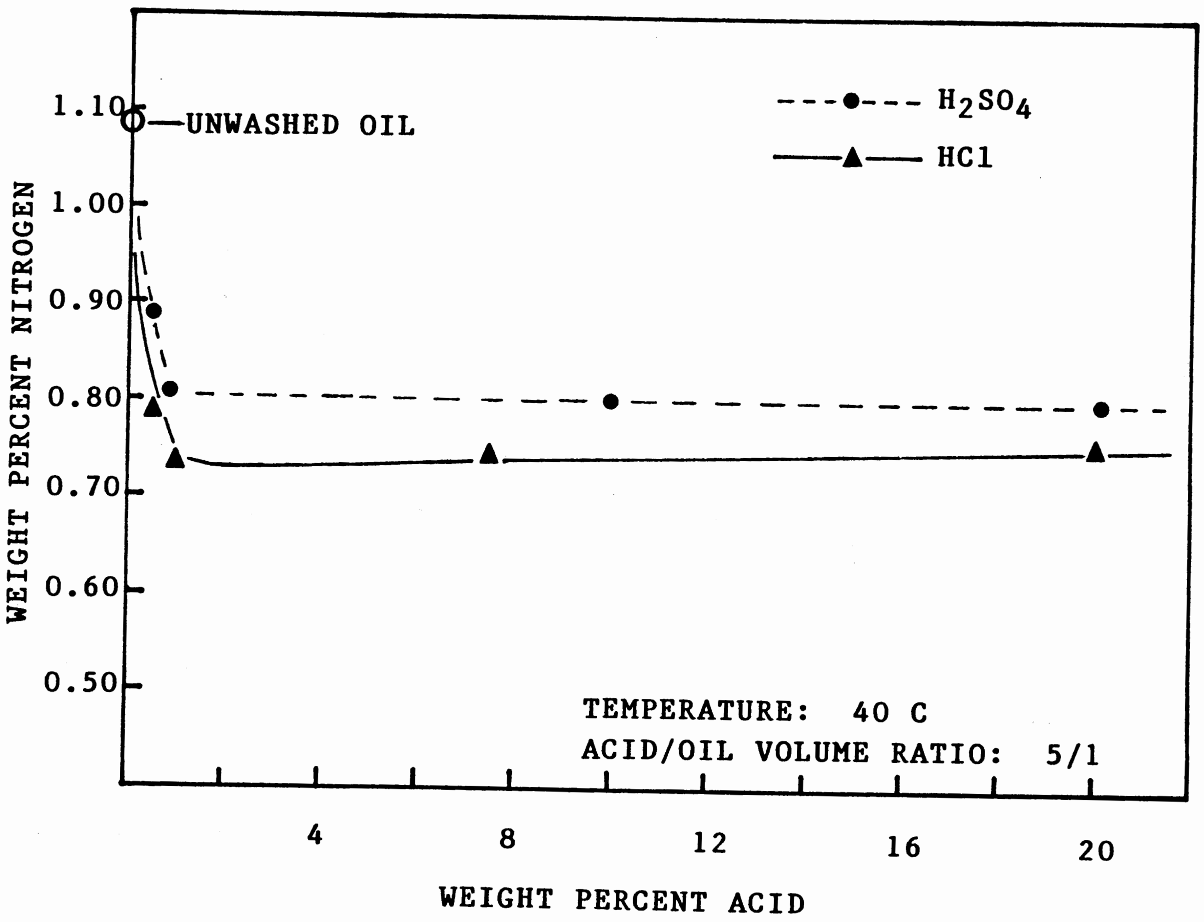

Figure 10. The Effect of Acid Concentration on the Removal of Nitrogen from SRC Heavy Distillate

the aqueous extracts from this series is given in Table VI. The data are also converted to percentage carbon lost from the oil phase. The data for hydrochloric acid show a nearly linear relationship between carbon concentration and acid concentration. However, the data for the sulfuric acid washes are scattered and higher in all cases than the HCL washes. In both cases, the concentration of carbon increases with increasing acid concentration.

Acid Solution/Oil Volume Ratio. The results showing the effect of the acid solution to oil volume ration are shown in Figure 11. Increasing the volume ratio of the aqueous solution to oil increased the nitrogen removal only up to a ratio of 5:1 with both hydrochloric and sulfuric acids. Again, the hydrochloric acid removed slightly more nitrogen than sulfuric acid.

Distillation

The distribution of nitrogen throughout the boiling range of raw and acid washed SRC heavy distillate is shown in Figure 12. The conditions of the wash were 1.0% HCl at 40 C (104 F) with an acid solution to oil volume ratio of 5:1.

The nitrogen concentration increases with increasing boiling point in both cases. The acid washed distillate shows a lower nitrogen concentration throughout the boiling range, and the difference is slightly larger between the two distillates in the lower boiling cuts.

TABLE VI

CARBON CONCENTRATION IN THE AQUEOUS PHASE FROM EXTRACTION XHDC

CONCENTRATION OF ACID (WEIGHT %)	CARBON CONCENTRATION IN AQUEOUS SOLUTION (WEIGHT %)	% CARBON LOST FROM OIL
SULFURIC ACID WASH		
1.0	1.58	8.5
2.0	2.33	12.6
10.0	2.02	11.3
20.0	2.14	12.8
HYDROCHLORIC ACID WASH		
1.0	0.78	4.1
2.0	0.83	4.4
10.0	1.39	7.6
20.0	1.81	10.0

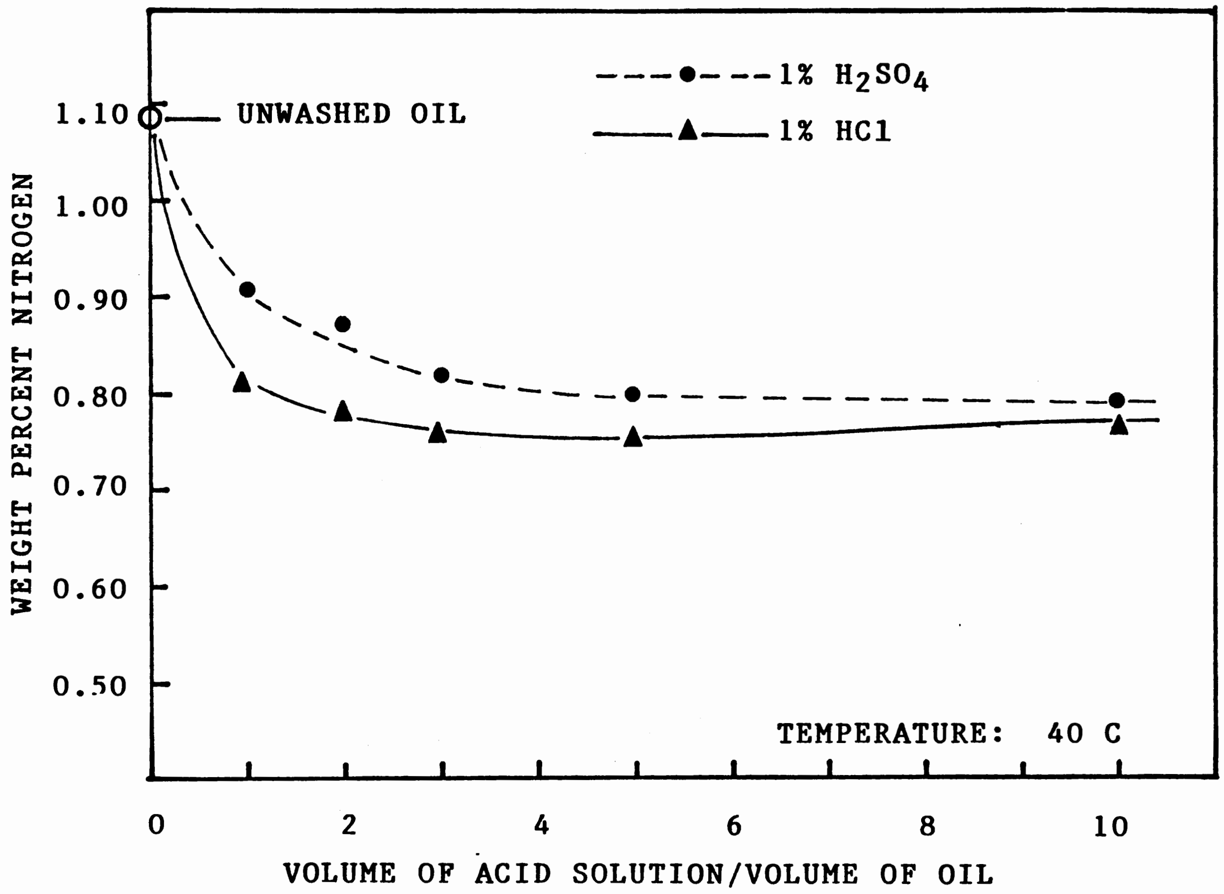

Figure 11. The Effect of Acid Solution/Oil Volume Ratio on the Removal of Nitrogen from SRC Heavy Distillate.

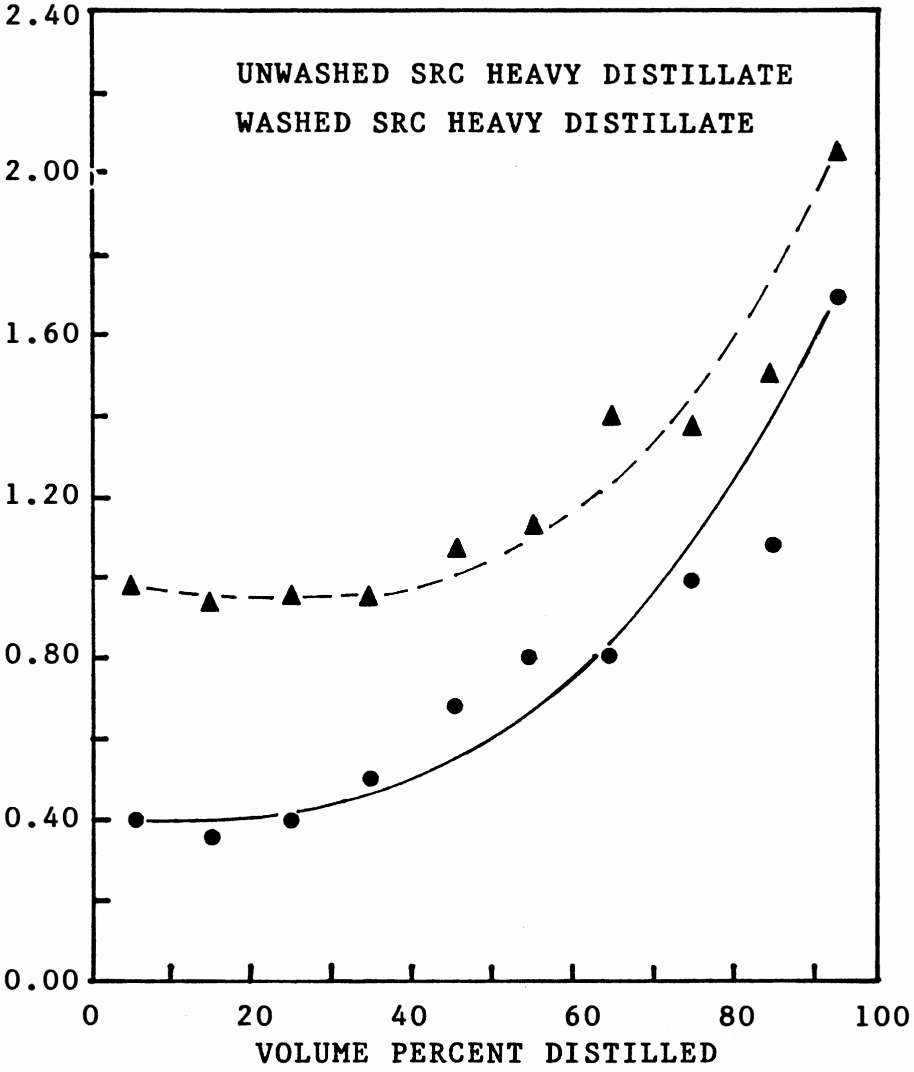

Figure 12. The Distribution of Nitrogen in Distillation Cuts of Washed and Unwashed SRC Heavy Distillate.

Hydrotreatment Results

Ten hydrotreatment runs were conducted to achieve the objectives outlined above. Five of the ten runs did not achieve their design objectives due to plugging problems. Those problems were confined to runs with hydrochloric acid washed Heavy Distillate as the feedstock. The properties of the two feedstocks, SRC Process solvent and SRC Heavy distillate, were given above. Two commercial Ni-Mo-alumina catalysts were used. In RPS and WPS runs the catalyst was HDN-30 from American Cyanamid Corporation. The Shell 324 catalyst was used in all other runs. Both catalysts have been used in previous studies with Solvent Refined Coal liquids (Chan, 1982; Chang, 1982; Bhan, 1981). The properties of both catalysts are given in Table VII. A description of the individual runs and the results obtained follows:

Process Solvent Hydrotreatment

Run RPS. The objective of the run was to establish a reference run for hydrotreatment of SRC Process Solvent. The operational parameters were 10.34 Mpa (1500 psig), 371 C (700 F), 1068 m^3H_2/m^3 (6000 SCF H_2/BBl) and LVHST of 1.5 hr. The operating procedure outlined above was followed. After 76 hours on stream the heating system failed due to a break in the ceramic beaded wire surrounding the aluminum blocks around the reactor. The system operated

TABLE VII

PROPERTIES OF CATALYSTS

	HDN-30	SHELL 324
CHEMICAL COMPOSITION (Wgt. %)		
NiO	5.0	3.4
MoO_3	20.5	19.3
SO_4	0.30	——
Na_2O	0.03	——
Alumina	Balance	Balance
PHYSICAL PROPERTIES		
Geometry	1.6 mm extrudate	1.6 mm extrudate
Surface Area (m^2/gm)	122	146
Pore Volume (cc/gm)	0.45	0.42
Most Frequent Pore Diameter (A)	84	118

in a stable mode up to the point of the heating system failure. The level of nitrogen removal decreased from 95% initially to 76% at shutdown and a steady deactivation with respect to nitrogen removal is evident. The sulfur removal fluctuated from 83% to 63% removed, however, no deactivation trend is evident from the data. The hydrogen concentration rose to 9.21% initially from a feedstock value of 7.51% indicating significant hydrogenation. Again, no significant deactivation with respect to hydrogen concentration, as indicated by the H/C molar ratio, is observed.

Run WPS. The objective of run WPS was to hydrotreat an acid washed feedstock and compare the rate of deactivation with respect to HDN, HDS and hydrogenation to that of run RPS. The Process Solvent was washed twice with 0.5% HCl in distilled water at a volume ratio of 5:1 aqueous solution to oil. The acid washes were followed by two washes with distilled water at the same volume ratio. All extractions were conducted at room temperature. No problems were encountered during the run and the scheduled 150 hours of on stream time were obtained. The feedstock was changed after 136 hours on stream from the washed Process Solvent to the raw Process Solvent.

A comparison of the HDN activity, HDS activity, and the H/C molar ratio with the data of run RPS are shown with least square fits in Figures 13, 14 and 15.

