

HYDRODENITROGENATION OF QUINOLINE IN A
TRICKLE BED REACTOR

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PREFACE

The objective of this study was to evaluate quinoline concentration effects and to obtain a better understanding of quinoline hydrodenitrogenation reaction network. A modified reaction network was proposed in this study. Increasing quinoline concentration in the feed mixture resulted in an increase in the catalyst decay rate.

I would like to express special thanks to my thesis adviser, Dr. Billy L. Crynes, for his guidance, patience, and understanding throughout this study. Appreciation is also extended to other committee members, Dr. Mayis Seapan and Dr. Gary L. Foutch, for their advice and encouragement.

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This thesis is dedicated to my parents, Mr. and Mrs. Shao-Lin Liu, for their sacrifice, understanding, and love.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Introduction.

The removal of undesirable nitrogen compounds from petroleum heavy residual and coal derived liquids is best achieved by catalytic hydrodenitrogenation (HDN). Some of these nitrogen compounds are heterocyclic and basic. They are also resistant to HDN. Basic nitrogen compounds when adsorbed on active sites can decrease catalyst activity significantly for hydrogenation, hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) reactions. Nitrogen poisoning will become important when heavy residual and coal derived liquids become more available as refinery feedstocks. However, such feedstock studies alone are not adequate for developing a clear understanding of catalyst deactivation mechanisms, because the complexity of the reactions involved makes the task of identifying the compounds and the role they play extremely difficult. One approach to this problem is by the use of model compounds as feedstocks instead of complex, heavy feedstocks.

There have been several studies using individual sulfur, nitrogen and oxygen compounds as feedstocks; however, most dealt with interactions between these compounds. The

present study was thus undertaken to determine how the catalyst is affected by a nitrogen compound.

Quinoline has been used in this study since it is a model compound representative of the heterocyclic nitrogen compounds found in substantial concentrations in petroleum residual and coal derived liquids. The activity tests were conducted in a catalyst life test unit (CLTU) which contains a trickle bed reactor. The objective of this study was to characterize catalyst deactivation as a function of quinoline concentrations in the feedstock and to obtain a better understanding of the quinoline HDN reaction network.

Literature Review

Heterocyclic Nitrogen Compounds in Petroleum Feedstocks and Synthetic Fuels

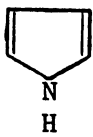

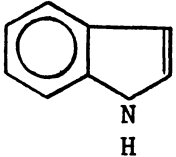
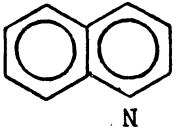
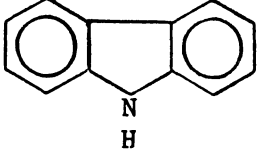
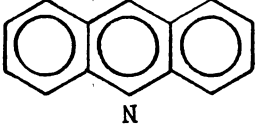
The heterocyclic nitrogen in petroleum and coal derived liquids is incorporated in five- or six-membered rings, most of which are unsaturated. These nitrogen compounds can be classified into basic and non-basic compounds. Pyridine, quinoline, and acridine are generally basic, while pyrrole and indole tend to be non-basic. In the catalytic hydrodenitrogenation of heavy feeds, these heterocyclic nitrogen compounds are most resistant to removal in comparison with sulfur and oxygen compounds.

Several studies on the nature of heterocyclic nitrogen compounds in petroleum feedstocks and synthetic fuels have been reported in the literature. Snyder (1970) found that

indole, pyridine and higher derivatives are present in a California crude. Further, he determined that the nitrogen content increases as the temperature reaches the boiling point range of the petroleum fraction. McKay, et al. (1976) reported that four types of basic nitrogen compounds are present in a high boiling crude oil distillate. They are pyridine benzologs (e.g. quinoline, benzoquinoline), diaza-compounds, amides, and carbazoles. In another study (Latham and Brandenburg, 1968), the classes of nitrogen compounds in the 130 to 350°C distillate fraction of a Wilmington petroleum were characterized. Cyclopentyl- and cyclohexylpyridines having C₁ - C₇ alkyl substituents on the rings are the predominant compounds in the 130 - 300°C fraction, and alkylquinolines are prevalent in the 300 - 350°C fraction. Characterization of coal-derived liquids carried out in several laboratories indicates that there are similar nitrogen compounds present in coal liquids and shale oil (Scheppele, et al., 1977).

Quader, et al. (1968) reported that pyridines, quinolines, pyrroles, indoles, and carbazoles are the principle heterocyclic nitrogen compounds in a coal tar prepared from a high volatile bituminous Utah coal by carbonization at 550°C. The presence of indole derivatives, acridines, benzoquinolines, carbazoles, and other compounds in a solvent refined coal (SRC) liquid product was reported by Boduszynski, et al. (1982). Some of these heterocyclic nitrogen compounds are shown in Table I. Non-heterocyclic nitrogen

TABLE I
REPRESENTATIVE HETEROCYCLIC NITROGEN
COMPOUNDS

FORMULA	STRUCTURE	NAME
C_4H_5N		Pyrrole
C_5H_5N		Pyridine
C_8H_7N		Indole
C_9H_7N		Quinoline
$C_{12}H_9N$		Carbazole
$C_{13}H_9N$		Acridine

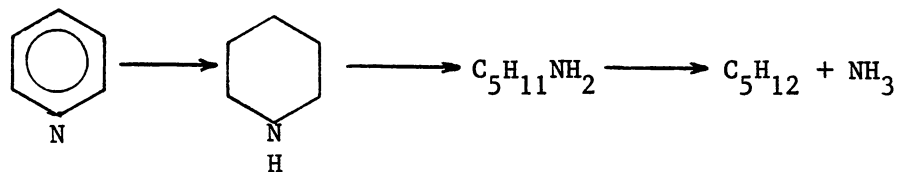
compounds are found in very small amounts and include aliphatic amines and nitriles. Such non-heterocyclic nitrogen compounds are generally easier to denitrogenate by catalytic hydrogenation than by the relatively unreactive heterocyclic compounds. Thus, they are not a serious problem (Cocchetto and Satterfield, 1976).

Hydrodenitrogenation

In the hydrotreating process, HDN always occurs together with HDO and HDS. In model studies (Odedunmi and Ollis, 1983a and 1983b), nitrogen compounds inhibited HDO and HDS reactions, while oxygen compounds inhibited HDN and HDS reactions. Although sulfur compounds inhibited some HDO reactions, they inhibited certain HDN reactions only at low temperatures while enhancing the same reactions at higher temperatures. Furimsky (1983) assumes that the hydrogenolytic cleavage of C-S, C-N, and C-O bonds is the rate-determining step in the opening of heterocyclic rings. He found two trends in the relative rates, HDS > HDO > HDN at low pressure; while HDS > HDN > HDO under high pressure conditions.

HDN of heterocyclic nitrogen compounds usually occurs by a complex reaction network involving initial hydrogenation of aromatic rings followed by carbon-nitrogen bond hydrogenolysis. This differs from HDS which involves mainly direct hydrogenolysis of carbon - sulfur bond. Several studies on HDN of heterocyclic nitrogen compounds have been

reported. McIlvried (1971) studied pyridine HDN and proposed a reaction network as shown below:

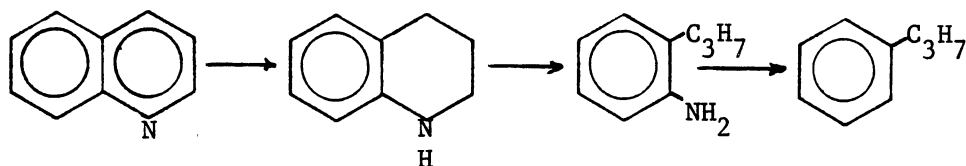


Sonnemans, et al. (1973) found first order behavior in this reaction, but the rate constant decreased with increasing pyridine concentration in the feedstock. McIlvried (1971) explained this behavior by fitting a Langmuir-Hinshelwood rate expression to both his own and Sonnemans' data. In this model there is strong inhibition of the reaction rate due to adsorption of basic nitrogen compounds. Different rate limiting steps were reported in pyridine HDN reactions. McIlvried (1971) reported cracking of piperidine as rate limiting at 315°C. Sonnemans and Mars (1973) presented data indicating that both hydrogenation and cracking have influence on overall rate at low temperature.

The HDN of pyrrole was reported by Smith (1957). The reaction probably occurred via saturation of the ring to pyrrolidine, opening the ring to form n-butyl amine, and finally cracking the amine to form n-butane and ammonia. Second order kinetics had been reported in this reaction (Cox and Berg, 1962).

Aboul-Gheit and Abdou (1973) used aniline, pyridine, pyrrole, quinoline, and indole in a study of HDN kinetics

over a $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst. The overall rate of reaction in each case was first order in the nitrogen compound. Flinn, et al. (1963) have used quinoline as a model nitrogen compound. There is general agreement in both studies about the reaction mechanism, which is



The various authors disagree on the rate limiting step, however, Flinn, et al. (1963) concluded that hydrogenation of the ring was a rate-limiting step. Aboul-Gheit and Abdou (1973) feel cracking of tetrahydroquinoline is a rate-limiting step. This controversy may result from the fact that each group of investigators used different catalysts and reaction conditions. El-Bishtawi (1986) studied HDN of quinoline, acridine, and their mixture. A pseudo first order kinetics model successfully fits the experimental data. Both quinoline and acridine in their mixture, interfere with each other's kinetics, usually reducing the reaction rates. The effect of quinoline on acridine is stronger than the effect of acridine on quinoline.

Satterfield, et al. (1978) studied the intermediate reactions in quinoline HDN in a vapor phase microreactor packed with presulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts. Reactor temperatures were varied from 230 to 420°C at pressures of 3.55

and 7.0 MPa. They reported that rapid equilibrium between quinoline and tetrahydroquinoline occurred at all reaction conditions. At lower temperatures this equilibrium favored 1,2,3,4-tetrahydroquinoline which then converted to either o-propylaniline or decahydroquinoline, but at higher temperatures the conversion rate of quinoline to 5,6,7,8-tetrahydroquinoline and subsequently to decahydroquinoline became significant.

The carbazole mechanism was proposed by Horne and MaAfee (1960). They considered that the denitrogenation of carbazole to biphenyl is plausible but also indicated that saturation of an aromatic ring prior to nitrogen removal is possible. Flinn, et al. (1963) suggested that one of the carbazole aromatic rings is hydrogenated and cracked to form an alkylated indole or indoline, which then proceeds by the usual mechanism.

Flinn, et al. (1963) also investigated several nitrogen compounds. They found that the basic nitrogen compound quinoline is the most difficult to decompose during hydrogenation, while aniline and n-butylamine, which are also basic, are most readily destroyed. The stability of the six-membered ring nitrogen compound is undoubtedly related to a resonance energy stabilization much like that which stabilizes benzene. The non-basic five-number ring compound indole is removed at an initial rate which is more than four times that of quinoline. Thus, they concluded that those nitrogen compounds containing an aromatic-type heterocyclic

ring are the most difficult to hydrogenate.

Little information is available on the kinetics of coal liquids HDN, Satchell (1974) in his HDN studies of raw anthracene oil observed second order kinetics to best fit the data obtained in a trickle bed reactor. Sivasubramanian (1977) observed first order kinetics accounting for catalyst partial wettability and liquid holdup to best fit the data for HDN of raw anthracene oil in a trickle bed reactor. This discrepancy is probably due to different operating temperatures and different catalysts used in their studies.

Catalysts

Typical hydrotreating catalysts usually consist of a combination of cobalt and molybdenum oxide, or nickel and molybdenum oxide, or nickel and tungsten oxide supported on alumina. The sulfide forms of such catalysts are more resistant to sulfur and nitrogen poison. Shih, et al. (1977), in a study of quinoline HDN found that sulfided NiMo/Al₂O₃ possesses higher hydrogenolysis activity and hydrogenation activity than the unsulfided catalysts. Satterfield and Yang (1983) studied hydrogen sulfide effect on quinoline HDN. They concluded that higher concentrations of hydrogen sulfide in the gas phase resulted in higher hydrogenolysis activity of the catalysts. This can be attributed to the effect of hydrogen sulfide in maintaining the more active sulfide state of the catalyst during the reaction.

The activity of sulfided catalysts also depends on the

pore size, surface area, and metal compositions. In general, sulfided NiMo/Al₂O₃ seems to have somewhat higher hydrogenation activity than sulfided CoMo/Al₂O₃. Furimsky (1979) reported that about 4% by weight more sulfur and nitrogen were removed from a petroleum heavy gas oil, at a pressure of 13.8 MPa and temperature of 400°C, when using a sulfided NiMo catalyst than when using a sulfided CoMo catalyst. Newton (1985) hydrotreated an SRC coal liquid in a trickle-bed reactor packed with different active metal catalysts. He concluded that the NiMo catalyst has the highest hydrogenation and HDN activities for this feedstock. In a hydrotreatment of raw anthracene oil study, Sivasubramanian and Crynes (1979) found that the rate of HDN was sensitive to changes in catalyst surface area available for reaction. A reduction in surface area results in a reduction of nitrogen removal.

The sizes of molecules in petroleum heavy feedstocks range between 2.5 nm and 15.0 nm, the largest fraction being around 5 nm (Tschemler and DeRuiter, 1963). The average pore size of typical catalysts used for hydrotreating these heavy feedstocks also falls in this range (Schuit and Gates, 1973). Since the diameter of the reactant molecules is comparable to the pore diameter, the ratio, λ , between the molecule diameter and the average pore diameter affects the diffusion of the molecules in the pores. Their diffusion coefficient decreases with increasing λ . However, for constant volume of a catalyst, the reaction rate increases with decreasing pore diameter because the area of the reacting

surface increases. These two opposing effects result in the existence of optimum pore size.

Inoguchi (1976) observed that catalysts with pore sizes around 10 nm have higher activity for the HDS of petroleum heavy residual, and vanadium removal is maximized when pore sizes range between 12 and 14 nm. Eigenson, et al. (1977) reported that a shift of average pore diameter from 7 to 15 nm increased the activity of MoO_3 supported on alumina in spite of a lower metals loading used for larger pore diameters. For coal liquefaction, Yen, et al. (1976) reported that a $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst with pore diameter of 20 nm performs better than a catalyst with pore diameter of 12 nm, even though the former has a lower surface area.

Catalyst Deactivation

Catalyst deactivation is commonly classified into three primary mechanisms: coking, metal deposition, and poisoning. Stiegel, et al. (1983) reported that the loss of catalyst activity can result from coverage of active sites by coke and trace metals, increased diffusional restrictions due to pore filling or blocking by deposition of coke and trace metals, and poisoning of active sites by the reversible and irreversible adsorption of heterocyclic compounds which reduces the number of active catalytic sites. Ann and Smith (1984) stated two different deactivation rates: a fast initial surface deactivation progressively poisoning from the pore mouth to the interior of a pore, and a slow deactiva-

tion due to physical deposition of metal products which eventually lead to pore plugging.

Catalyst deactivation by coking has been studied quite extensively. Beazer (1984) studied the effects of hydro-treating coal-derived liquids by temperature zoning in a two-stage trickle bed reactor. Experiments were carried out varying the top zone temperature between 400 and 500 C, while maintaining the bottom zone at 400 C. He concluded that increasing the top zone temperature from 400 to 450 C had a beneficial effect on the catalyst HDN activity, but the temperature above 450°C had a detrimental effect on the catalyst HDN activity due to significant coke formation. Similar results had been observed by Ahmed (1979).

Ozawa and Bischoff (1968) concluded that intraparticle diffusivities do not change significantly in the case of ethylene cracking on silica-alumina catalysts, but this only represents experiments where coke deposition on the catalyst is below 1%. However, Levinter, et al. (1967) reported losing up to 50% of surface area through coke deposition, which indicates severe pore blockage and size reduction. In a laboratory investigation of the hydroprocessing of a coal liquid, Chang (1982) observed that coke deposition causes a severe reduction in the pore size distribution and results in reducing catalyst efficiency. Chang further developed a parallel fouling model, which incorporated a variable diffusivity and intrinsic activities as function of coke deposition. This model is able to predict catalyst life base on

pore size and pellet size of the catalyst.

A number of empirical models have been proposed to relate catalyst activity to catalyst coke content. Ozawa and Bischoff (1968) found that a linear relationship of activity and coke content satisfactorily represented deactivation data with an empirical constant which exhibited an exponential temperature dependence. Takeuch, et al. (1966) observed that an empirical hyperbolic model was required to relate activity to catalyst-coke content data. The empirical parameter in this model exhibited a dependence not only upon the reaction temperature but also upon the composition of feedstock. Dumez and Froment (1976) found that an empirical exponential relationship was required to describe catalyst activity-coke content data, with an empirical parameter which did not exhibit systematic trends with either temperature or feed composition.

The deposition of metals on the catalyst surface generally occurs slowly over the life of the catalyst, but its effect, like that of coke, is an increase in the intraparticle diffusion resistance caused by pore filling or blocking (Pracher, et al., 1978). For hydroprocessing coal liquids and petroleum residuum, several metals commonly found in these heavy feedstocks caused a permanent loss of catalyst activity; however, the extent of deactivation was a function of particular metals (Kovach, et al., 1978). Iron, sodium, calcium, and magnesium in their oxide states cause the greatest degree of deactivation. Titanium present as an

oxide did not cause any loss in catalyst activity; however, when present as an organometallic salt, it adsorbed easily on the catalyst surface and caused significant deactivation.

Recently, mass transfer effects and poisoning reactions were included in deactivation models which can predict catalyst deactivation by coke formation and metal deposition. Tamm, et al. (1981) summarized that the majority of these models were based on a pore-plugging mechanism which assumed a diffusion-limited demetalation reaction in the catalyst pores. Metal deposition takes place preferentially near the entrance of a pore and eventually causes pore plugging. Kodama, et al. (1980) expanded the pore-plugging model by assuming that both the effective surface area for reactions and the effective diffusivities for reactants decrease proportionally with the total amount of metal and coke deposits. The advantage of their model was that some adjustable parameters can be used in many cases.

Kittrell (1986) developed two models to predict catalyst poisoned by pyridine. The first model predicted the period when reversible pyridine adsorption and irreversible coke formation were simultaneously poisoning the fresh catalyst. The second model predicted the period when coke formation had reached a steady-state level and only reversible pyridine adsorption was occurring on the catalyst surface. Both models were supported by experimental data.

Heterocyclic nitrogen compounds contained in crude oil and synthetic fuels always inhibit catalyst activity more

than other compounds, because basic nitrogen compounds react with the acid centers on the catalysts (Thomas, 1970). Tarrer, et al. (1985) reported that the poison effects of basic nitrogen compounds such as quinoline and 4-methylquinoline were found to be greater than those of some oxygen-containing compounds such as 1-acenaphthenol and 9-phenanthrol and some multiring aromatics such as acenaphthene and phenanthrene. Kirsch, et al. (1959) blended a synthetic gasoline from heptane and heptene with thiophene added to represent sulfur at a level of 0.4wt%. An addition of 0.2wt% of pyridine to this feed decreased desulfurization from 80% to 60% (CoMo/Al₂O₃ catalyst). Hydrogenation of olefins also dropped from 85% to 52%. After pyridine was removed from the feed, desulfurization returned to its original level, but some hydrogenation activity was permanently lost.

Two pure compounds studies also show the detrimental effects of nitrogen compounds on HDS. Desikan and Amberg (1964), using a pulse reactor, investigated the effect of pyridine on thiophene HDS. They found that pyridine reversibly poisoned HDS activity but irreversibly poisoned the hydrogenation activity of the catalyst (CoMo/Al₂O₃). Adding this to the results of some pyridine adsorption/desorption experiments, they concluded that there are two types of HDS on sulfided CoMo/Al₂O₃ catalysts. The authors classified one as very strongly acidic and the other as weaker in acidity. Both sites have HDS activity, but only the strong acid sites have hydrogenation activity. Pyridine apparently poisoned

both sites, but it affected the strong acid site more adversely; therefore, hydrogenation was more severely retarded than desulfurization. Lipsch and Schuit (1969) also used a pulse reactor to study the effect of pyridine on thiophene HDS. They also concluded that pyridine is adsorbed on two types of catalyst sites, but only one of these sites showed HDS activity. Pyridine poisoned thiophene HDS; however, the effect was not as large as the results Desikan and Amberg observed. The discrepancy between these studies may lie in the fact that Desikan and Amberg used a pre-sulfided catalyst while Lipsch and Schuit did not.

Satterfield, et al. (1975) studying the simultaneous HDS of thiophene and the HDN of pyridine proposed that two kinds of catalytic sites exist on a sulfided CoMo/Al₂O₃ catalyst: Site I has HDS activity and is very sensitive to poisoning by nitrogen bases; Site II shows much less HDS activity, and is less susceptible to pyridine poisoning. Sivasubramanian and Crynes (1980) hydrotreated raw anthracene oil, a coal liquid, with and without quinoline over the same catalysts at the same operating conditions. Increased nitrogen concentration had a detrimental effect on sulfur removal. This supports the theory that two types of HDS sites may be present in CoMo alumina catalysts.

In a study of the effect of hydrogen sulfide on the HDN of quinoline, Yang and Satterfield (1983) also postulated two kinds of catalytic sites to exist on a sulfided NiMo/Al₂O₃ catalyst. Based on their study, the characteris-

tics of two types of sites can be summarized as follows:

Type I sites: (1) are sulfur vacancies associated with molybdenum atoms, (2) can facilitate hydrogenation and dehydrogenation reactions as well as the direct extrusion of sulfur from thiophene, (3) are easily poisoned by nitrogen bases, and (4) there remains the possibility that these sites facilitate hydrogenolysis.

Type II sites: (1) are Bronsted acid sites, consisting of H^+ on the surface either from a promoter added to the catalyst (e.g. phosphate) or from the dissociation of H_2S on the surface or from the support, (2) facilitate hydrogenolysis, cracking, and isomerization that involve a carbonium ion mechanism, and (3) are comparatively less vulnerable to poisoning by nitrogen bases, though nitrogen compounds easily poison the protonic acid centers of cracking catalysts.