The nitrogen concentration in the product of run WPS is slightly higher initially at 0.13% compared to that

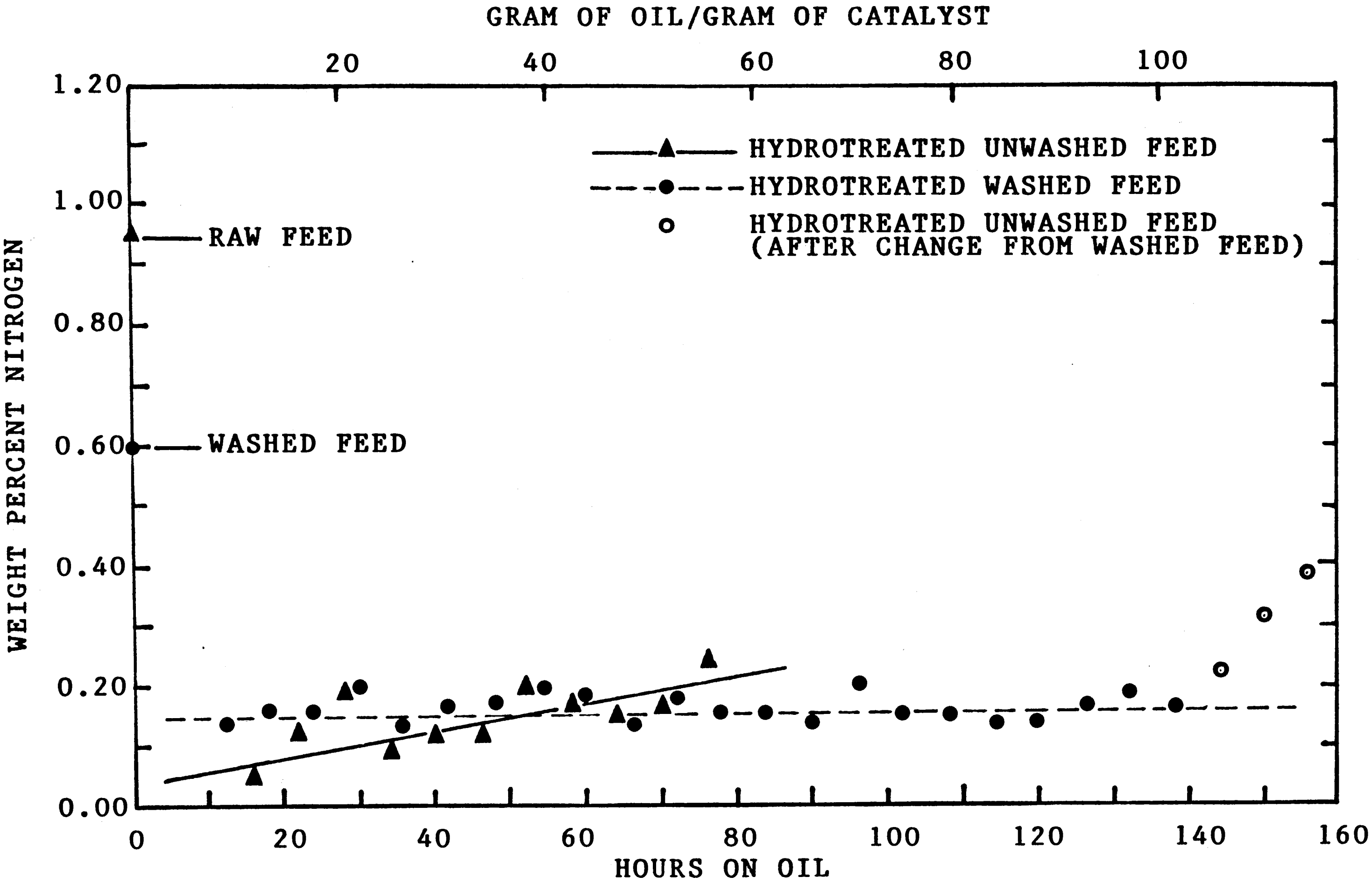

Figure 13. Comparison of the Hydrodenitrogenation Activity for Acid Washed and Unwashed SRC Process Solvent

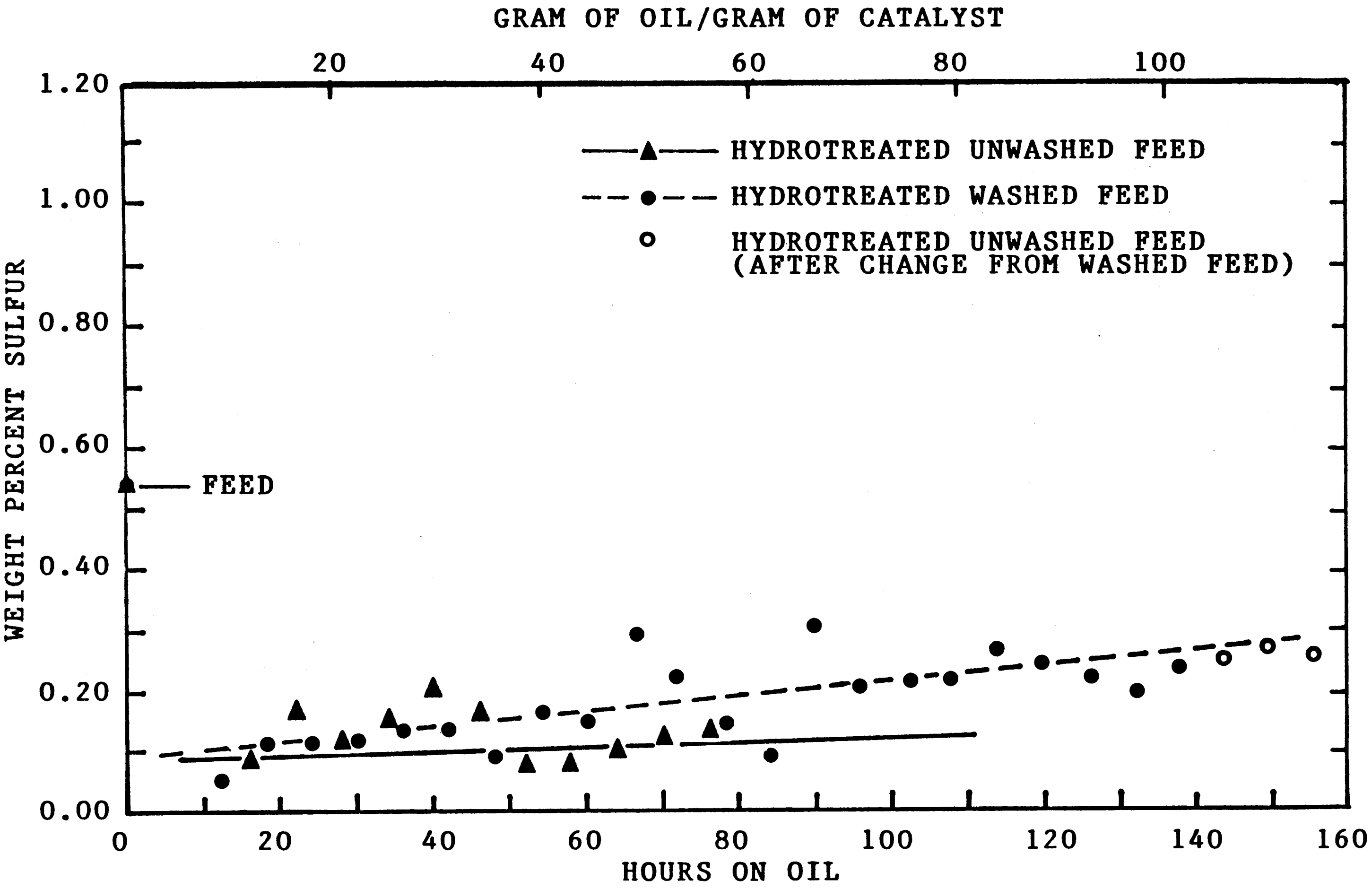

Figure 14. Comparison of Hydrodesulfurization Activity for Acid Washed and Unwashed SRC Process Solvent

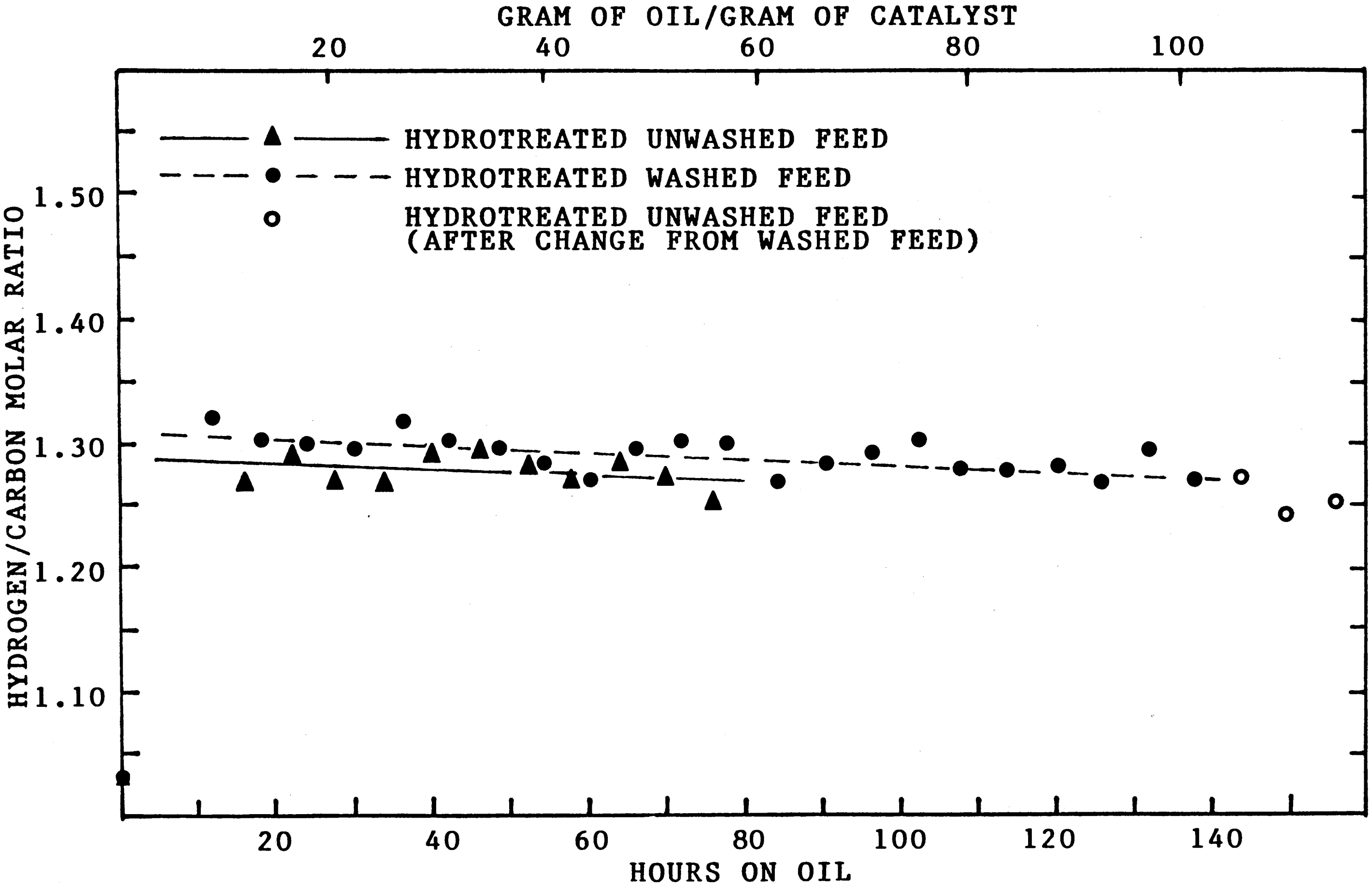

Figure 15. Comparison of the Hydrogen/Carbon Molar Ratio for Products of Hydrotreatment of Acid Washed and Unwashed SRC Process Solvent

of run RPS at 0.05%. However, very little change in the nitrogen concentration occurs up to 138 hours. During the last 20 hours on stream, while the feedstock was raw process solvent, the concentration increased from 0.21% to 0.38%.

The hydrodesulfurization activity, shown in Figure 14 indicates a slow deactivation with respect to sulfur removal. Although the initial concentrations are essentially the same, a least squares fit of the data indicates a higher deactivation rate for the acid washed feed. There is no apparent difference in the sulfur concentration after changing to the raw feed at 138 hours.

There is very little difference in the level of hydrogenation with respect to the hydrogen/carbon molar ratio as seen in Figure 15. Products from both runs show a significant increase in the hydrogen concentration. The rate of deactivation with respect to the molar ratio is approximately the same for both runs.

Samples from approximately 30 hours on stream from both runs were subjected to ASTM distillations. The results are shown in Figures 16 and 17. Both samples show significantly lower boiling points in all cuts relative to the feedstock. There is very little difference, however, between the two hydrotreated samples. The sample from run WPS with washed feed shows a very slight decrease in boiling points compared to that from run RPS.

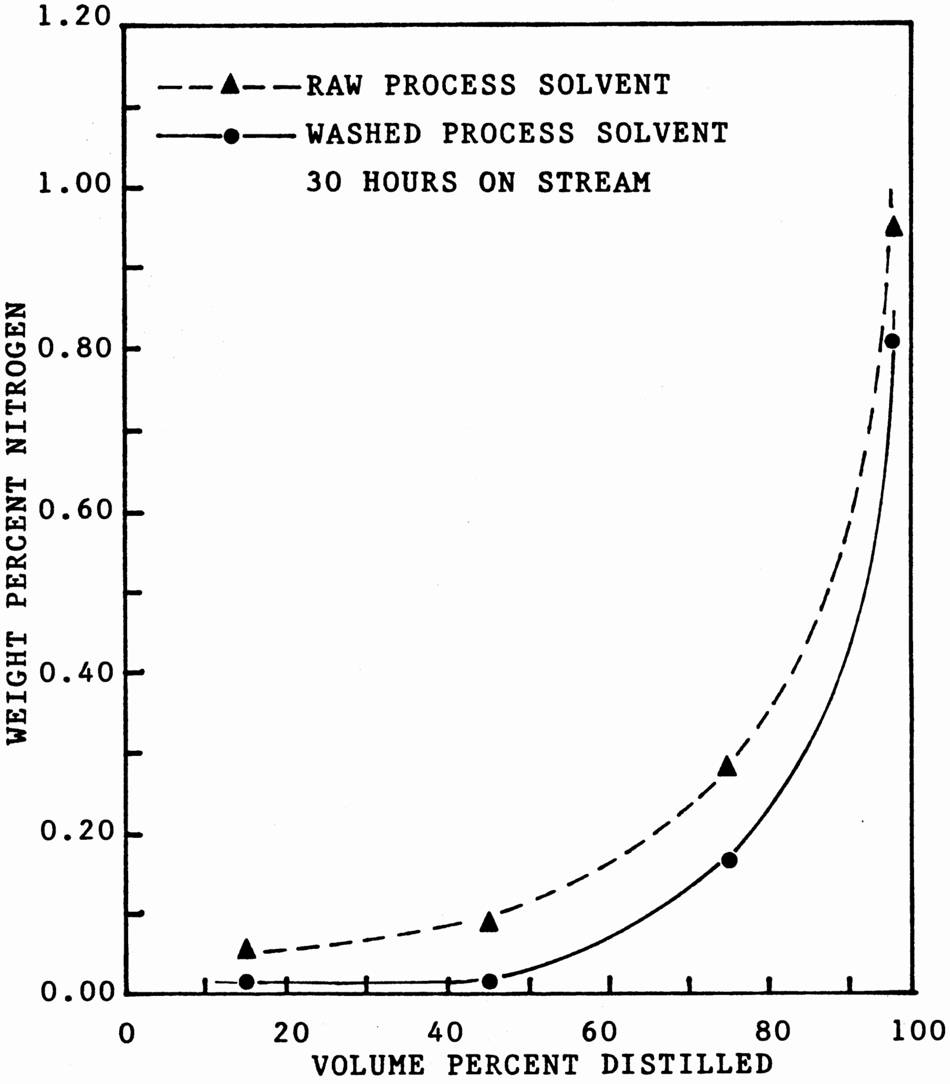

Figure 16. Distribution of Nitrogen in Hydrotreated Washed and Unwashed SRC Process Solvent