The extent of nitrogen compound poisoning depends on the specific nitrogen compounds in the feedstocks. Plank and Nace (1955) provided information on the relative inhibition effects of a variety of nitrogen compounds. By use of the alkylation of cumene over a silica-alumina catalyst at $425^\circ C$, the following order of decreasing inhibitor strength was obtained: imidazole > quinoline, quinoline > pyrrole, pyridine > piperidine, indole > decylamine, n-butylamine > aniline. The poisoning powers of basic nitrogen compounds related to their proton affinities were studied by Lau, et al. (1978). In their study, the proton affinity was determined by measuring the gas-phase proton transfer reaction

between a nitrogen base and the NH_4^+ ion. Although replacing the NH_4^+ ion with a catalyst as the proton source will affect the absolute proton affinity value, the relative order should remain unchanged. They concluded that a basic nitrogen compound with higher proton affinity is also a stronger poison.

Summary

This literature review can be summarized as follows:

1. There are similar nitrogen compounds present in coal liquids and petroleum residuum. Most of them are five- or six-member rings and are unsaturated.

2. The nitrogen content increases with increasing boiling point of the fuel fraction.

3. Basic nitrogen compounds are resistant to HDN.

4. HDN of heterocyclic nitrogen compounds proceeds via saturation of the heterocyclic ring followed by ring fracture at a carbon-nitrogen bond. Nitrogen is then removed from the resulting amine or aniline as ammonia.

5. HDN of nitrogen compounds containing a six-member ring is more difficult than that of five-member rings.

6. Hydrotreating catalysts are usually CoMo or NiMo on alumina.

7. NiMo catalysts are somewhat more suitable than CoMo for HDN.

8. Catalyst deactivation by coking and trace metals decrease the diffusion coefficient of reactant molecules in

catalyst pores.

9. Basic nitrogen compounds react with catalyst acidic sites and inhibit the hydrotreating process.

10. Two kinds of catalytic sites exist on sulfided NiMo catalysts. Site I is easily poisoned by basic nitrogen compounds while Site II is not.

CHAPTER II

EXPERIMENTAL PROCEDURE

All experimental runs were performed in a trickle bed reactor located at the Hazardous Reaction Laboratory, Oklahoma State University. A schematic diagram of the experimental system is presented in Figure 1. The system includes an automatic shutdown design and an alarm mechanism so that it could run unattended. A metering pump (Lewa FL-3) delivered the feedstock at a constant rate. A calibration of the pump is present in Appendix C. Hydrogen pressure was maintained by a regulator, and flow was controlled by needle valves located upstream and downstream of the reactor. The exit gas flow rate was measured by a wet test meter. Three central heaters were connected to an automatic temperature controller which maintained the operating temperature. Reactors were made from 316 stainless steel, had an inside diameter of 1.3cm (0.515in) and used 86cm (34in) in length. The liquid and gas streams were combined in a tee at the top of the reactor and passed cocurrently down to the catalyst bed. Separation of the fluids into gas and liquid phases was performed in two consecutive separation tanks located downstream of reactor. The gases from the separation tank were then scrubbed with 20% NaOH solution before venting. Liquid

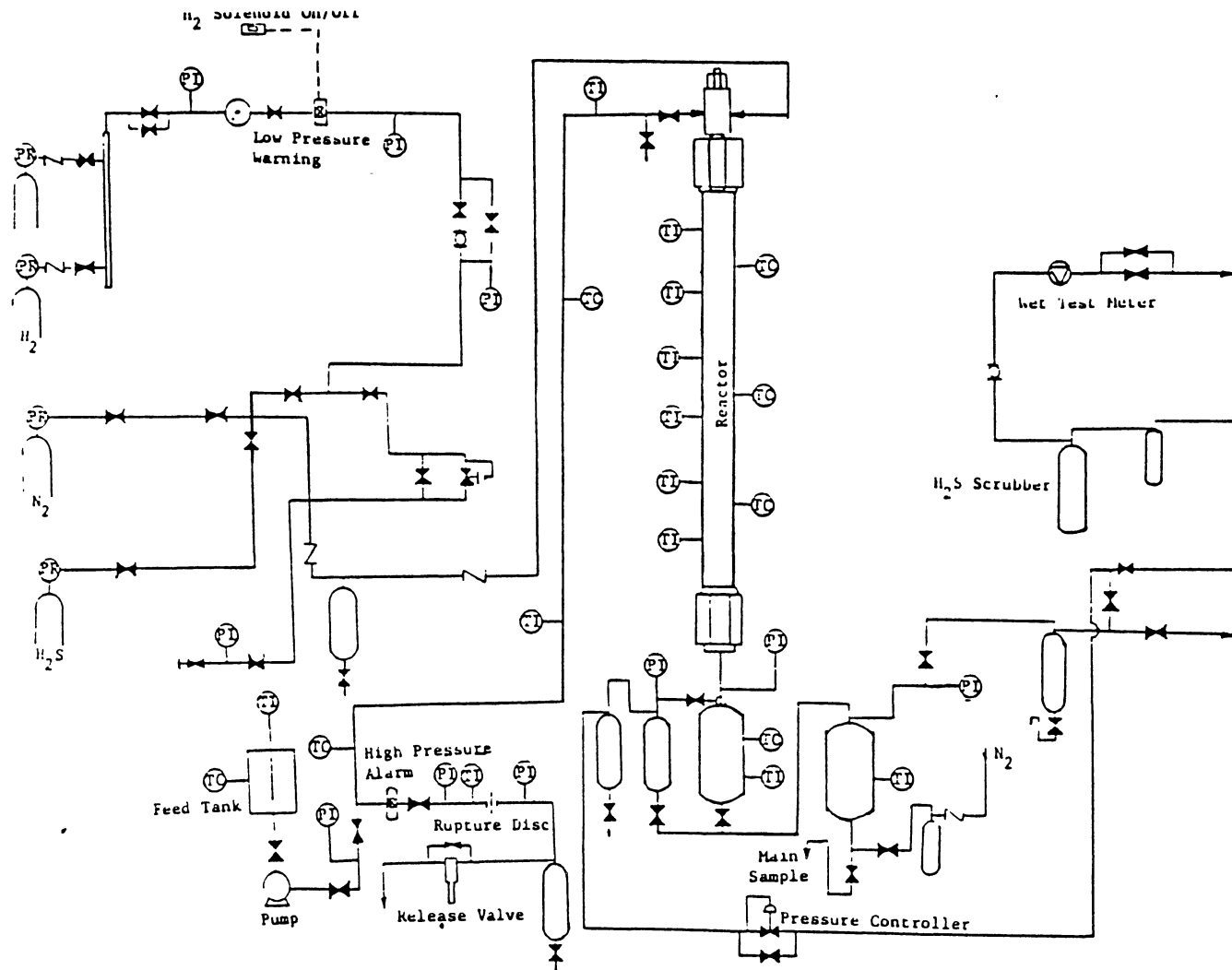


Figure 1. Schematic Diagram of Experimental System

products were collected at regular time intervals.

The experimental equipment and procedure used in this study are the same as those used by Chang (1982). Chang gave a detailed description of the equipment, thus only brief mention will be made here.

Preparation

0.025 kg catalysts were packed into the middle part (0.25m) of the reactor. The top and the bottom zones of the reactor were filled with glass beads. A profile of reactor bed is shown in Figure 2. The reactor was then installed and a pressure test was performed with nitrogen at operating pressure to ensure that the system was leak free.

Catalyst Calcining and Presulfiding

Based on previous work done by Chang (1982), Bhan (1983), and Newton (1985), catalysts were calcined under nitrogen with a pressure of 1.4MPa and a flow rate of $1.2 \times 10^{-2} \text{ m}^3/\text{h}$. The temperature was raised to operating level at a rate of 120°C/h. This procedure was used for 4h to remove water and air from the system. After calcining, the catalysts were sulfided at 0.55MPa with $3 \times 10^{-2} \text{ m}^3/\text{h}$ mixture of H_2 and $\text{H}_2\text{S}(5\%)$ for 3h at operating temperature.

Startup

The reactor was pressurized to the operating level and the Lewa metering pump was started and set at the highest

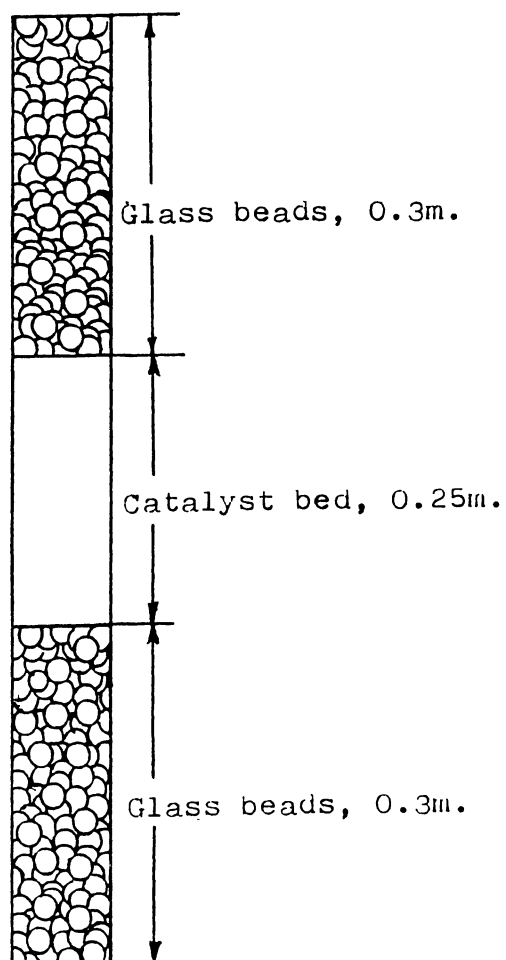


Figure 2. Profile of Catalyst Bed

flow rate so that the liquid line could be filled with oil within 0.5h. When the pressure gauge on the liquid line began increasing (which meant that the liquid line has been filled with oil), the valve before the reactor entrance was opened to let the oil flow into the reactor. After 0.5h, the pump was set at the desired normal flow rate.

Normal Operation

Maximum deviations of 3°C in temperature with both position and time and 345 kPa(50psi) in pressure were considered acceptable during normal operation.

The temperature profile along the catalyst bed was continuously recorded on a twenty-four point strip chart recorder. The pressure was also recorded continuously on a twelve-point strip chart recorder. Liquid samples were taken every 6 or 12h.

Shutdown

During shutdown the oil feed was stopped and the reactor heaters were shut off. Reactor pressure was maintained at the normal operating value, and hydrogen flow was allowed to pass through the system until ambient temperature was reached. The reactor was then disconnected from the system, and ends were capped.

Catalyst Sample Analysis

Catalyst pellets were randomly selected for analysis.

Spent catalysts from each run were extracted with tetrahydrofuran (THF). The Soxhlet apparatus was used for 24h to remove soluble material. The catalysts were then regenerated by controlled combustion for 24h at a temperature of 600°C. Coke content was determined by the difference in weight between catalysts before and after regeneration. Corrections were made due to the weight changes of oxidation of metal sulfide. Both spent and regenerated catalysts were characterized in terms of pore volume, surface area and pore size distribution by using a Quantochrome Porosimeter Model 60.

Liquid Sample Analysis

Liquid samples were analyzed by a Hewlett Parkard 5890 gas chromatograph equipped with a thermal conductivity detector and a 60m capillary column Model DB-1, supplied by J and W Inc. The calibration details of the gas chromatograph are given in Appendix D. A set of three samples was taken and the average of the peak sizes was used in calculation.

CHAPTER III
EXPERIMENTAL PARAMETER AND
CATALYST

Seven experimental runs were conducted in this study. In each run, the operating pressure was maintained at 12.4MPa (1800psi). Liquid volume hourly space time was used in this study. It is defined as volume of catalyst section per liquid volumetric flow rate. Table II summarizes the general information of each run. Runs PDA and PDB were made as preliminary runs and were of duration of 120h. The operating temperatures of these two runs were 370°C (700°F) and space times were 2.3h and 1h, respectively. These operating conditions were typical for hydrotreating heavy feedstocks conditions. However, adjustment had to be made because quinoline HDN conversion was too extensive (29-96%) for a definitive study. Subsequent runs were made at 350°C (660°F) for 72h with space time of 0.5h. Run PDG was a duplicate of Run PDF to determine overall reproducibility. In this study, the carrier liquid was to be pure and without affecting the quinoline HDN reactions; hence, n-hexadecane was chosen. Different weight percents of quinoline (10, 20 and 30 wt%), mixed with n-hexadecane, were used as feedstocks in these runs. The nitrogen contents of these three weight percents were 1.08%, 2.16%, and 3.24%, respectively.

TABLE II
OPERATING CONDITIONS OF EXPERIMENTAL RUNS

Run	Quinoline(wt%)*	Temperature(°C)	Pressure(MPa)	Space Time(h)	Duration(h)
PDA**	10	370	12.4	2.3	120
PDB**	10	370	12.4	1.0	120
PDC	10	350	12.4	0.5	120
PDD	30	350	12.4	0.5	72
PDE	20	350	12.4	0.5	72
PDF	10	350	12.4	0.5	72
PDG	10	350	12.4	0.5	72

* Mixed with n-hexadecane

** Samples taken every 12h after 48h time on stream

In general, nitrogen content of heavy petroleum and coal liquid feedstocks fall in these ranges (Crynes, 1981). A list of chemicals used in this study is presented in Appendix A.

A commercial catalyst, Topsøe TK-771, was used for this study. This catalyst was chosen because it is suitable for HDN and was new from a new vendor which we wanted to evaluate. Note that catalyst bed was 0.25m in length and 0.025kg in weight, except those of runs PDA and PDB were 0.5m and 0.05kg, respectively. Table III shows the properties of this catalyst, and Figure 3 shows that the most frequent pore size is 9.8nm. Differences between vendor's and our data were because of the different methods used in analysis.

TABLE III
 PROPERTIES OF CATALYST, TK-771 (Topsøe)

Chemical Composition*	wt%
NiO	3.4
MoO	14
Al ₂ O ₃	balance
Physical Properties	
Surface Area, m ² /kg	200* x 10 ³ (253)**
Pore Volume, m ³ /kg	0.470* x 10 ⁻³ (0.570)**
Geometry	1.6mm extrudates

* Vendor's data

** Measured by Autoscan Porosimeter (average value)

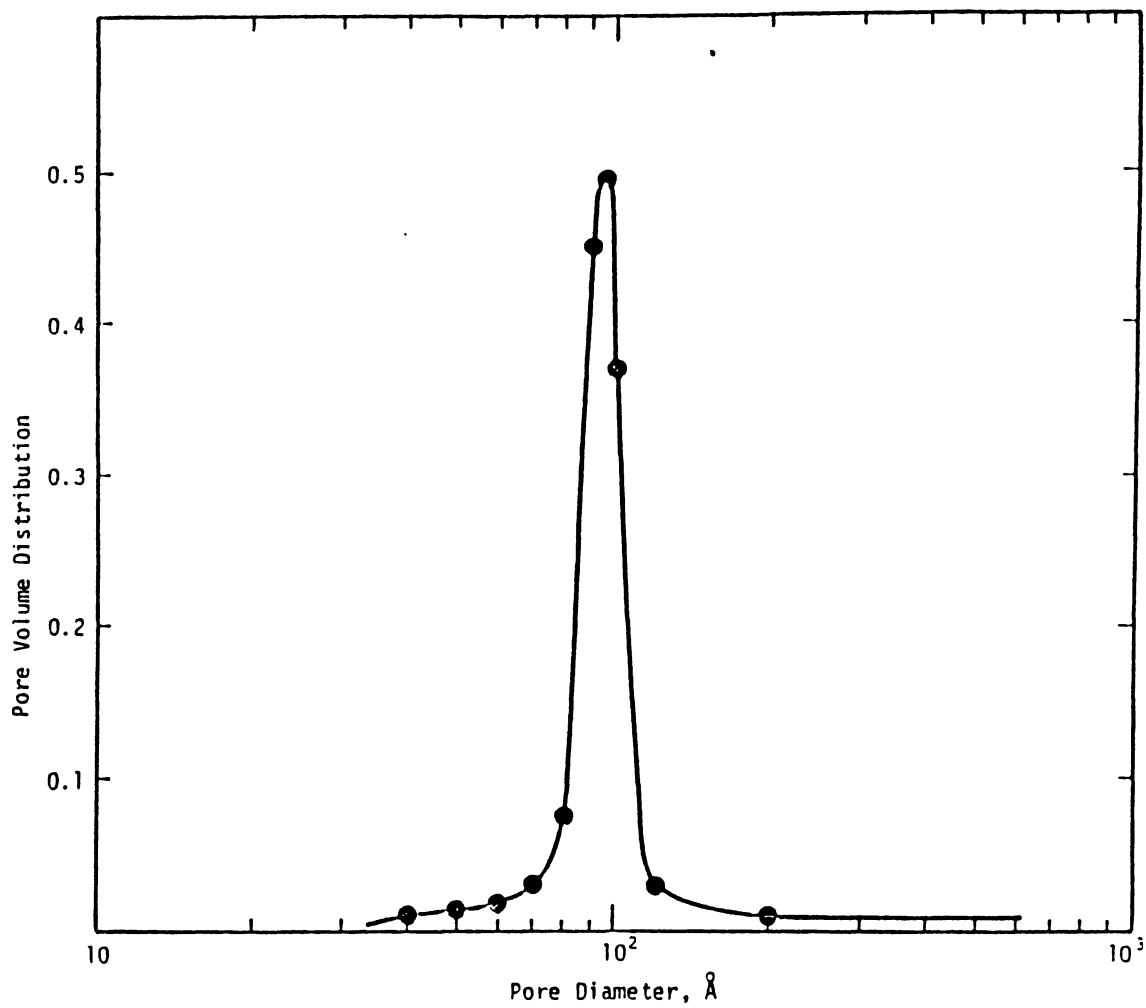


Figure 3. Pore Size Distribution of Fresh Catalyst TK-771 (Topsøe)

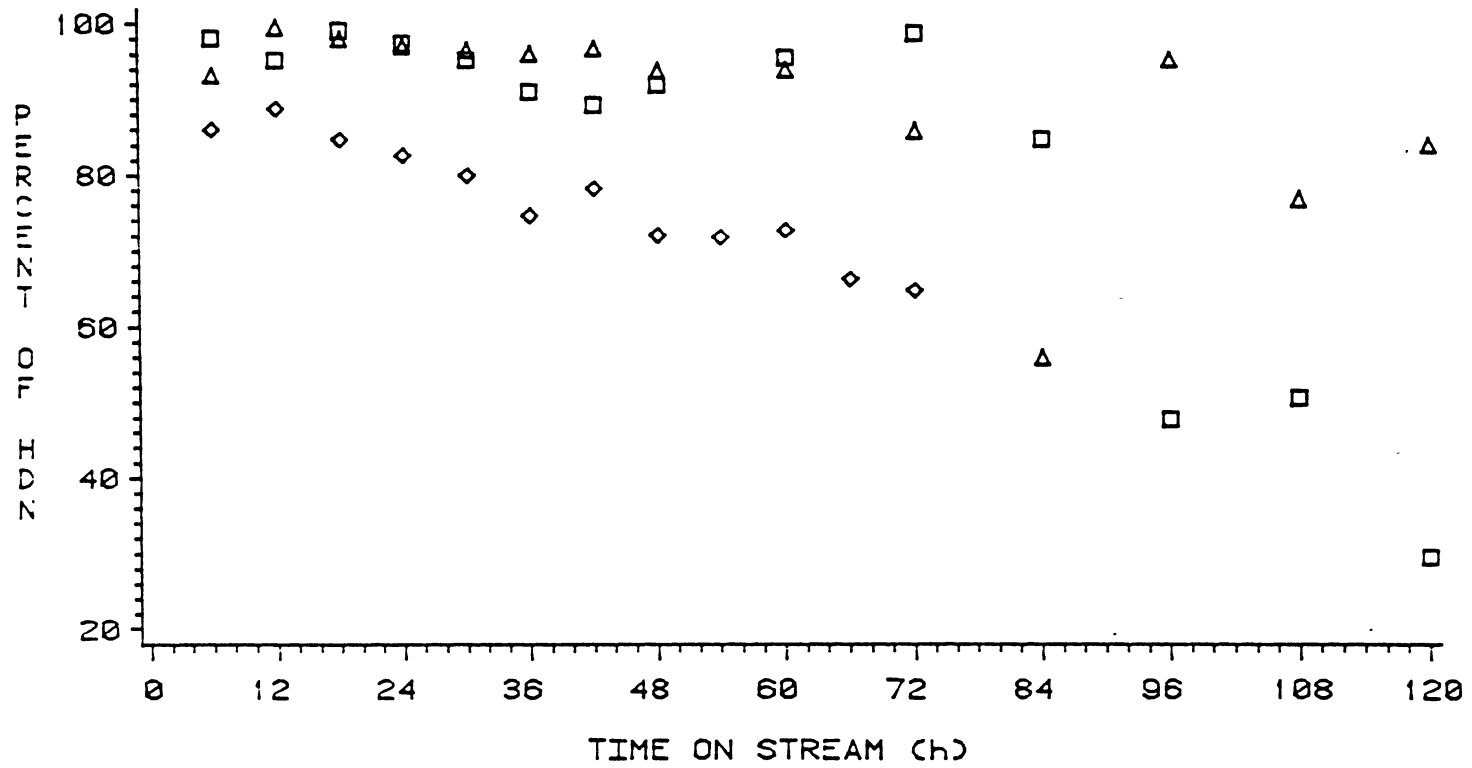
CHAPTER IV

RESULTS AND DISCUSSION

In this chapter data are presented graphically, but the tabular results are given in Appendix B. Following a review of the preliminary runs, the reaction network is discussed, and then concentration effect and catalyst properties results are covered. The precision of the study is discussed last.