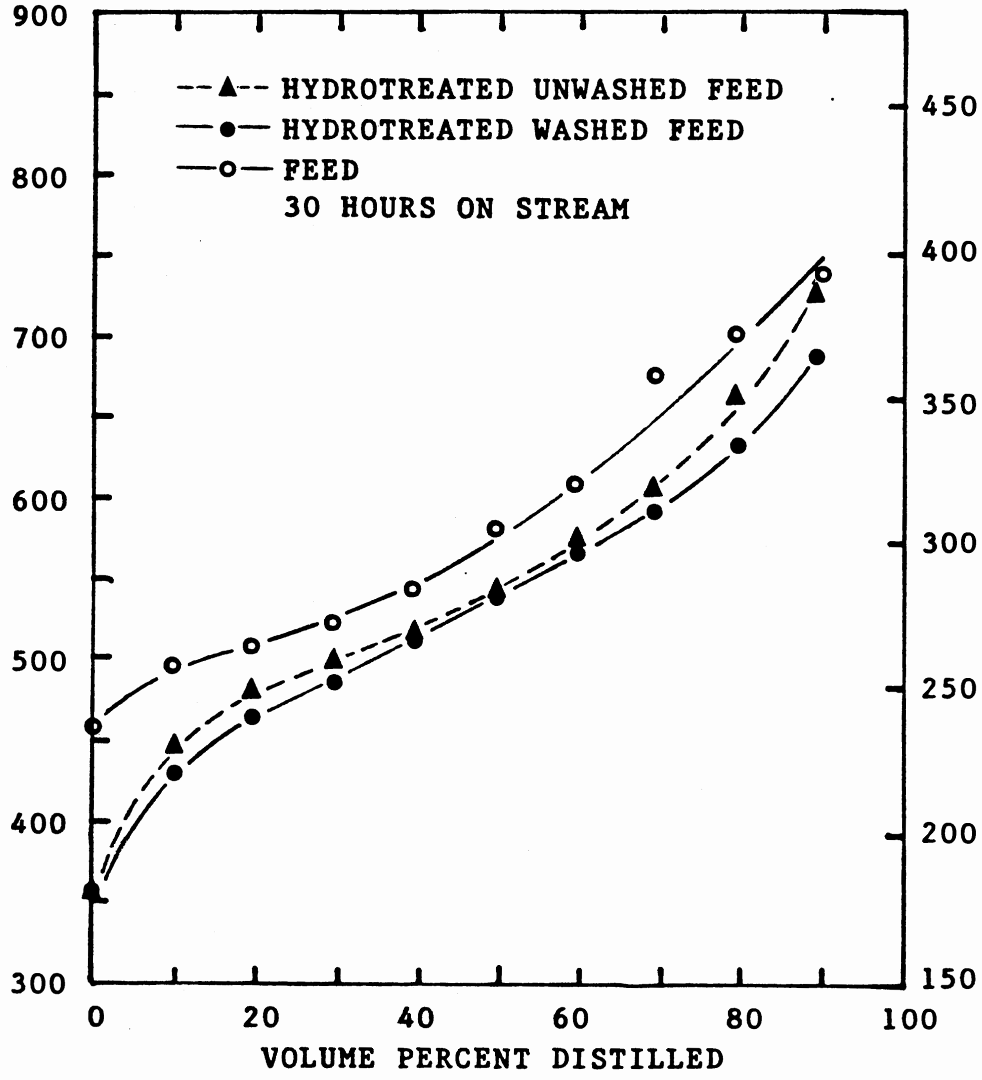

Figure 17. Boiling Points of Distillation Cuts from Hydrotreated Washed and Unwashed SRC Process Solvent

Run RPSS. The objective of run RPSS was to obtain reference data as in run RPS. The only difference between the two was the catalyst (Shell 324 in run RPSS). The run lasted for a total of 230 hours of oil-catalyst contact. Samples were analyzed for nitrogen, carbon and hydrogen. The Shell 324 catalyst proved to be a very active catalyst under the operating conditions employed. The denitrogenation activity indicates an initial deactivation from startup to 74 hours as seen in Figure 18. After 74 hours no significant deactivation occurs. The hydrogenation data in Figure 19 also show a slight decrease in activity during the first 74 hours after which no significant deactivation occurs.

The objective was to follow run RPSS with a run using an acid washed feed. Due to the lack of significant deactivation during RPSS no such run was conducted.

Heavy Distillate Hydrotreatment

Run RHD. The objective of run RHD was to provide reference data for comparitive purposes as in run RPS. Since the Shell 324 catalyst was shown to be a very active in the previous run (see also Chang, 1982), it was chosen for this and all subsequent runs. SRC Heavy Distillate was chosen as the feedstock for this series due to the higher concentration of nitrogen and the higher boiling characteristic of the liquid.

Run RHD and subsequent runs were conducted using the CLTU reactor system described in the previous chapter.

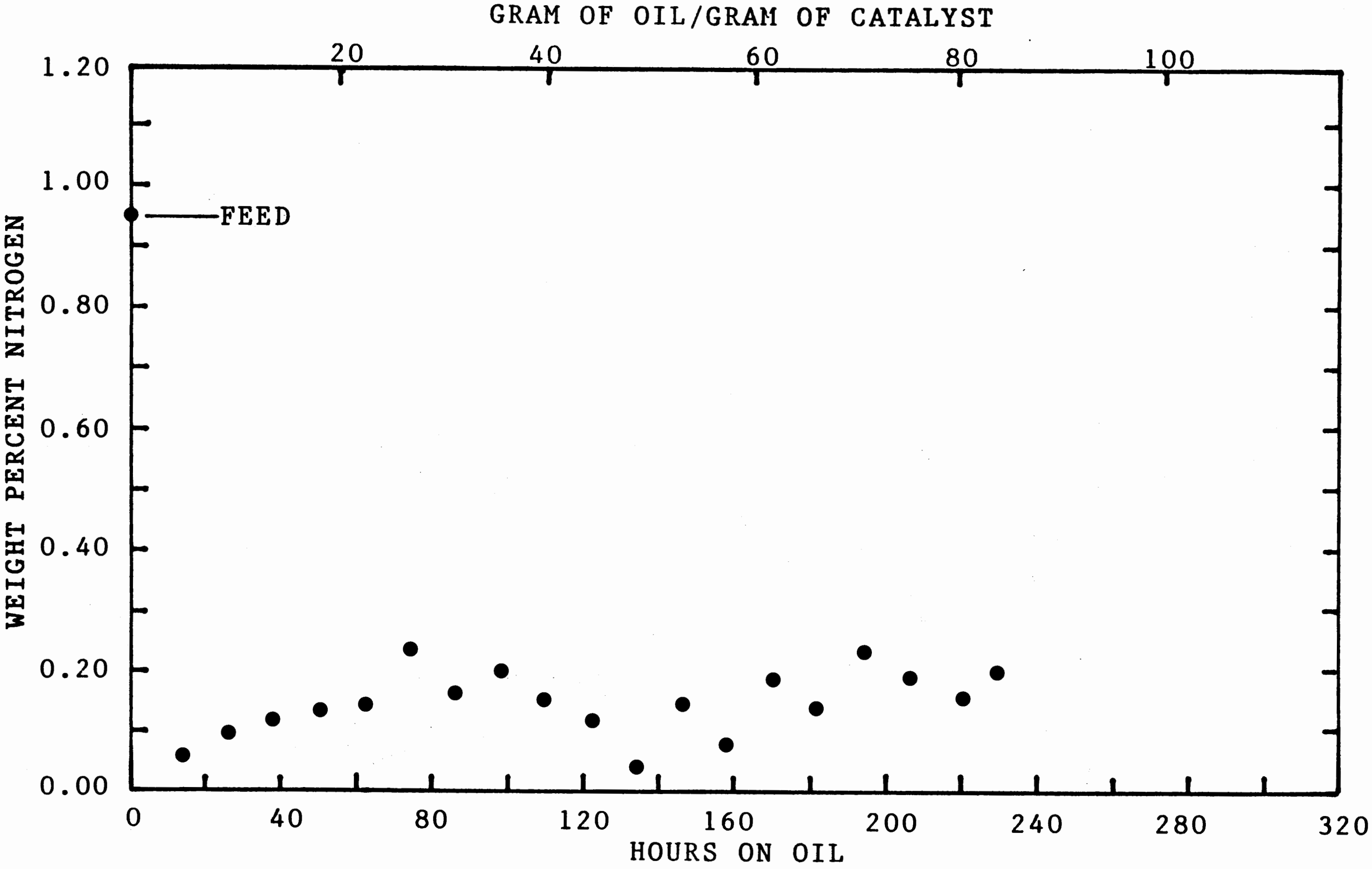

Figure 18. Hydrodenitrogenation Activity for Run RPSS

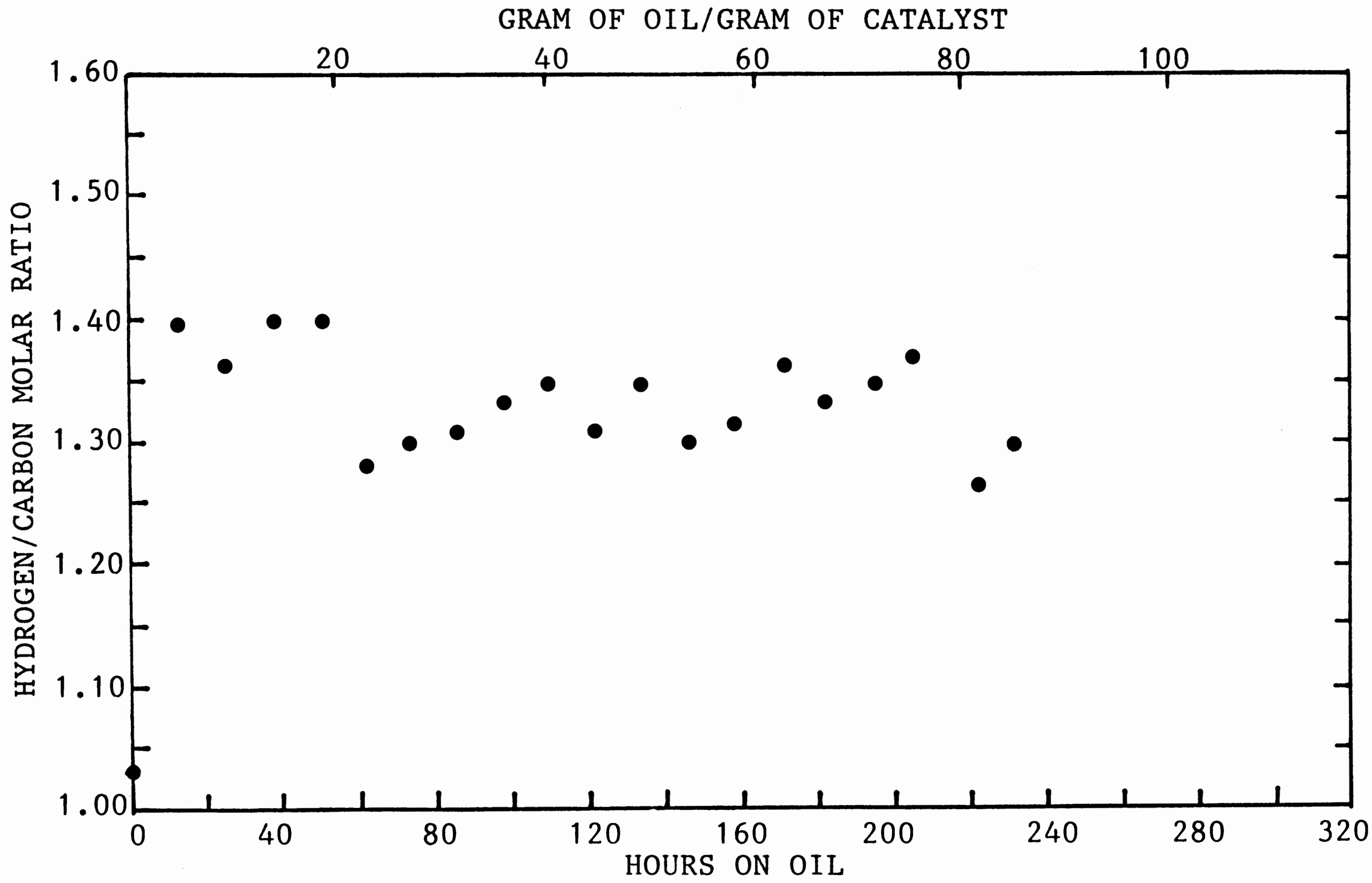

Figure 19. Hydrogen/Molar Ratio for Hydrotreated Products from Run RPSS.

The operating conditions were chosen to achieve a high initial catalyst activity with respect to HDN, HDS, and hydrogenation. The operational parameters were 413 C (775 F), 10.34 MPa (1500 psig), 1780 M^3H_2/M^3 (10000 SCF H_2/BBL oil) and 1.25 hour LVHST. The operational procedure outlined previously was followed. No problems were encountered during the scheduled 319 hours on stream. The nitrogen concentration is reduced from 1.09 % in the feed to 0.18 % initially. The denitrogenation activity appears to increase slightly up to 67 hours after which a steady deactivation occurs. Very little deactivation is seen from the desulfurization data. The level of hydrogenation as indicated by the hydrogen/carbon molar ratio decreases steadily throughout the run.

WHHD Series

Four runs were conducted in this series which utilized SRC Heavy Distillate washed with Hydrochloric Acid Solutions as the feedstock. The objective was to compare the effect of the washed feedstock on HDN, HDS and hydrogenation activity of the catalyst with run RHD. Plugging problems occurred in all four runs resulting in pressure fluctuations and, as a result, no run from the series achieved the objective. A description of the four runs follows:

Run WHHDa. The feedstock was prepared by the washing of SRC Heavy Distillate with one percent HCl using the temperature controlled extraction apparatus described previously. The extraction was conducted at 40 C with an acid solution to oil ratio of 3:1. The acid wash was followed by a single wash with distilled water at the same conditions.

The operational procedure used in run RHD was followed. After 30 hours on stream a pressure differential occurred over the reactor indicating partial plugging. After 44 hours on stream the reactor was shut down due to wide pressure fluctuations and hazardous pressure differentials. No analysis of any samples was attempted.

The reactor was dismantled after shutdown and the plugging material was found immediatly following the reactor tube exit and prior to the first gas-liquid separation bomb. A qualitative analysis indicated the material to be ammonium chloride.

Run WHHDb. The source of the chlorine was thought to be from the hydrochloric acid wash. The feedstock for Run WHHDb was then washed once with HCl as in WHHDa followed by two washes with distilled water. A heating system for the tubing from the reactor exit to the first gas-liquid separation bomb was installed.

Pressure fluctuations occurred 25 hours after startup. The problem became severe after 40 hours on stream and the reactor was again shut down. The tubing following the reactor was dismantled and the same crystalline material was found.

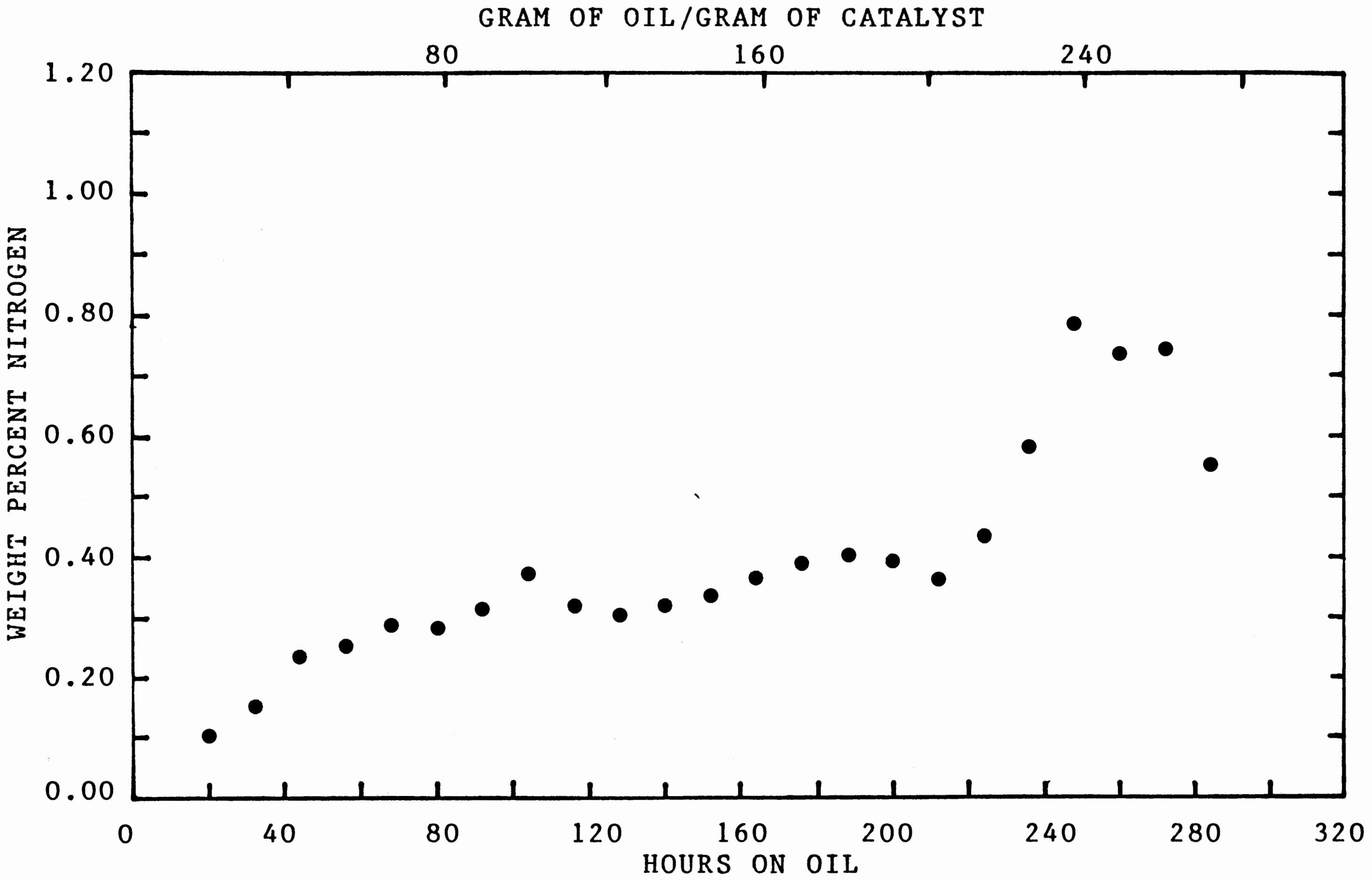

Figure 20. Hydrodenitrogenation Activity for Run WHHDd

Run WHHDc. The tubing below the reactor was shortened and the heating system improved. No changes were made in the washing procedure for the feed stock from the previous run.

Pressure fluctuations again occurred after 103 hours on stream. The run was continued for another 29 hours when the reactor plugged completely. The same material was again found to be responsible for the plugging.

Run WHHDd. The Heavy Distillate feedstock for run WHHDd was washed once with HCl as before followed by three washes at a one to three ratio. All other parameters and operating conditions were the same as the previous runs.

Pressure fluctuations started after 44 hours on stream, although less severe than in previous runs. The run was allowed to continue although the pressure fluctuated 100 psig from the design pressure of 1500 psig. Samples were analyzed for Nitrogen, sulfur, carbon and hydrogen. The denitrogenation data is presented in Figure 20.

WSHD Series

The WSHD series consists of three hydrotreatment runs, two of which were prematurely shut down due to plugging problems. The third and last run was successfully completed with no operational problems occurring.The objective of this series was the same as in the WHHD series. The feedstock was the same in all three runs and was prepared by washing the Heavy Distillate once with 1% sulfuric acid followed by two washes with distilled water. No major changes in the reactor system were made following the WHHD run series.

<u>Run WSHDa</u>. Run WSHDa was operated for 72 hours before plugging forced a premature shutdown. Upon dismantling the reactor, the plug was found at the top of the upper zone of glass beads in the reactor tube. All plugging material was within one inch of the reactor entrance. The plugging material appeared to be polymer type material. No analysis was attempted on the plug. The samples taken during the run were analyzed for nitrogen concentration.

<u>Run WSHDb</u>. The one millimeter diameter glass beads in the top and bottom inert zones were replaced with 3 millimeter diameter glass beads for this run. No other alterations were made.

A plug again occurred after 92 hours on stream. The behavior of the plug was such that the pressure downstream from the reactor declined in a linear fashion with no fluctuations. The time from the first indication of the plug to the point of mandatory shutdown was relatively short.

The reactor was dismantled and the material was again found to be the polymer type substance located in the top one inch of the reactor tube in the glass bead zone. Samples taken throughout the run were analyzed for nitrogen.

<u>Run WSHDc</u>. For this run the reactor tube was loaded without an inert zone of glass beads above the catalyst zone. Six millimeter diameter glass beads were used in

the lower inert zone. No other changes in equipment or procedure were made.

No problems were encountered during the scheduled 302 hours on stream. The pressure remained stable throughout the run with no indications of plugging at any time. Samples were taken at 12 hour intervals and analyzed for nitrogen, carbon, hydrogen and sulfur. The run is referred to as WSHD in further discussions.

A comparison of the HDN, HDS and hydrogenation activity (as H/C molar ratio) of run WSHD with that of run RHD is shown in Figures 21, 22 and 23.

The denitrogenation activity from Figure 21 shows a higher initial activity for run WSHD with 95% of the nitrogen removed and consistantly lower concentrations of nitrogen throughout the run. However, the percentage removal relative to the feed concentration is approximately the same in both runs. The concentration increases in a linear fashion in both runs and the rate of deactivation appears to be the same.

The Shell 324 catalyst maintained a high level of desulfurization activity in both runs RHD and WSHD as seen in Figure 22. Essentially no deactivation is seen in run RHD. Although the initial activity appears to be the same, the concentration in run WSHD decreases after 30 hours on stream in and remains negligible for the following 250 hours. Only the last two samples again show significant sulfur concentration.

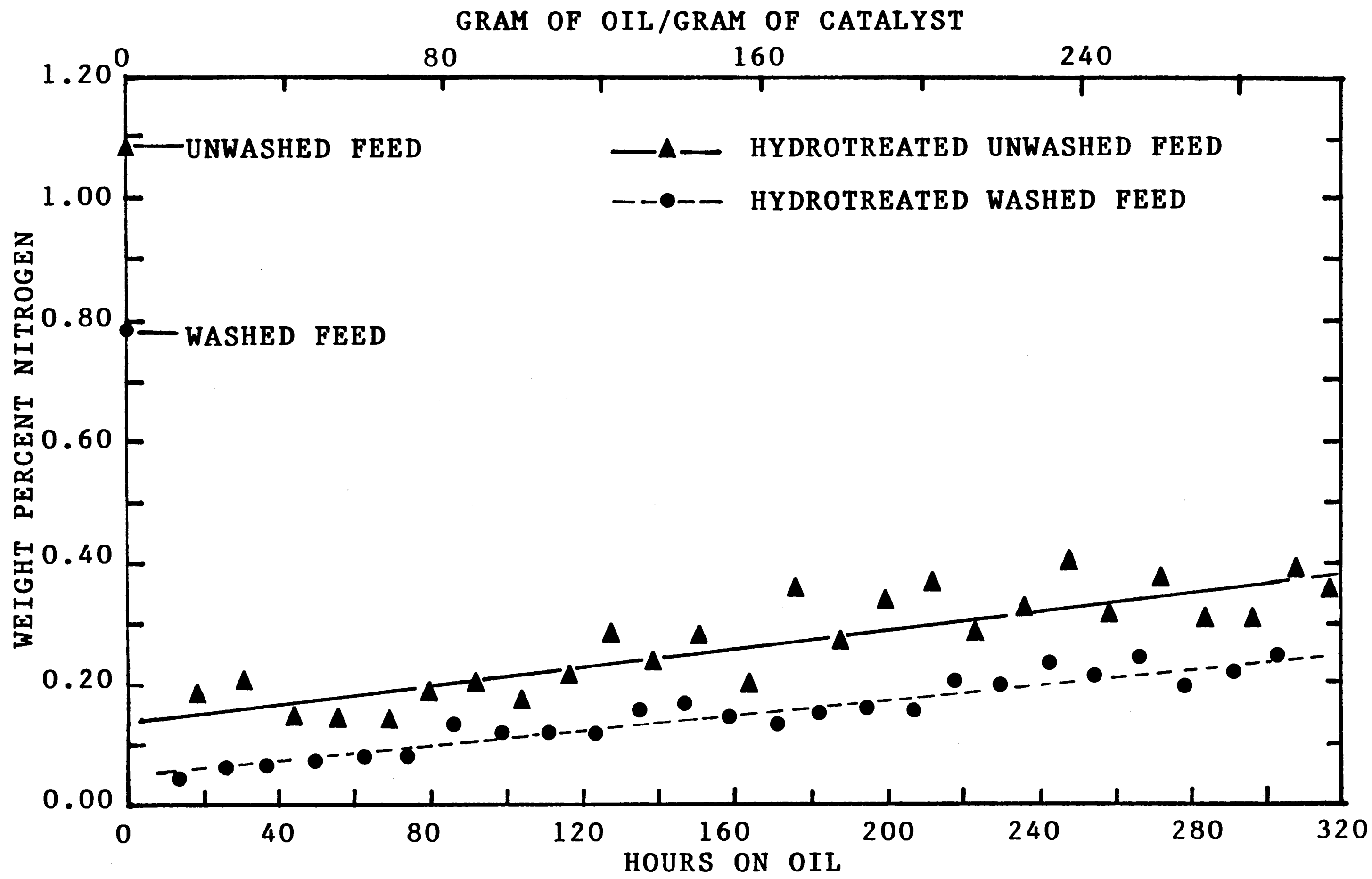

Figure 21. Comparison of the Hydrodenitrogenation Activity for Raw and Sulfuric Acid Washed SRC Heavy Distillate

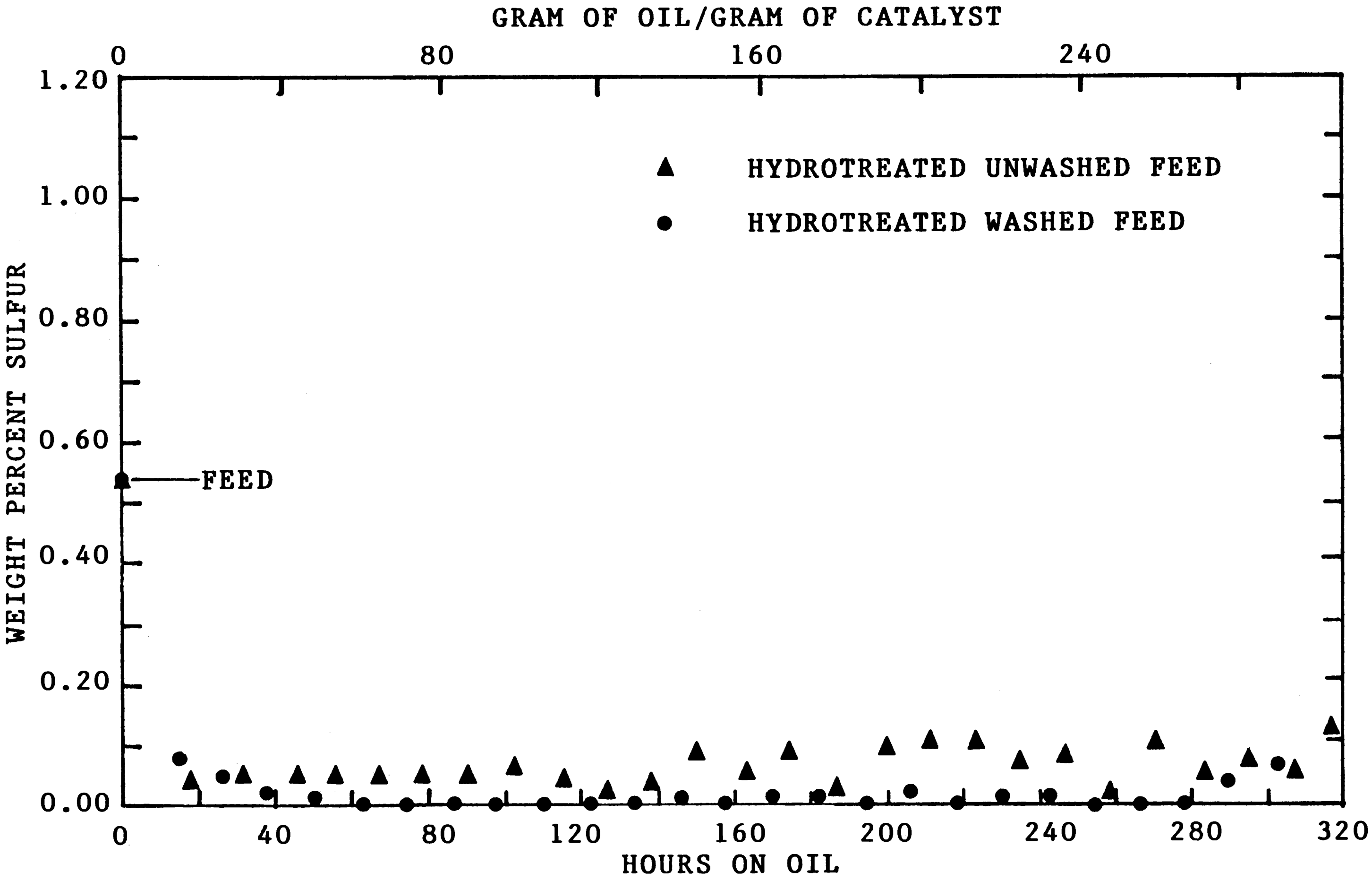

Figure 22. Comparison of the Hydrodesulfurization Activity for Raw and Sulfuric Acid Washed SRC Heavy Distillate