Preliminary Runs

Preliminary runs were made (PDA and PDB) to establish a basic data set and to decide reasonable conditions for the study. catalyst deactivation is shown by loss of nitrogen removal ability. An example of a calculation is presented in Appendix F. The percents of HDN from runs PDA and PDB are presented in Figure 4. Results from run PDA revealed that the catalyst had a constant nitrogen removal ability (90% - 96%) through 84h but decayed rapidly after that. Apparently there is a saturation level of poison that accumulates on the catalyst before rapid decay begins. The rather high space time (2.3h) resulted in significant nitrogen removal at first - too high for this study. Therefore, run PDB was made at a space time of 1h. Nitrogen removal from run PDB showed the same general trend as that from run PDA. In



NOTATION □ □ □ PDA(LVHST=2.3h) Δ Δ Δ PDB(LVHST=1h)
 ◇ ◇ ◇ PDF(LVHST=0.5h)

Figure 4. Percent of HDN from Runs PDA, PDB, and PDF

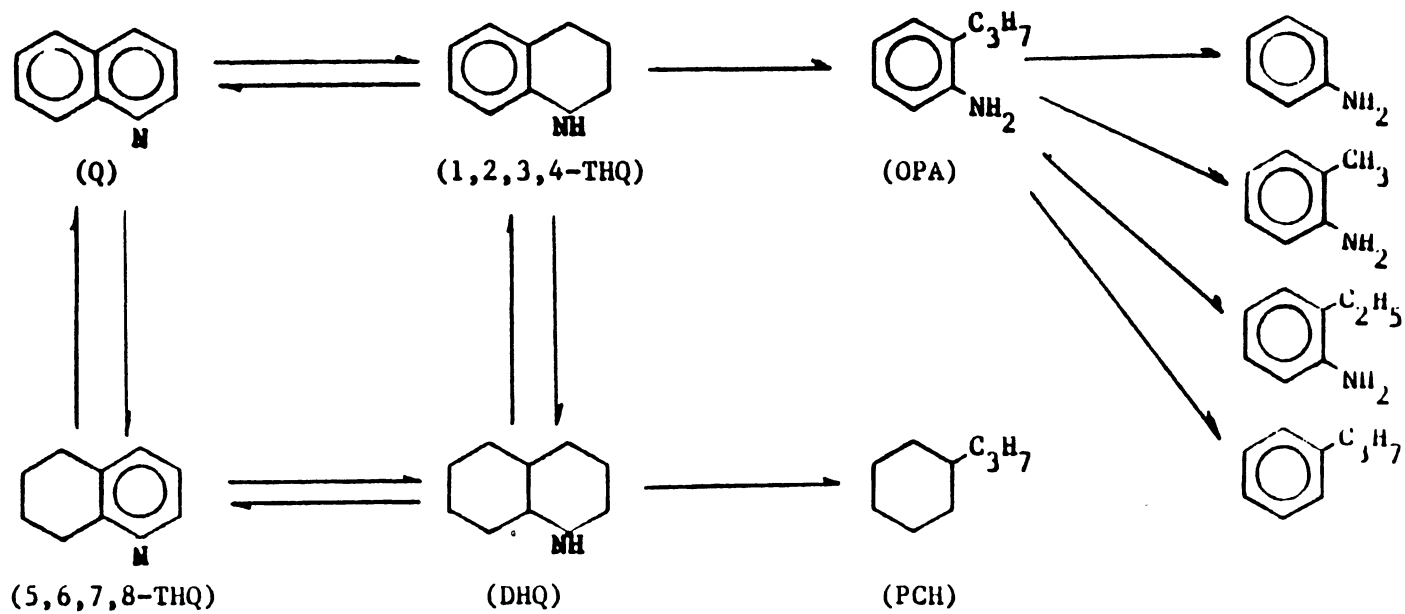
considering both operating temperature (370°C) and space time, runs PDC to PDG were made at 350 C instead of 370°C and space time was further reduced to 0.5h. No significant effect on data comparison from run to run after 72h time on stream was expected; therefore, experimental run duration was reduced to 72h as shown in Table II. These changes were made to have suitable conditions (reasonable conversion levels) for the study. Figure 4 also presents percent of HDN from run PDF, which had the same quinoline concentration (10wt%) as runs PDA and PDB. Results show that the established conditions had a better performance for this study than the conditions of runs PDA and PDB.

Poor product distributions were found in run PDC (Table IX, Appenidx B). A valve located upstream of the reactor malfunctioned and was found after this run. Thus, run PDC was considered to be unsuccessful and results from this run will not be covered.

Reaction Network

Seapan, et al. (1985) studied the reaction network of catalytic HDN of quinoline. From their model (Figure 5), the major products of quinoline HDN, propylbenzene and propylcyclohexane, are formed from the reaction intermediates, 1,2,3,4-tetrahydroquinoline (1,2,3,4-THQ), 5,6,7,8-tetrahydroquinoline (5,6,7,8-THQ), decahydroquinoline (DHQ), and o-propylaniline (OPA).

Some specific compounds from runs PDD to PDF are



Q : Quinoline
 1,2,3,4-THQ : 1,2,3,4-tetrahydroquinoline
 5,6,7,8-THQ : 5,6,7,8-tetrahydroquinoline

DHQ : Decahydroquinoline
 OPA : O-propylaniline
 PCH : Propylcyclohexane

Figure 5. Quinoline HDN Reaction Network (Seapan, et al., 1985)

presented in Figures 6 - 11. Among these runs, mole percents of 1,2,3,4-THQ, DHQ, and OPA in liquid samples increased with time of catalyst-liquid contact, but that of propylcyclohexane decreased. There is no significant change in 5,6,7,8-THQ and propylbenzene. From a view of resonance energy, the formation of 1,2,3,4-THQ and 5,6,7,8-THQ should be comparable. But actually the concentration of 1,2,3,4-THQ is much higher than that of 5,6,7,8-THQ. This can be explained as follows: (1) The active sites on the catalyst surface are considered to be acidic; hence, the affinity of a molecule to the catalyst surface is dominated by the molecule's basicity. When quinoline is adsorbed on the catalyst surface, the hydrogenation of its pyridine ring should occur readily because of the interaction of its nitrogen unpaired electrons with the acid site. (2) The reaction rate constant of 5,6,7,8-THQ \rightarrow DHQ is higher than that of 1,2,3,4-THQ \rightarrow DHQ; therefore, most of 5,6,7,8-THQ reacts to DHQ (Shih, et al., 1977).

Within a molecule a C-N bond has a greater opportunity than a C-C bond to be on an active site because of adsorption of the N atom on the catalyst surface. In this study, only a small amount of benzene, cyclohexane, and ethylcyclohexane (generally less than 1 mole% each) were detected. No trace amount of aniline, toluidine, and ethylaniline were found. These compounds are most likely formed through C-C bond cracking of 1,2,3,4-THQ. Thus, C-C bond breakage is not as prevalent as C-N bond breakage in quinoline HDN