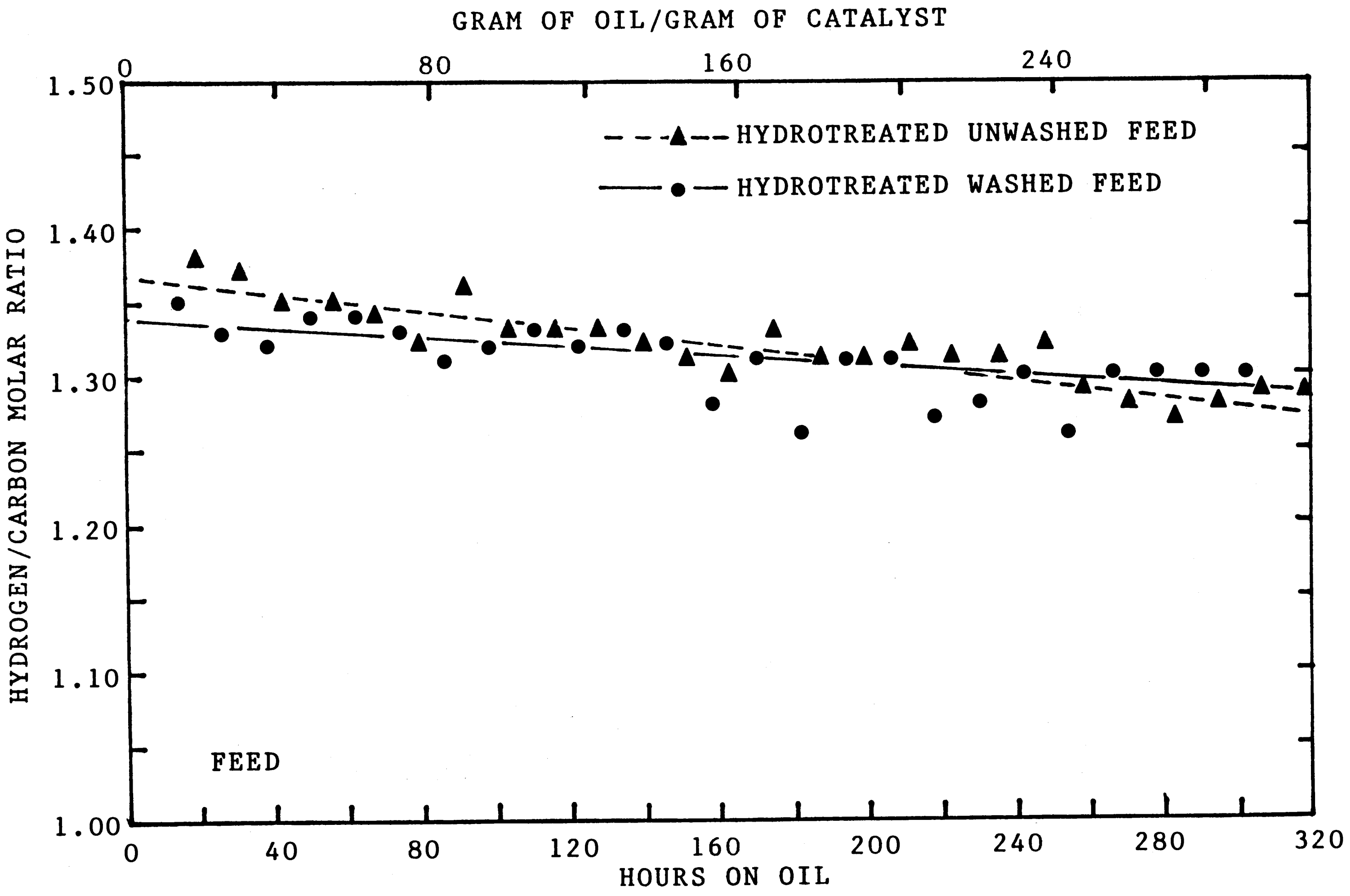

Figure 23. Comparison of the Hydrogen/Carbon Molar Ratio for Hydrotreated Products of Sulfuric Acid Washed and Unwashed SRC Heavy Distillate

A comparison of the hydrogen/carbon molar ratio for runs RHD and WSHD is shown in Figure 23. There is no significant difference between the two runs in this respect. Both show substantial hydrogenation relative to the feedstock and a gradual decrease in the molar ratio throughout the run.

Samples taken after 30 hours on stream were subjected to ASTM distillation. The distillate was separated as distlled into 0-30%, 30-60% and 60% to end point volume fractions. Each of the cuts plus the residue was analyzed for nitrogen, carbon and hydrogen. The results are shown in Figures 24 and 25. The boiling points do not vary significantly up to 20% distilled and the distillate from run WSHD shows only slightly lower boiling points beyond 20% distilled. After 275 hours on stream run RHD shows slightly lower boiling points in nearly all cuts.

The nitrogen concentration in the various distillation cuts after 30 hours on stream is shown in Figures 26 and 27. The only data that differs significantly is that of the 60%-endpoint cut with a lower concentration for the acid washed feed. After 275 hours the difference is more significant. All the cuts from run WSHD show lower nitrogen concentrations. The datum for the residue for the washed feed is essentially the same at 275 hours as at 30 hours. For the raw feed, however, the nitrogen concentration in the distillate residue increases substantially from the 30 hour to the 275 hour sample.

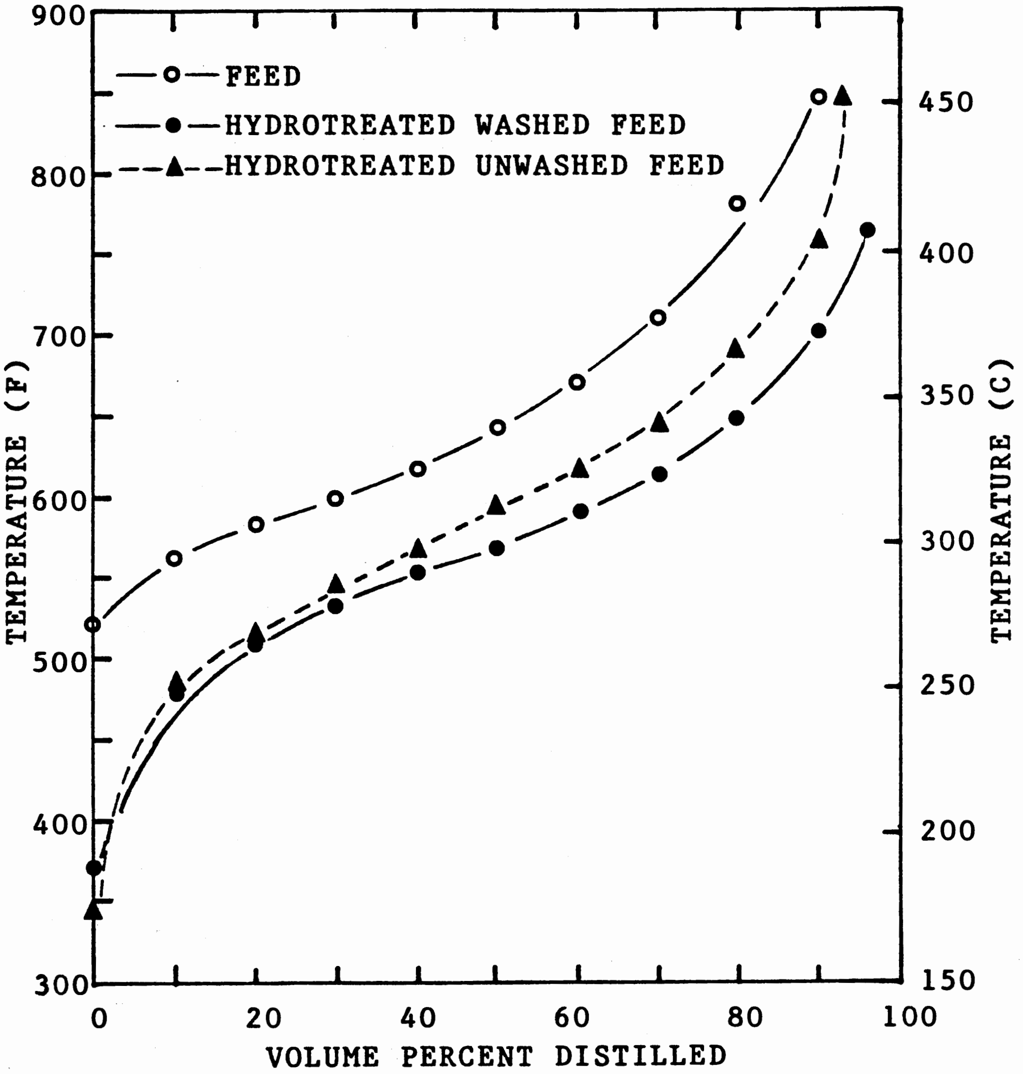

Figure 24. Boiling Points of Distillation Cuts from Hydrotreated Washed and Unwashed SRC Heavy Distillate after 30 Hours on Stream

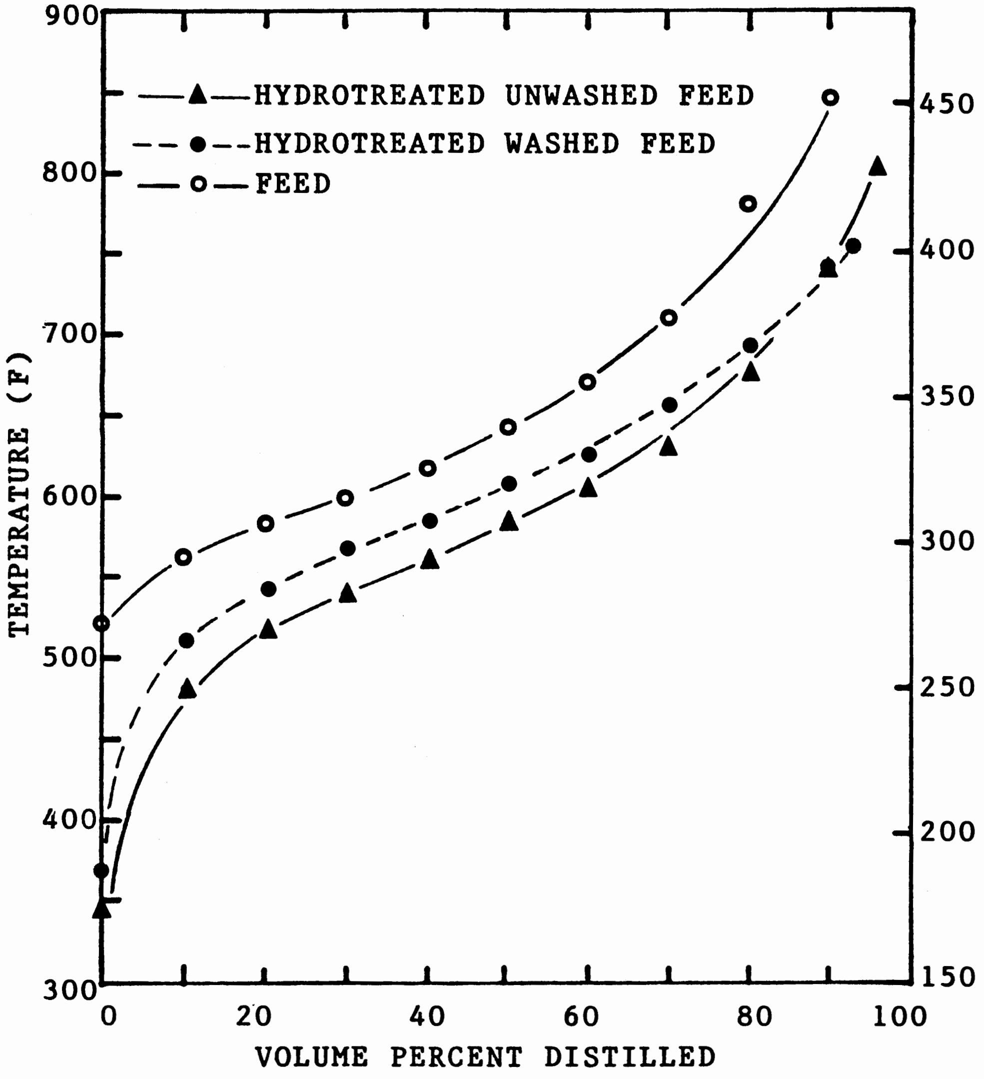

Figure 25. Boiling Points of Distillation Cuts from Hydrotreated Washed and Un-Washed SRC Heavy Distillate after 275 Hours on Stream

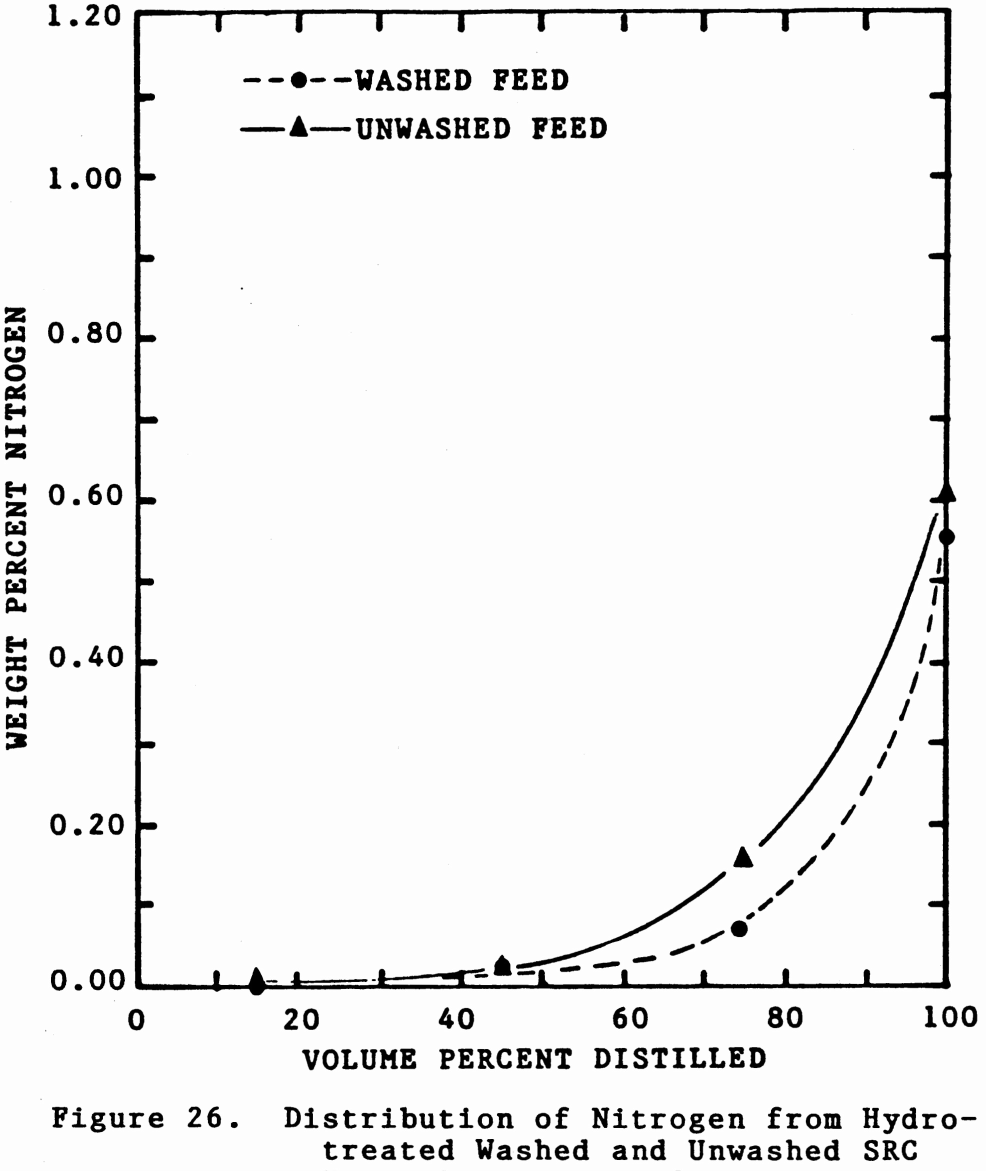

Figure 26. Distribution of Nitrogen from Hydrotreated Washed and Unwashed SRC Heavy Distillate after 30 Hours on Stream.

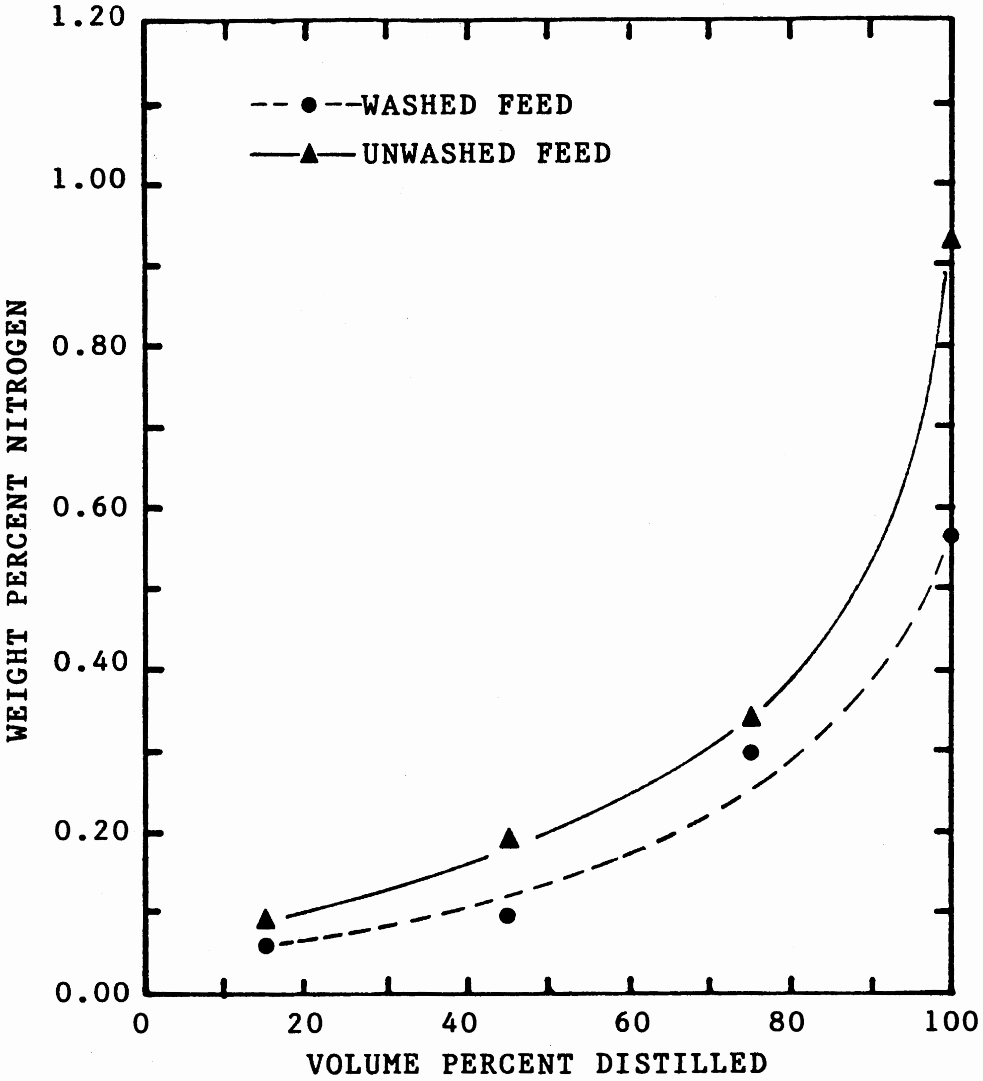

Figure 27. Distribution of Nitrogen from Hydrotreated Washed and Unwashed SRC Heavy Distillate after 275 Hours on Stream.

The raw and acid washed feedstocks and several product samples from various points throughout runs RHD and WSHD were analyzed for basic nitrogen using the method outlined in the previous chapter. The results, shown in Figure 28, indicate very little difference in basic nitrogen in the hydrotreated products although the basic nitrogen concentration in the feed is decreased substantially from the acid washing.

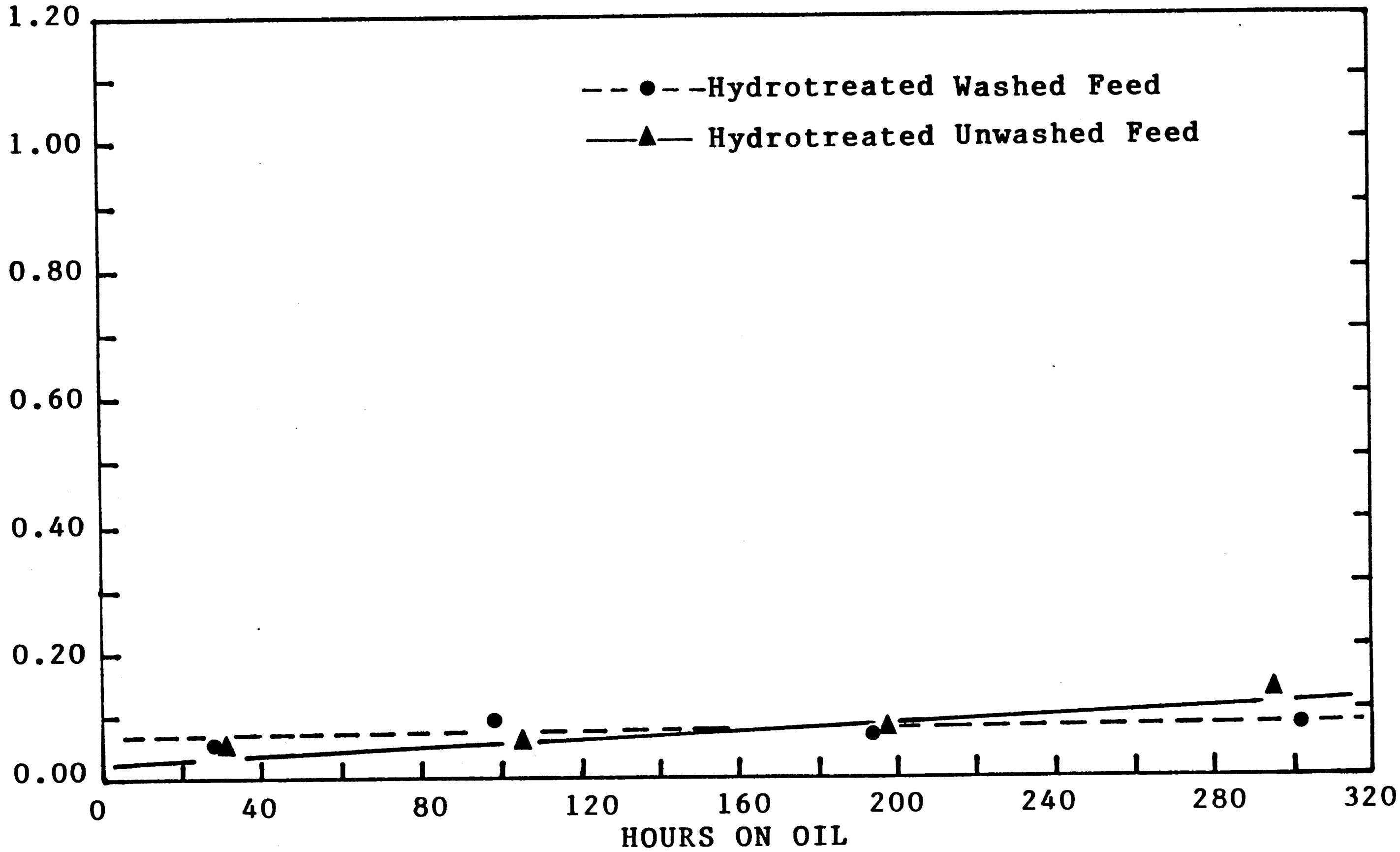

Figure 28. Basic Nitrogen Concentration in Hydrotreated Products of Acid Washed and Unwashed SRC Heavy Distillate.

CHAPTER V

DISCUSSION OF RESULTS

The first objective of this study was to investigate the feasibility of removing basic nitrogen compounds from SRC liquids by acidic extraction. The effectiveness of the acid washes as well as adverse effects on the liquid will be discussed. The effect of temperature, acid concentration and acid solution/oil volume ratio will also be discussed.

Of the ten hydrotreatment runs conducted, only two sets were of significant value for camparison between the raw and acid washed feedstocks. However, other runs did provide relevant information on the reproducibility of the hydrotreatment data. The following aspects of the hydrotreatment results will be discussed:

1. Comparison of raw and acid washed products of hydrotreatment with respect to hydrogenation, hydrodenitrogenation and hydrodesulfurization.
2. Comparison of distillation products of hydrotreated products.
3. Reproducibility and precision of the data.

Extraction of Nitrogen Compounds

The ability to extract nitrogen compounds from the organic phase into the aqueous phase depends upon:

1. Breaking of intermolecular bonds in the organic phase.
2. Diffusion of the molecule through the organic phase.
3. Solubility of the molecule in the aqueous phase.

Due to the relatively large concentration of heterocompounds in SRC liquids, significant dipole-dipole interaction should exist leading to strong intermolecular bonding. Hydrogen bonding should be a major factor in heterocompound solubility in both organic and liquid phases. Pure component solubility data, therefore, may not be a good indicator of extractiblity from a multicomponent liquid.

Basic nitrogen compounds have been shown to form hydrochlorides readily (Schweighart, 1975) and several investigators have utilized hydrochloric acid to separate basic nitrogen fractions in coal derived liquids for analytical purposes (Bodzek et al., 1979; Paudler and Cheplen, 1979; Schweighart et al., 1978). The results from the preliminary extraction study, shown in Figure 7, indicate a small amount of nitrogen compounds are extracted using water alone. These compounds could be basic, acidic or neutral nitrogen compounds. However, the formation of the salt is evidently necessary for removal of a significant amount of nitrogen compounds. The largest removal shown for the process solvent is 38% which was a multiple washing with two acid and two water washes. The basic nitrogen concentration of the raw and acid washed process solvent is 0.48% and 0.16% respectively. The amount of nitrogen removed is less than the total basic nitrogen indicating that either not all basic nitrogen formed the acid salt or the salt was not extracted from the organic phase.

The effect of agitation time on nitrogen removal, as shown in Figure 8, indicates very little additional removal after 5 minutes of mixing. If diffusion resistance through the organic phase is a significant factor, an exponential decline in the nitrogen concentration of the organic phase would be expected. Diffusion resistance, then, does not appear to be significant.

The effect of temperature on nitrogen removal from SRC Heavy Distillate, shown in Figure 9, is not significant for hydrochloric acid washes. An increase is observed for the sulfuric acid wash from 25 C to 40 C beyond which the effect again is not significant. The temperature would affect the rate of diffusion, the formation of the salt and the solubilities in both phases. Since diffusional resistance is not considered significant, the hydrochloride salt appears to have a higher solubility in the aqueous phase than the corresponding sulfuric acid salt.

The effect of increasing acid concentration also indicates a maximum at approximately one weight percent acid. However, in this study acid concentrations were restricted to below twenty weight percent. Lin and Holy (1978) used sulfuric acid concentrations of 5, 50 and 90% to extract nitrogen from two coal derived liquids. As seen in Figure 27, extraction of GU 145R Product #38 (Gulf Oil Company) showed a 32% removal of nitrogen with both 5% and 50% acid concentrations. The removal is increased to 55% with a 90% acid concentration. With the H-Coal liquid, increasing the acid concentration from 5% to 50% increased the removal of nitrogen slightly from 64% to 71% removed. At 90% acid concentration, the removal was increased to 95%. These results indicate little or no increase in removal from an increase in acid concentration from 5% to 50%. The results obtained using a 5% concentration are similar to those obtained in this study for SRC liquids.

The distillation data shown in Figure 12 indicate the nitrogen concentration in the Heavy Distillate increases with increasing boiling temperature. Wilson and co-workers (1982) also observed a similar trend in SRC I Process Solvent. The acid washed heavy distillate shows the same trend although the difference in concentration between the raw and washed liquids is greater in the lower boiling cuts. This would indicate removal of a greater percentage of lower molecular weight nitrogen compounds.