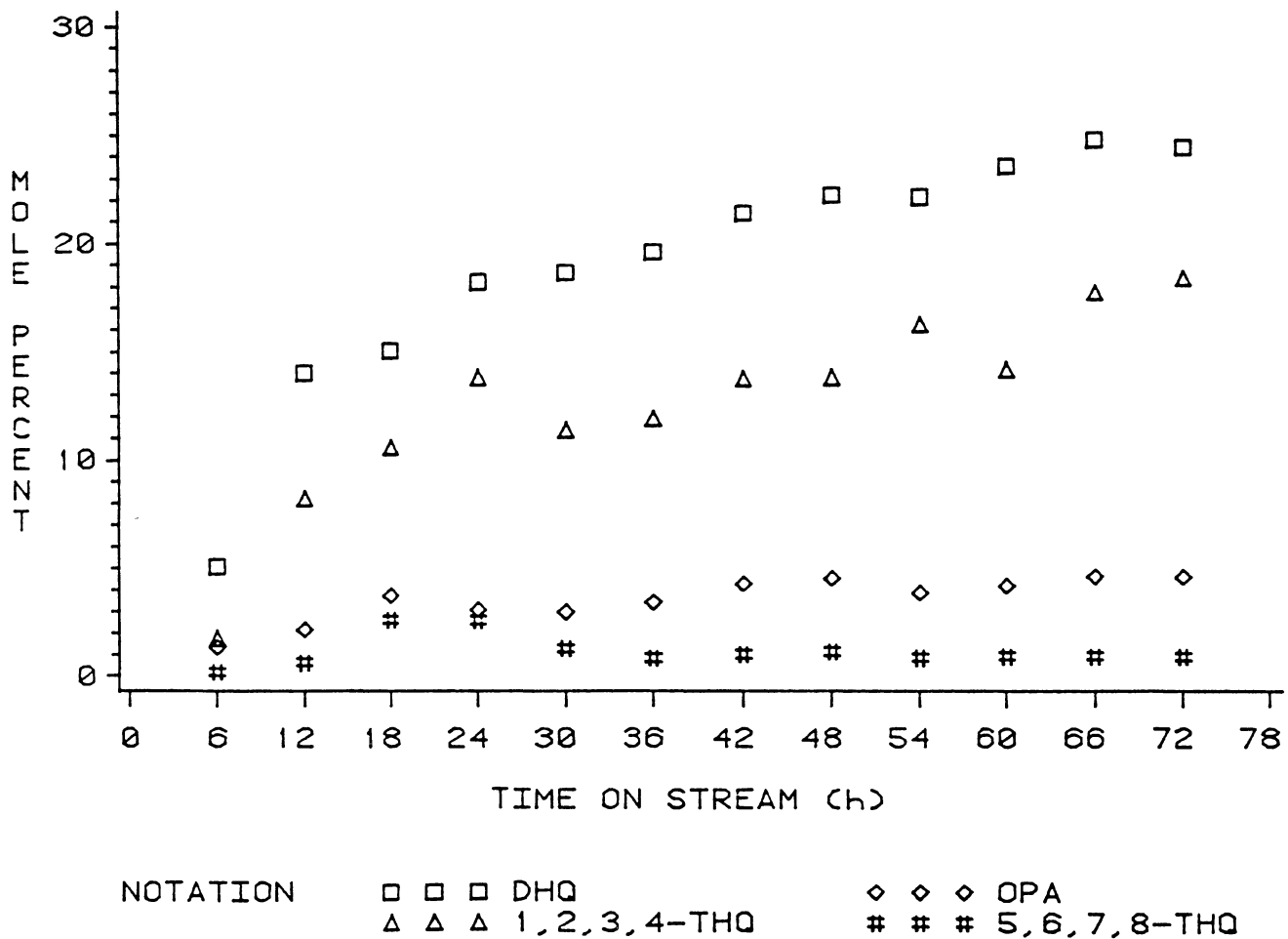
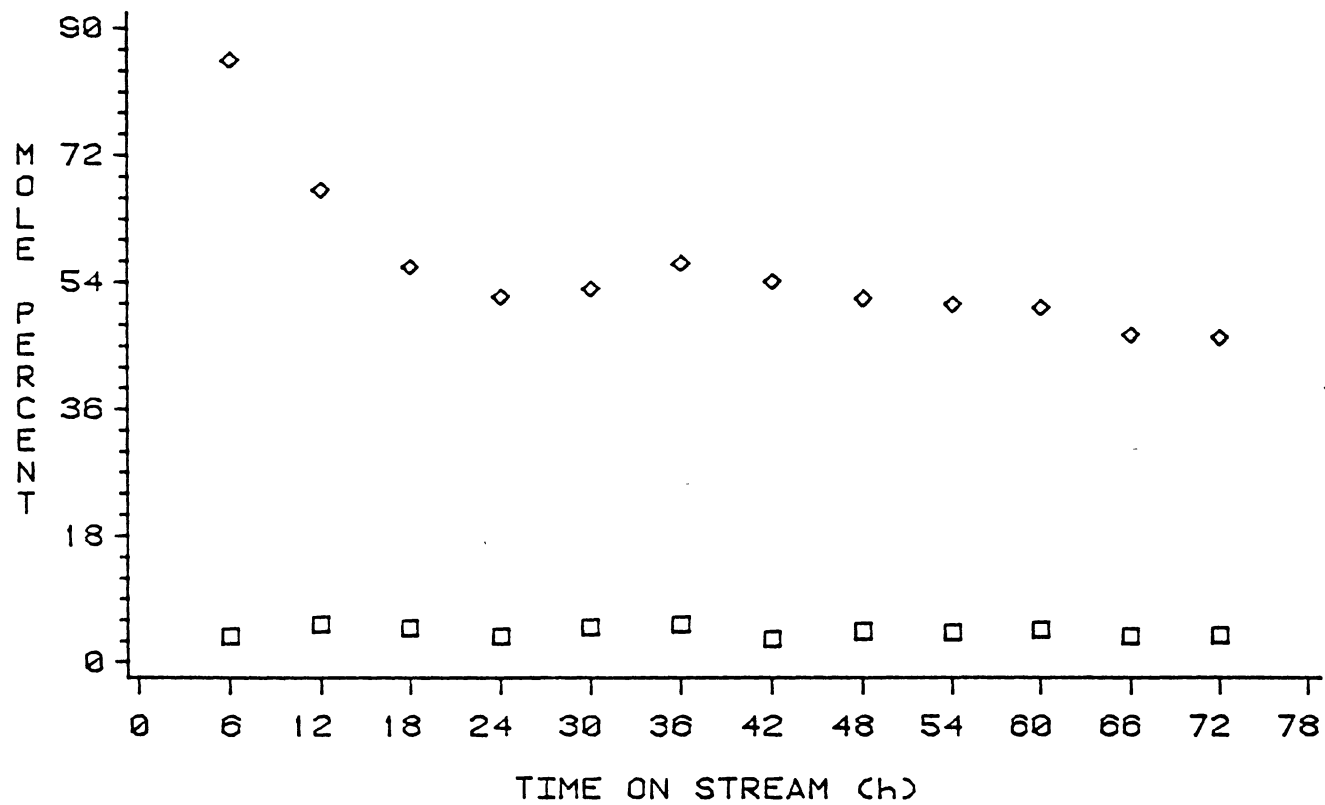
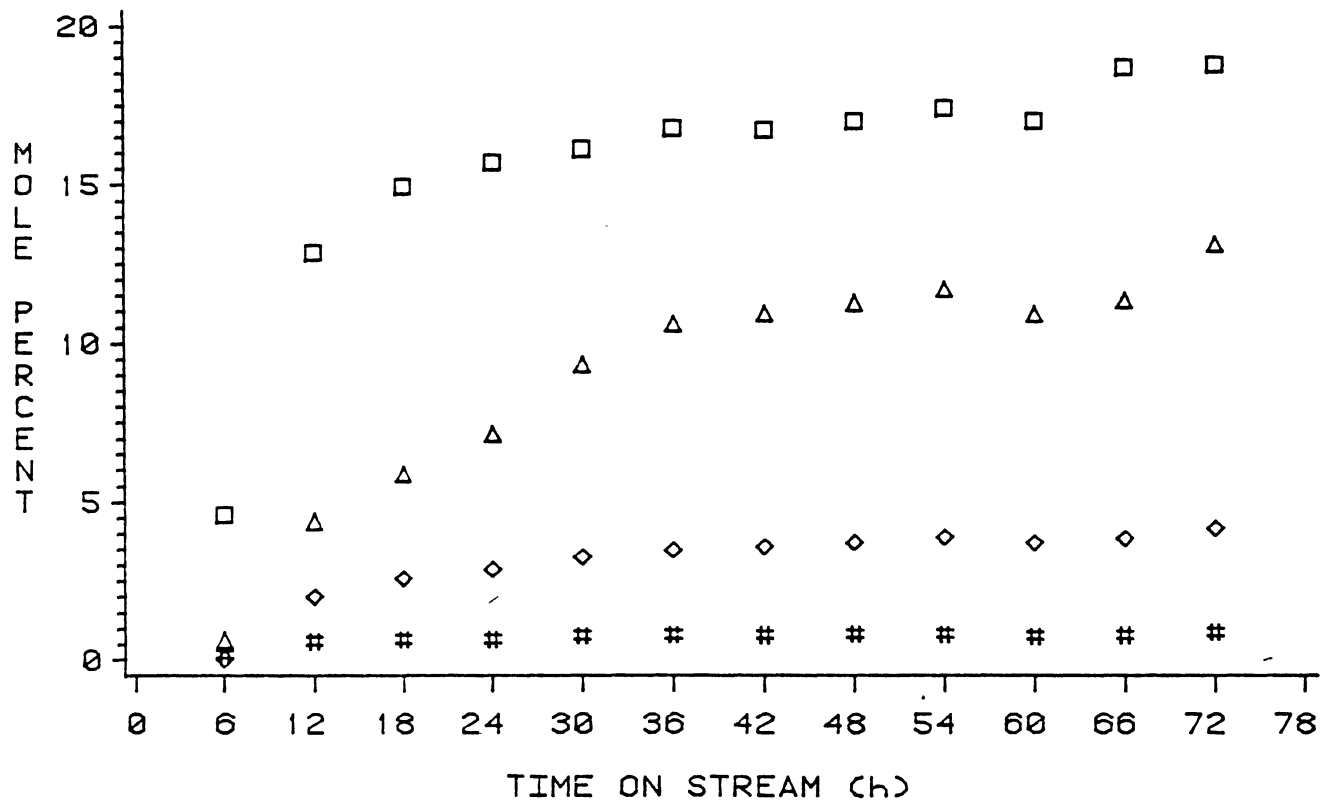


Figure 6. Concentration of Intermediates with Time, Run PDD(30%Q)



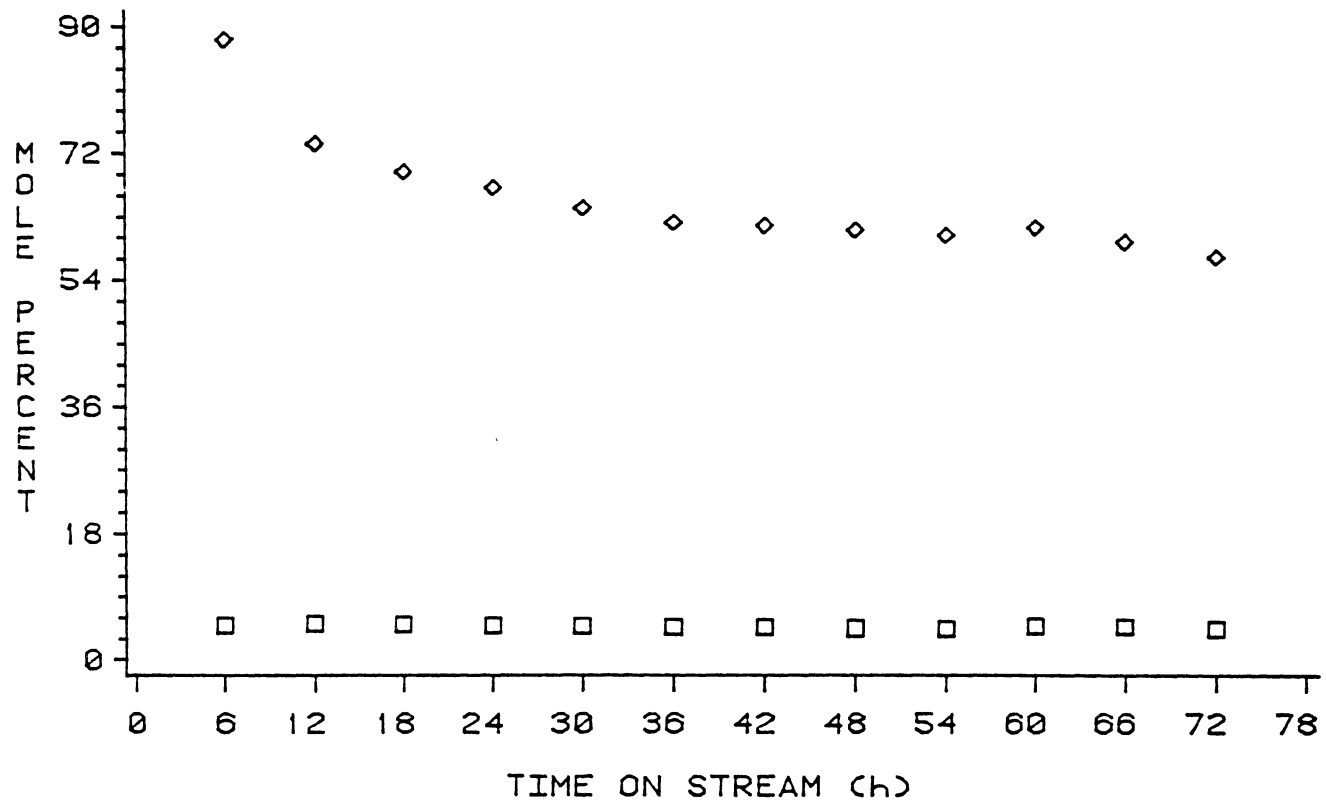
NOTATION □ □ □ PB ◇ ◇ ◇ PCH

Figure 7. Concentration of Major products with Time, Run PDD(30%Q)