The Effect of Acid Washing On Hydrotreatment

Process Solvent Hydrotreatment

The unscheduled shutdown of run RPS after 76 hours limits comparisons between hydrotreatment of the raw feed of run RPS and acid washed feed of WPS. However, several

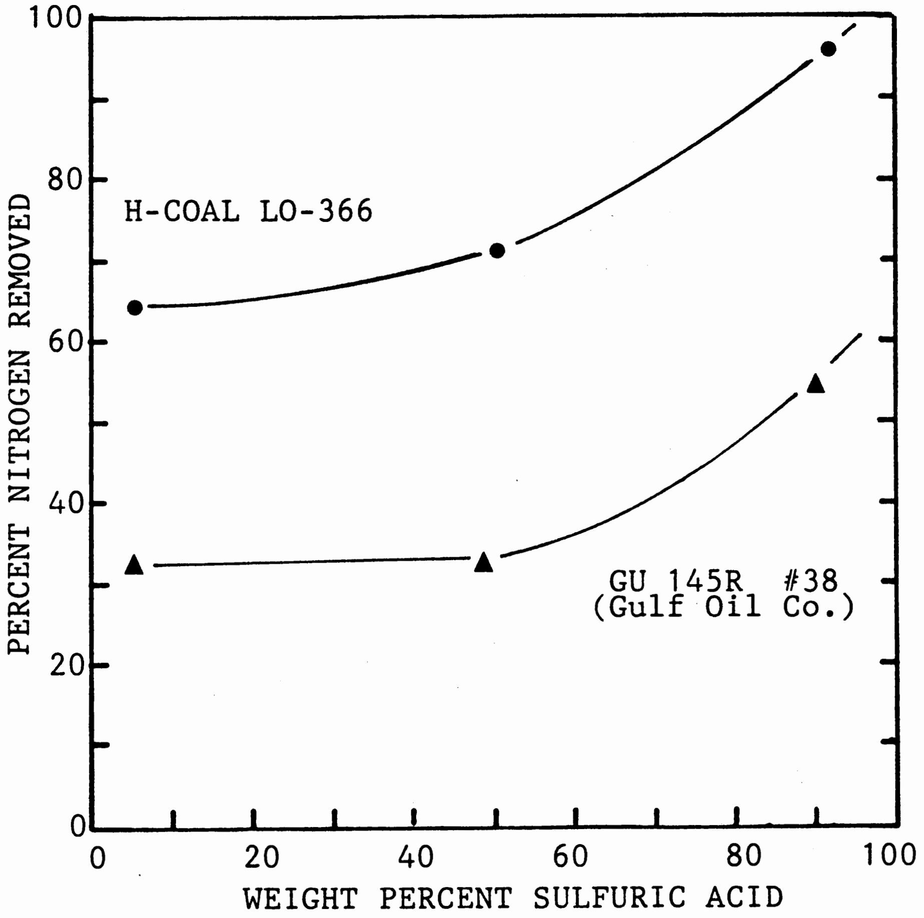

Figure 29. The effect of Acid Concentration on Nitrogen Removal from Coal Derived Liquids (Lin and Holy, 1978)

differences are noted. The initial concentrations of nitrogen in run WPS are slightly higher than that of run RPS. Although nearly 40% of the nitrogen was removed in the acid washed feed the concentration in the hydrotreated product is no better than the unwashed feedstock. The compounds removed by acidic extraction from Process Solvent are appearently those most easily converted during hydrotreatment.

The least square fit of the denitrogenation data indicates slight deactivation for the raw feedstock and essentially no deactivation for the washed feed. The increase in nitrogen concentration after switching to the raw feed in run WPS could be caused by several different factors:

1. Catalyst poisoning by basic nitrogen compounds.
2. A relative increase due to the greater concentration of nitrogen in the raw feed.
3. The absence of the chloride ion which was present during the first 138 hours of oil catalyst contact.

As mentioned previously, adsorption of basic nitrogen compounds may be either reversible or irreversible. The possibility exists that a reversible adsorption equilibrium existed while under the washed feed. After switching to the raw feed, the basic nitrogen concentration increased and the adsorption-desorption equilibruim was maintained. If the increase was simply due to the relative difference in the feeds, that difference should also be present in the initial stages of the runs. Coking does not appear to be a factor due to the rapid increase in the concentration.

Another explanation is that the chloride ion present in the washed feed (from the HCl wash) accounts for the lack of deactivation up to the 138 hour point and the absence of the ion after that point accounts for the decrease in denitrogenation activity. This phenomenon has been reported by other investigators. Gates and Katzer (1980) reported increased denitrogenation activity after addition of fluoride to a sulfided Ni-Mo/alumina catalyst. Massoth et al. (1981) reported increased hydrodesulfurization activity after addition of fluoride and chloride ions to Co-Mo/Silica alumina catalyst. Recently Chan (1982) reported the presence of chloride (from titanocene dichloride added to the feed) as a possible explanation for increased catalyst activity during hydrotreatment of an SRC liquid.

The hydrodesulfurization data indicates a greater deactivation with the acid washed feed than with the raw feed. Gates, et al (1979), reported that quinoline and its reaction intermediates inhibit carbon-nitrogen and carbon-sulfur bond scission as well as hydrogenation reactions. If the lack of deactivation with respect to hydrodenitrogenation is due to a reduced inhibiting effect in the acid washed feed, a similar trend would be expected in the hydrodesulfurization and hydrogenation activity.

Heavy Distillate Hydrotreatment

Comparison of runs RHD (raw Heavy Distillate feed) and WSHD (sulfuric acid washed Heavy Distillate) produced several significant differences. The nitrogen concentration in the initial products were substantially lower in WSHD than RHD. This difference was not present in the initial products of raw and washed Process Solvent. The difference between the two sets of runs appears not to be due to the amount of total or basic nitrogen present in the acid washed feed relative to the raw feed, but due to the type of nitrogen compound present. Acid washing of Process Solvent reduced the basic nitrogen concentration by 65%. With Heavy Distillate, acid washing reduced the basic nitrogen concentration by 45%. Even though acid washing was more effective in reducing the total nitrogen and basic nitrogen concentrations in the case of Process Solvent, the effect of acid washing is much more pronounced in the initial product samples of Heavy Distillate.

There is a consistant deactivation throughout the run, however. Chang (1982) has suggested that poisoning by basic nitrogen compounds should be significant only during the first few hours of a run and that deactivation by coke formation should be the primary deactivation mechanism. The two runs do not exhibit a difference in the rate of deactivation even though there is a difference in the amount of product nitrogen throughout the run. Poisoning, then, does not appear to be the primary deactivation mechanism since a reduction of nitrogen compounds does not affect the overall deactivation rate.

The hydesulfurization data shows a significant increase in the activity after 40 hours on stream. A possible explanation is the absence of certain nitrogen compounds due to the extraction which inhibit hydrodesulfurization. Satterfield and co-workers (1975) reported a severe inhibiting effect due to pyridine on hydrodesulfurization of thiophene over a wide range of temperatures.

No definite conclusions can be drawn from the hydrogen/ carbon molar ration for the two runs. Both show significant hydorgenation activity and also indicate a slight deactivation throughout the run.

Distillation

The nitrogen concentration in the feedstocks tends to increase with increasing boiling point. The trend is even more pronounced in the hydrotreated products. The hydrotreated product of the acid washed Process Solvent, after 30 hours on stream, shows a slightly lower concentration of nitrogen in all boiling cuts. Both products show a high concentration in the residue and the difference between the two is not significant. An almost identical trend is again seen after 30 hours of oil catalyst contact in the hydrotreatment of raw and acid washed Heavy Distillate. After 275 hours the product from the acid washed feed shows slightly less nitrogen in all cuts with the largest difference in the residue.

Due to the mechanism of denitrogenation, whereby the saturation of the ring is necessary before C-N bond breakage, a higher conversion of lower boiling compounds is expected with both feedstocks. The significant difference in the nitrogen concentration of the residue after 275 hours is not expected. Previous distillation data has shown the majority of nitrogen removal is due to relatively lower molecular weight compounds. The difference in the concentrations in the residue at that point should not be due to a relative difference in the feedstocks.

Reproducibility and Precision

The reproducibility of the experimental data depends upon the procedure as well as the accuracy of the analytical equipment. The overall reproduciblity can be seen from the run series WSHD where two runs were ended prematurely due to plugging. No changes were made in the acid washing procedure for the three runs. The only changes made in the hydrotreatment procedure were the larger glass beads in the upper inert zone in run WSHDb and the removal of the glass beads from the upper inert zone in WSHDc. These changes should have a negligible effect on the results. Very good agreement in nitrogen concentrations was observed in the initial samples with measurements of 0.04%, 0.04%, and 0.05%. The hydrogen concentrations showed a greater variation with measurements of 9.62%, 9.65%, and 10.02%. Other samples up to the point of plugging also showed good agreement.

An estimate of the accuracy of nitrogen analysis is seen from the standard deviations from the analysis of runs RHD and WSHD given in Table XVII in Appendix A. The deviations range from 0.000 to 0.028 for run RHD and to 0.046 for WSHD. The samples with concentrations lower than 0.10% are relatively less accurate than those at larger concentrations. Bhan (1981) observed similar results in measuring nitrogen concentrations of an SRC Process Solvent. Measurements of the hydrogen concentrations in samples from runs RHD and WSHD showed a maximum standard deviation of 0.15 and 0.13 respectively. These results indicate high reproducibility and accuracy.

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APPENDIX A

EXPERIMENTAL DATA

TABLE VIII

RESULTS FOR RUN RPS

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
FEED		0.95		0.54		7.51	86.51	1.03	4.49
RPS-2	16	0.05	95	0.09	83	9.21	86.88	1.27	3.37
RPS-3	22	0.11	88	0.16	70	9.35	87.22	1.29	3.16
RPS-4	28	0.17	82	0.12	78	9.29	88.03	1.27	2.39
RPS-5	34	0.09	91	0.15	72	9.21	87.10	1.27	3.45
RPS-6	40	0.12	87	0.20	63	9.25	86.04	1.29	4.39
RPS-7	46	0.12	87	0.16	70	9.25	85.76	1.29	4.71
RPS-8	52	0.20	79	0.07	87	9.28	89.31	1.28	1.01
RPS-9	58	0.17	82	0.08	85	9.37	89.37	1.27	1.01
RPS-10	64	0.15	84	0.10	81	9.30	87.47	1.28	2.98

TABLE VIII (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
RPS-11	70	0.17	82	0.12	78	9.37	88.32	1.27	2.02
RPS-12	76	0.23	76	0.13	76	9.14	87.40	1.25	3.10

FEED: SRC PROCESS SOLVENT; *BY DIFFERENCE

TABLE IX

RESULTS FOR RUN WPS

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
FEED		0.95		0.54		7.51	86.81	1.32	4.54
WPS-2	12	0.13	78	0.07	87	9.52	86.56	1.32	3.72
WPS-3	18	0.16	73	0.12	78	9.41	86.96	1.30	3.35
WPS-4	24	0.16	73	0.12	78	9.38	86.86	1.30	3.48
WPS-5	30	0.20	67	0.12	78	9.35	86.91	1.29	3.42
WPS-6	36	0.13	78	0.13	76	9.55	86.84	1.32	3.35
WPS-7	42	0.16	73	0.13	76	9.44	86.88	1.30	3.39
WPS-8	48	0.17	72	0.09	83	9.34	87.02	1.29	3.38
WPS-9	54	0.19	68	0.17	69	9.27	86.79	1.28	3.58
WPS-10	60	0.18	70	0.15	72	9.22	86.90	1.27	3.55
WPS-11	66	0.14	77	0.29	46	9.30	86.76	1.29	3.51

TABLE IX (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
WPS-12	72	0.18	70	0.21	61	9.35	86.55	1.30	3.71
WPS-13	78	0.15	75	0.14	74	9.41	86.90	1.30	3.40
WPS-14	84	0.15	75	0.09	83	9.23	87.03	1.27	3.50
WPS-15	90	0.14	77	0.31	43	9.19	86.43	1.28	3.93
WPS-16	96	0.20	67	0.20	63	9.28	86.50	1.29	3.82
WPS-17	102	0.15	75	0.22	59	9.33	86.64	1.30	3.66
WPS-18	108	0.15	75	0.22	59	9.18	86.30	1.28	4.15
WPS-19	114	0.14	77	0.26	52	9.20	86.39	1.28	4.01
WPS-20	120	0.14	77	0.24	56	9.24	86.90	1.28	3.48
WPS-21	126	0.17	72	0.22	59	9.21	86.75	1.27	3.65
WPS-22	132	0.19	68	0.20	63	9.28	86.50	1.29	3.83
WPS-23	138	0.17	72	0.23	57	9.20	86.68	1.27	3.72

TABLE IX (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
WPS-24**	144	0.21	78	0.25	54	9.18	86.72	1.27	3.64
WPS-25**	150	0.31	67	0.26	52	8.95	86.88	1.24	3.60
WPS-26**	156	0.38	60	0.25	54	9.02	86.63	1.25	3.72

FEED: WASHED SRC PROCESS SOLVENT; WASH: 0.5% HCl

*BY DIFFERENCE; **UNWASHED SRC PROCESS SOLVENT

TABLE X

RESULTS FOR RUN RHD

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
FEED		1.09		0.54		7.61	89.03	1.03	1.73
RHD-2	19	0.18	83	0.04	93	10.08	87.65	1.38	2.05
RHD-3	31	0.20	82	0.05	91	10.04	87.92	1.37	1.99
RHD-4	43	0.14	87	0.05	91	9.96	88.39	1.35	1.46
RHD-5	55	0.14	87	0.05	91	10.02	89.06	1.35	0.73
RHD-6	67	0.14	87	0.05	91	9.94	88.79	1.34	1.08
RHD-7	79	0.23	78	0.05	91	9.80	89.41	1.32	0.51
RHD-8	91	0.20	82	0.05	91	10.01	88.92	1.35	0.82
RHD-9	103	0.17	84	0.06	89	9.89	89.11	1.33	0.77
RHD-10	115	0.21	81	0.04	92	9.85	89.00	1.33	0.90
RHD-11	127	0.28	74	0.02	96	9.77	88.23	1.33	1.70

TABLE X (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
RHD-12	139	0.23	79	0.03	94	9.84	89.45	1.32	0.45
RHD-13	151	0.28	74	0.08	85	9.75	87.85	1.33	2.04
RHD-14	163	0.20	82	0.05	91	9.67	89.08	1.30	1.20
RHD-15	175	0.34	68	0.09	83	9.70	87.84	1.33	2.03
RHD-16	187	0.27	75	0.02	96	9.67	88.81	1.31	1.48
RHD-17	199	0.33	70	0.10	81	9.65	88.38	1.31	1.54
RHD-18	211	0.36	67	0.10	81	9.66	88.02	1.32	1.86
RHD-19	223	0.28	74	0.10	81	9.62	88.44	1.31	1.56
RHD-20	235	0.32	71	0.06	89	9.66	88.29	1.31	1.67
RHD-21	247	0.39	64	0.07	87	9.64	87.89	1.32	2.01
RHD-22	259	0.30	72	0.02	96	9.58	89.04	1.29	1.06
RHD-23	271	0.37	66	0.10	81	9.43	88.57	1.28	1.53

TABLE X (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
RHD-24	283	0.30	72	0.05	91	9.50	89.93	1.27	0.22
RHD-25	295	0.30	72	0.07	87	9.56	89.43	1.28	0.64
RHD-26	307	0.38	65	0.05	91	9.50	88.66	1.29	1.41
RHD-27	319	0.35	68	0.12	78	9.52	88.89	1.29	1.12

FEED: SRC HEAVY DISTILLATE; *BY DIFFERENCE

TABLE XI

RESULTS FOR RUN WSHD

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
FEED		0.79		0.54		7.47	89.40	1.00	1.80
WSHD-2	14	0.04	95	0.06	89	10.02	89.10	1.35	0.78
WHSD-3	26	0.07	91	0.05	91	9.89	89.20	1.33	0.79
WSHD-4	38	0.07	91	0.02	95	9.50	89.03	1.32	0.99
WSHD-5	50	0.08	90	<0.02	98	9.98	89.46	1.34	0.47
WSHD-6	62	0.09	89	<0.02	>98	9.95	84.30	1.34	0.66
WSHD-7	74	0.09	89	<0.02	>98	9.90	89.18	1.33	0.83
WSHD-8	86	0.13	84	<0.02	>98	9.69	89.09	1.31	1.09
WSHD-9	98	0.12	85	<0.02	>98	9.79	88.97	1.32	1.12
WSHD-10	110	0.12	85	<0.02	>98	9.87	89.33	1.33	0.68
WSHD-11	122	0.12	85	<0.02	>98	9.79	89.03	1.32	1.06