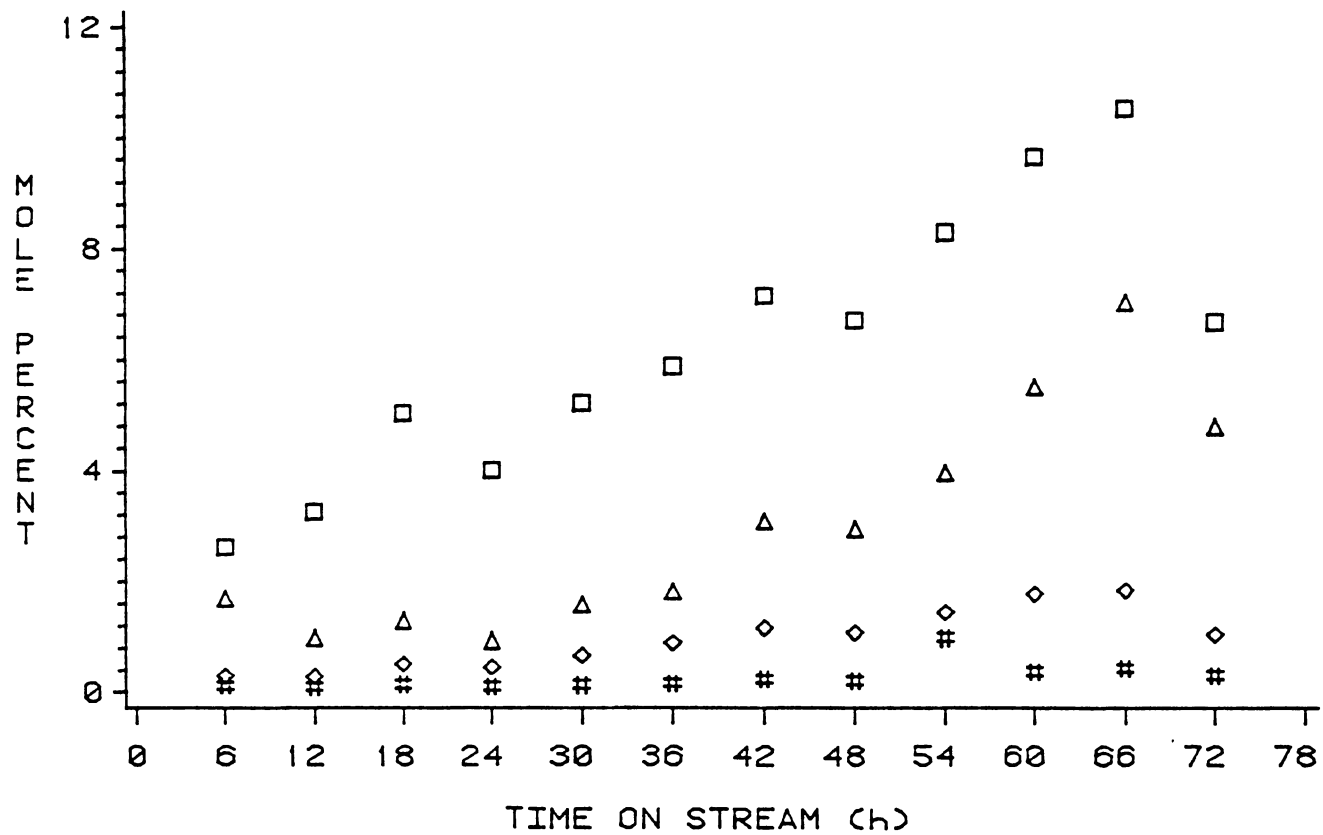
NOTATION □ □ □ DHQ ◇ ◇ ◇ OPA
 △ △ △ 1,2,3,4-THQ # # # 5,6,7,8-THQ.

Figure 8. Concentration of Intermediates with Time, Run PDE(20%Q)



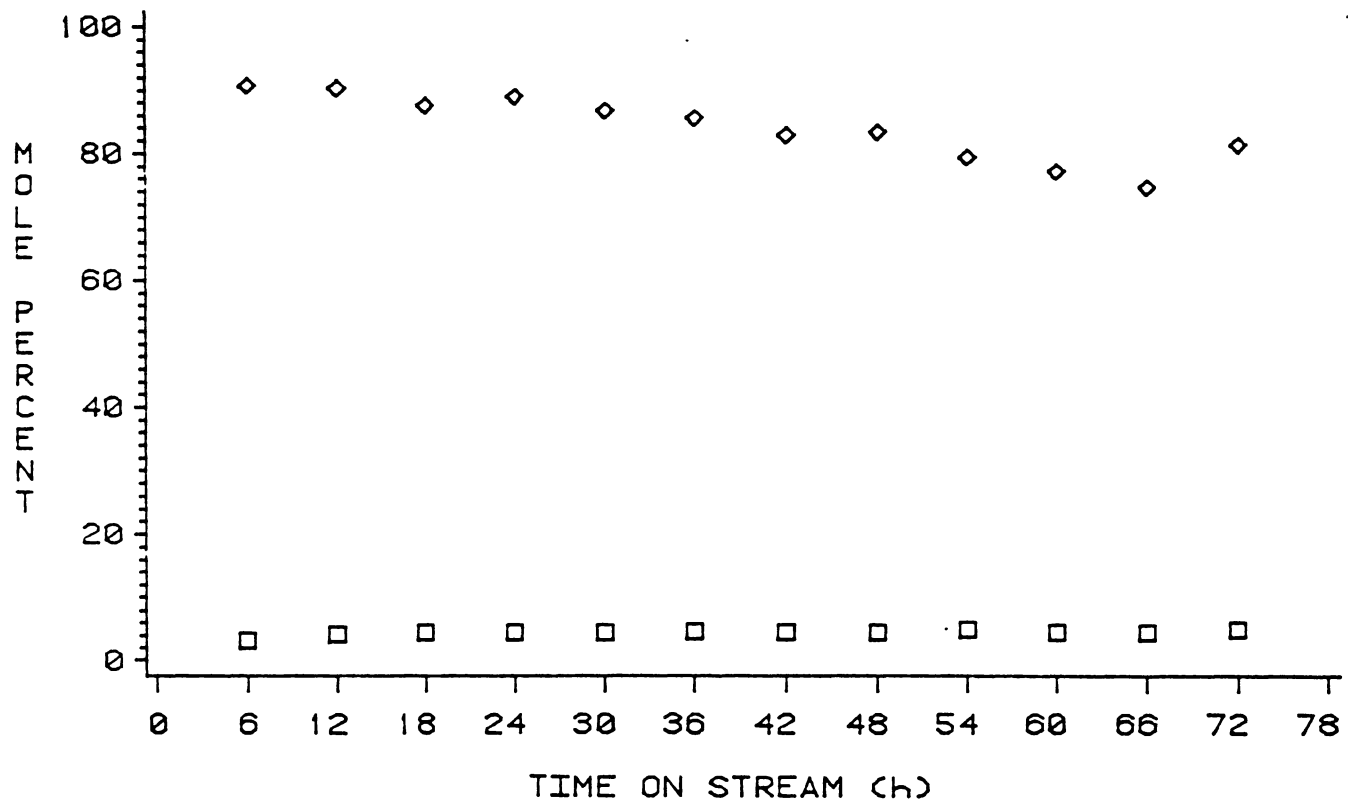
NOTATION □ □ □ PB ◇ ◇ ◇ PCH

Figure 9. Concentration of Major products with Time, Run PDE(20%Q)



NOTATION □ □ □ DHQ ◇ ◇ ◇ OPA
 △ △ △ 1,2,3,4-THQ # # # 5,6,7,8-THQ

Figure 10. Concentration of Intermediates with Time, Run PDF(10%Q)



NOTATION □ □ □ PB ◇ ◇ ◇ PCH

Figure 11. Concentration of Major products with Time, Run PDF(10%Q)

reaction.

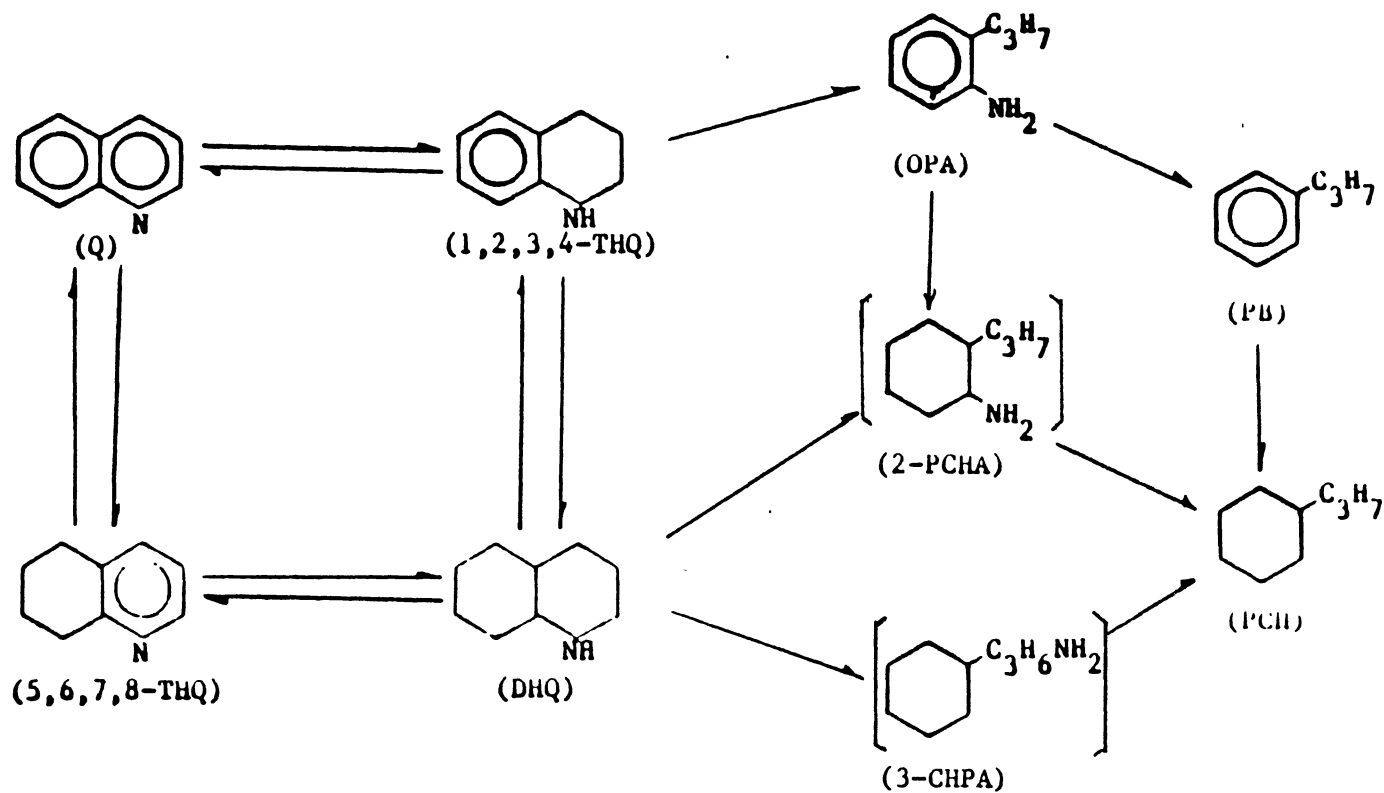
Stengler, et al. (1964) reported that the C-N bond of an aromatic ring is much stronger than the C-N bond of an alkylamine, because the unpaired electrons of the N atom in an aromatic amine is involved in the resonance of the ring π -electrons. The inference of this is that the C-N bond of the benzene ring is more difficult to break than the bond of N atom with a CH_2 structure in 1,2,3,4-THQ. Therefore, the intermediate of 1,2,3,4-THQ reacts to OPA rather than 3-phenylpropylamine. Hydrogenation was easier than hydrogenolysis in 1,2,3,4-THQ at the operating conditions (350°C and 12.4MPa). The concentration of DHQ is much higher than that of OPA. There is not much difference between the strengths of the two C-N bonds of DHQ. Either bond goes through hydrogenolysis to form 2-propylcyclohexylamine (2-PCHA) or 3-cyclohexylpropylamine (3-CHPA). 2-PCHA can also be formed from hydrogenation of OPA; therefore, reaction steps $\text{DHQ} \rightarrow 2\text{-PCHA}$, $\text{DHQ} \rightarrow 3\text{-CHPA}$, and $\text{OPA} \rightarrow 2\text{-PCHA}$ are probably involved in the quinoline HDN reaction network. These two compounds may be present in only small amounts because deamination of alkylamine can occur readily (Stengler, et al., 1964). No attempt was made to identify these two compounds because no reference samples could be found for calibration. Under typical reaction conditions hydrogenation of propylbenzene, which is most likely, occurs from the denitrogenation of OPA, to propylcyclohexane (Gultekin, et al., 1984). Therefore, a modification of the Seapan's

(1985) reaction network is proposed in Figure 12.