TABLE XI (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
WSHD-12	134	0.16	80	<0.02	>98	9.87	89.01	1.32	0.96
WSHD-13	146	0.17	78	<0.02	>98	9.85	89.89	1.32	0.09
WSHD-14	158	0.14	82	<0.02	>98	9.50	89.03	1.28	1.33
WSHD-15	170	0.13	84	<0.02	>98	9.71	89.23	1.31	0.92
WSHD-16	182	0.15	81	<0.02	>98	9.46	90.32	1.26	0.06
WSHD-17	194	0.16	80	<0.02	>98	9.73	89.35	1.31	0.76
WSHD-18	206	0.16	80	0.02	98	9.68	88.94	1.31	1.20
WSHD-19	218	0.20	75	<0.02	>98	9.44	89.57	1.27	0.79
WSHD-20	230	0.19	76	<0.02	>98	9.48	88.79	1.28	1.53
WSHD-21	242	0.23	71	<0.02	>98	9.66	89.21	1.30	0.89
WSHD-22	254	0.21	73	<0.02	>98	9.49	90.17	1.26	1.26
WSHD-23	266	0.24	70	<0.02	>98	9.74	89.63	1.30	0.39
WSHD-24	278	0.19	76	<0.02	>98	9.68	89.58	1.30	0.55

TABLE XI (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
WSHD-25	290	0.21	73	0.03	94	9.64	89.15	1.30	0.97
WSHD-26	302	0.24	70	0.04	93	9.53	87.66	1.30	2.53

FEED: WASHED SRC HEAVY DISTILLATE; WASH: 1% H_2SO_4;

*BY DIFFERENCE

TABLE XII

RESULTS FOR RUN WHHD

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
FEED		0.78		0.54		7.58	89.35	1.02	1.75
WHHD-2	20	0.10	87	0.10	81	9.27	90.34	1.23	0.19
WHHD-3	32	0.15	81	0.14	74	9.11	90.22	1.20	0.08
WHHD-4	44	0.23	71	0.07	87	8.98	90.66	1.17	0.06
WHHD-5	56	0.25	68	0.03	94	8.75	90.64	1.16	0.33
WHHD-6	68	0.29	63	0.19	65	8.60	89.73	1.15	1.19
WHHD-7	80	0.29	63	0.05	91	8.69	88.80	1.17	2.17
WHHD-8	92	0.32	59	0.07	87	8.65	89.48	1.16	1.40
WHHD-9	104	0.37	53	0.15	72	8.29	88.76	1.12	2.43
WHHD-10	116	0.32	59	0.15	72	8.28	88.71	1.12	2.52
WHHD-11	128	0.30	62	0.07	87	8.35	89.23	1.12	1.45

TABLE XII (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
WHHD-12	140	0.32	59	0.09	83	8.52	90.27	1.13	0.80
WHHD-13	152	0.33	58	0.15	72	8.73	89.78	1.10	1.51
WHHD-14	164	0.36	54	0.22	59	8.32	89.95	1.11	1.15
WHHD-15	176	0.39	50	0.25	54	8.29	90.11	1.10	0.95
WHHD-16	188	0.40	49	0.19	80	8.35	89.06	1.11	2.00
WHHD-17	200	0.39	50	0.25	54	7.78	89.76	1.04	1.82
WHHD-18	212	0.36	54	0.25	54	8.12	89.39	1.09	1.88
WHHD-19	224	0.43	45	0.23	57	8.20	89.43	1.10	1.69
WHHD-20	236	0.58	20	0.24	56	8.17	89.13	1.10	1.88
WHHD-21	248	0.78	0	0.25	52	8.30	88.14	1.13	2.52

TABLE XII (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
WHHD-22	260	0.73	6	0.27	50	8.38	84.50	1.19	6.12
WHHD-23	272	0.74	5	0.30	44	7.79	82.92	1.12	8.25
WHHD-24	284	0.54	31	0.30	44	8.10	88.79	1.09	2.27

FEED: WASHED SRC HEAVY DISTILLATE; WASH: 1% HCl

*BY DIFFERENCE

TABLE XIII

RESULTS FOR RUN RPSS

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
FEED		0.95		0.54		7.51	86.81	1.32	4.54
RPSS-2	14	0.06	94			10.19	88.13	1.39	
RPSS-3	26	0.10	89			9.74	85.71	1.36	
RPSS-4	38	0.11	88			10.23	87.69	1.40	
RPSS-5	50	0.13	86			9.83	85.61	1.39	
RPSS-6	62	0.14	85			9.13	85.64	1.23	
RPSS-7	74	0.23	76			9.35	86.03	1.30	
RPSS-8	86	0.16	83			9.35	84.54	1.31	
RPSS-9	98	0.20	79			9.64	87.11	1.33	
RPSS-10	110	0.15	84			9.50	85.07	1.34	
RPSS-11	122	0.12	87			9.31	85.36	1.31	

TABLE XIII (Continued)

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%S	%S REMOVED	%H	%C	H/C MOLAR RATIO	%O*
RPSS-12	134	0.04	95			9.57	85.41	1.34	
RPSS-13	146	0.15	84			9.48	87.64	1.30	
RPSS-14	158	0.05	95			9.75	88.72	1.32	
RPSS-15	170	0.18	81			9.84	86.30	1.37	
RPSS-16	182	0.13	86			9.62	86.83	1.33	
RPSS-17	194	0.23	76			9.89	87.95	1.34	
RPSS-18	206	0.19	80			9.84	86.01	1.33	
RPSS-19	221	0.16	83			9.62	87.53	1.26	
RPSS-20	230	0.20	79			9.51	87.78	1.30	

TABLE XIV

RESULTS FROM RUN WHHDc

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%C	%H
FEED		0.76		89.35	7.58
WHHDc-2	14	0.09	88	89.25	9.62
WHHDc-3	26	0.06	92	88.95	9.65
WHHDc-4	38	0.05	93	88.60	9.59
WHHDc-5	50	0.16	79	85.95	9.47
WHHDc-6	62	0.14	82	89.15	9.19
WHHDc-7	74	0.19	74	87.96	9.15
WHHDc-8	86	0.23	70	88.18	8.43
WHHDc-9	98	0.32	58	88.30	9.07
WHHDc-10	110	0.23	70	88.48	8.64
WHHDc-11	122	0.26	66	87.99	8.65
WHHDc-12	134	0.28	64	88.70	8.45
WHHDc-13	146	0.33	57	87.76	8.37
WHHDc-14	158	0.34	56	85.46	8.70
WHHDc-15	170	0.22	71	81.78	9.20
WHHDc-16	182	0.30	61	88.39	8.86
WHHDc-17	194	0.34	56	88.20	8.76

TABLE XV

RESULTS FROM RUN WSHDa

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%C	%H
FEED		0.79		89.40	7.47
WSHDa-2	18	0.05	94	89.48	9.65
WSHDa-3	30	0.06	92	88.66	9.61
WSHDa-4	42	0.08	90	88.34	9.48
WSHDa-5	54	0.08	90	89.12	9.59
WSHDa-6	66	0.09	89	88.93	9.45
WSHDa-7	72	0.14	82	88.56	9.52

TABLE XVI

RESULTS FROM RUN WSHDb

SAMPLE NUMBER	HOURS ON OIL	%N	%N REMOVED	%C	%H
FEED		0.79		89.40	7.47
WSHDb-2	20	0.04	95	88.34	9.62
WSHDb-3	32	0.04	95	88.19	9.72
WSHDb-4	44	0.04	95	88.41	9.55
WSHDb-5	56	0.10	87	88.41	9.64
WSHDb-6	68	0.08	90	88.92	9.58
WSHDb-7	80	0.11	86	89.35	9.44
WSHDb-8	92	0.14	82	89.54	9.54

TABLE XVII

PRECISION OF NITROGEN ANALYSIS

SAMPLE	MEAN (%)	STANDARD DEVIATION	MEAN (%)	STANDARD DEVIATION
	RUN RHD		RUN WSHD	
2.	0.180	0.030	0.043	0.015
3.	0.200	0.010	0.067	0.023
4.	0.137	0.012	0.067	0.012
5.	0.143	0.023	0.087	0.023
6.	0.143	0.006	0.090	0.020
7.	0.230	0.017	0.093	0.026
8.	0.196	0.021	0.127	0.023
9.	0.166	0.006	0.120	0.026
10.	0.210	0.000	0.123	0.006
11.	0.277	0.015	0.120	0.000
12.	0.233	0.021	0.160	0.000
13.	0.283	0.006	0.167	0.023
14.	0.196	0.006	0.143	0.023
15.	0.343	0.032	0.127	0.025
16.	0.266	0.006	0.150	0.010
17.	0.330	0.020	0.160	0.010
18.	0.357	0.012	0.160	0.017

TABLE XVII (Continued)

SAMPLE	MEAN	STANDARD DEVIATION	MEAN	STANDARD DEVIATION
	RUN RHD		RUN WSHD	
19.	0.283	0.015	0.203	0.012
20.	0.323	0.015	0.190	0.017
21.	0.393	0.006	0.226	0.006
22.	0.296	0.012	0.210	0.046
23.	0.370	0.017	0.240	0.017
24.	0.300	0.000	0.186	0.153
25.	0.300	0.017	0.213	0.006
26.	0.380	0.000	0.237	0.006
27.	0.354	0.064		

APPENDIX B

HYDROTREATMENT AND ANALYTICAL PROCEDURE

Hydrotreatment Procedure

The operational procedure was essentially the same for both reactors and can be separated into six separate steps:

1. Reactor Loading
2. Calcination
3. Catalyst Presulfiding
4. Startup
5. Normal Operation and sampling
6. Shutdown

The differences in the reactor tubing for each system were discussed in the previous section. The only difference between the two systems in reference to the loading procedure was the amount of catalyst and inert material packed. The stainless steel screen was first placed and wedged between the fittings at the bottom of the reactor. A test was made for snugness of the fit. The thermowell was then put in place and glass beads are poured around the thermowell while gently tapping the sides of the tube. At one or two inch intervals the beads were tamped. A 50 mesh screen was placed on top of the lower zone to separate it from the catalyst zone. The catalyst was then added from a preweighed amount with tapping and tamping as before. Again, a 50 mesh screen was placed at the top of the zone. The remainder of tube was filled with glass beads leaving approximately 1/2 inch at the top of the reactor open. A screen was placed around the thermowell at the entrance of the reactor.

Calcination

After loading, the reactor tube was connected in place and the system was pressururized and tested at 1800 psig with nitrogen. The calcination procedure was then started by a gradual heating of the reactor to 482 C (900 F) with nitrogen flowing through the system at 1.2 cubic feet per hour. The system was maintained at 50 psig. After one hour, the temperature was reduced to 232 C (450 F) and maintained for eight hours.

Presulfiding

The reactor was maintained at 232 C while stopping the nitrogen flow and gradually reducing the pressure. A mixture of 5% H_2S in H_2 was started flowing through the reactor at three cubic feet per hour and maintained for three hours.

Startup

After presulfiding for the three hour period, the H_2S mixture was shut off and a very light nitrogen purge was started. The temperature controller and the power stats were simultaneously turned up and set at 15-20 C below the operating temperature. This allowed some margin for "hot spotting" at the top of the catalyst bed which normally occurs during the startup period. Prior to the startup period, the oil was run through the tubing from the pump to the closed valve immediately prior to the reactor entrance. The oil feed system was then effectively isolated and pressurized to the operating pressure. The reactor was also gradually pressurized during the heating process. The hydrogen flow was started when the system was initially stable at 1500 psig. The oil feed line valve was opened starting the oil flow no more than 5 minutes after the start of the hydrogen flow. The temperature of the catalyst bed was monitored and adjustments made accordingly. Stable hydrogen flow, temperature and pressure were obtained within 20 minutes of initial hydrogen flow.

Normal Operation

The system was considered to be in stable operation if pressure variations were less than 15 psig and temperature variations in the catalyst bed were minor. The latter criterion required a value judgement due to the highly exothermic reactions. The temperature and pressure were monitored and recorded as described previously at several points throughout the system. The pump was refilled approximately every 12 hours using valves to isolate the pump and feed storage tank. The pump was then depressurized by manually rotating the piston in reverse. The pump was then filled and the feed system repressurized. The refilling procedure normally takes 3 minutes.

Shutdown

A final sample was taken before the shutdown procedure is started. The hydrogen flow was then stopped and the pumped was stopped followed by closing valves to isolate the oil feed system. All temperature controls were turned off and a nitrogen purge was started. The purge was continued for 12 hours or until total cooling of the system had occurred.

Sample Analysis

Oil and aqueous samples from the extraction experiments were analyzed for nitrogen, carbon and hydrogen in all cases. Selected samples were analyzed for sulfur and basic nitrogen. Samples from the hydrotreatment study were analyzed for nitrogen, sulfur, hydrogen, and carbon. Again, selected samples were analyzed for basic nitrogen. Samples from selected periods from all runs were distilled under ASTM procedures and volumetric cuts analyzed for nitrogen, hydrogen and carbon concentration.

Nitrogen, Hydrogen and Carbon Analysis.

A Perkin-Elmer Model 240B Elemental Analyzer was used for nitrogen, carbon and hydrogen determination. The system is based on differences in thermal conductivities of H_2O, CO_2, and nitrogen oxides.

Samples of one to three milligram were weighed on a Perkin-Elmer AD-2 Autobalance then placed into an aluminum capsule which, in turn, was placed into the analyzer using a quartz ladle. The elemental analyzer started a twelve minute cycle by purging the system with helium to remove contaminants. The sample then was pushed into a combustion zone (950- 1000 C) under oxygen atmosphere. The combustion products 11(CO_2, H_2O and NO_x) then passed through a reduction tube filled with cuprin (maintained at 650 C) where the nitrogen oxides were reduced to molecular nitrogen. The gasses were then pushed through the system with helium as a carrier gas. The sample passed through a series of thermal conductivity cells and traps which selectively removed the gasses. The thermal conductivities of the gasses were measured before and after the removal of a particular gas and the difference determined the relative concentration of the gas.

Sulfur Analysis

The sulfur concentration was determined using a Leco Automatic Sulfur Analyzer which consisted of an automatic titrator (model 532-000) and an induction furnace (model 521-500). The sample was combusted in an oxygen atmosphere to give SO_2 which was passed to a solution of hydrochloric acid, starch and potassium iodate which have undergone the following reaction:

$$KIO_3 + 5KI + 6HCL \rightarrow 3I_2 + 6KCL + H_2O$$

The iodine reacted with the starch to give a blue color. The SO_2 obtained by combustion then undergoes the following reaction:

$$SO_2 + I_2 + H_2O \quad > \quad H_2SO_4 + 2HI$$

KIO_3 solution is added from a buret automatically to maintin the end point. The analysis takes approximately 15 minutes per sample and the total amount titrated is used to calculate the amount of sulfur against a known standard sample.

ASTM Distillation

The feedstocks and selected samples were distilled at 20 mm Hg according to the procedure outlined by ASTM D-1160 pressure. The volumetric cuts were collected for further analysis.

Basic Nitrogen Analysis

Selected samples were analyzed for basic nitrogen by electrometric titration using the procedure outlined by UOP Method 269-59. A Fisher Accumet Model 610A PH meter was used as the voltmeter.

VITA

Steve Wilkinson

Candidate for the Degree of

Master of Science

Thesis: THE EFFECT OF ACID WASHING ON THE HYDROTREATMENT OF SOLVENT REFINED COAL LIQUIDS

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