Concentration Effect

Two kinds of catalytic sites which exist on sulfided NiMo/Al₂O₃ catalyst have been mentioned in the literature review (Yang and Satterfield, 1983). Site I is a sulfur vacancy associated with molybdenum which is responsible for hydrogenation and hydrogenolysis reactions and is easily poisoned by nitrogen compounds. Site II is a Bronsted acid which is responsible for hydrogenolysis and is less sensitive to nitrogen poisoning. Percents of nitrogen removal of runs PDD, PDE, and PDF are given in Figure 13. The HDN activity of the catalyst shows a dependence on the concentration of quinoline in the feedstocks. As the quinoline concentration was decreased from 30% to 10%, the percentage of nitrogen removal increased. Results also show that catalyst deactivation from runs PDD and PDE decreased rapidly during the first 24h time on stream while that from run PDF decreased steadily. Apparently sufficient nitrogen can block both active sites. Run PDF did not show the same trend as runs PDD and PDE due to its lowest concentration of quinoline (10%) in the feed.

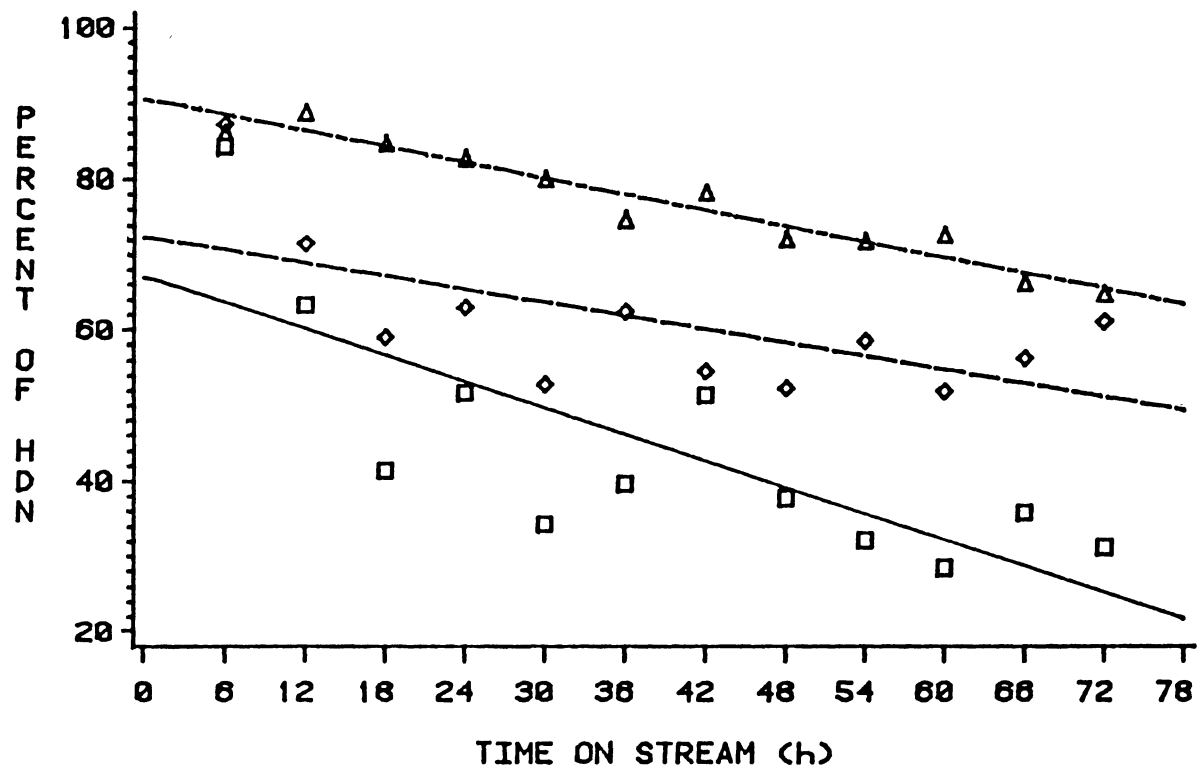
In a study of pyridine poisoning of thiophene HDS, Desikan and Amberg (1963) found that two kinds of active sites poisoned by nitrogen compounds were governed by an adsorption-desorption mechanism, i.e., nitrogen compounds strongly adsorb on and slowly desorb from one site, and



Q : Quinoline
 1,2,3,4-THQ : 1,2,3,4-tetrahydroquinoline
 5,6,7,8-THQ : 5,6,7,8-tetrahydroquinoline
 DHQ : Decahydroquinoline

OPA : O-propylaniline
 2-PCHA : 2-propylcyclohexylamine
 3-CHPA : 3-cyclohexylpropylamine
 PB : Propylbenzene
 PCH : Propylcyclohexane

Figure 12. Modification of Quinoline HDN Reaction Network



NOTATION □-□-□ PDD(30%Q) ◆-◆-◆ PDE(20%Q) ▲-▲-▲ PDF(10%Q)

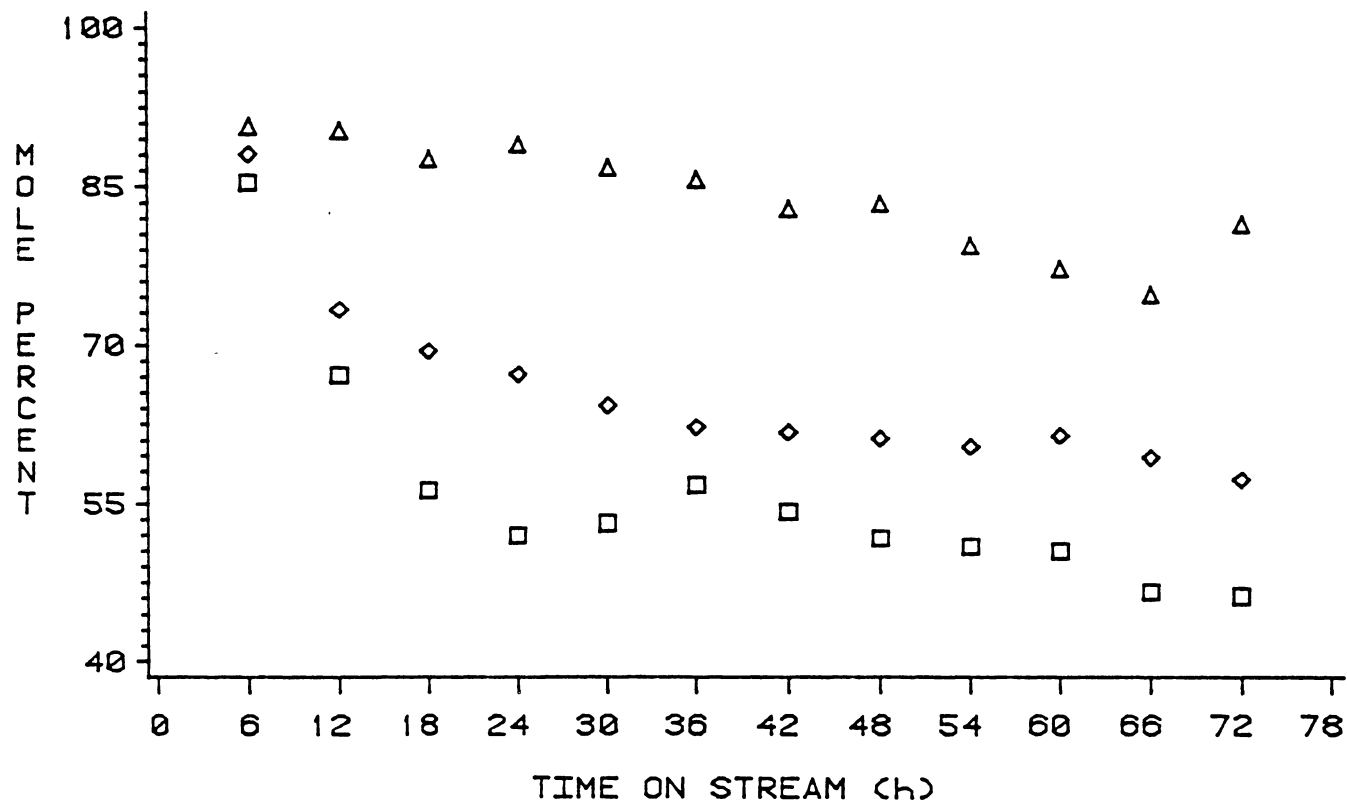
Figure 13. Percent of HDN, Run PDD(30%Q), PDE(20%Q), and PDF(10%Q)

weakly adsorb on and quickly desorb from the other site. In another study, Tarrer, et al. (1985) found that the poisoning effect of quinoline on hydrogenation of naphthalene is partially reversible. The inference of these is that the Type I site nitrogen poisoning is partially reversible even though it is sensitive to nitrogen compounds. Presumably the adsorption of basic nitrogen compounds on acid sites during the run have contributed to the initial decline in catalyst activity; however, these compounds likely had little effect on the long-term deactivation, as discussed below.

Catalyst deactivation usually relates to coke formation which may be due to the irreversible adsorption of nitrogen bases (Bartholomew, 1984). Generally, quinoline (a basic species) had a greater opportunity to adsorb on acidic sites than did n-hexadecane (a neutral species) and simple thermal decomposition of n-hexadecane would be negligible at the reaction temperatures. Therefore, coke contribution from n-hexadecane played an insignificant role in this study. Results showed that coke content increased with increasing quinoline concentration (see later). Coke blockage of active sites is responsible for catalyst deactivation after nitrogen compounds accumulate on the catalyst. Therefore, deactivation during the early portion of the run accelerates due to an accumulation of poisons until the nitrogen level on the catalyst reaches a saturated level and the overall deactivation rate diminishes to reflect the background of coking. Some catalyst deactivation was also due to loss of metal

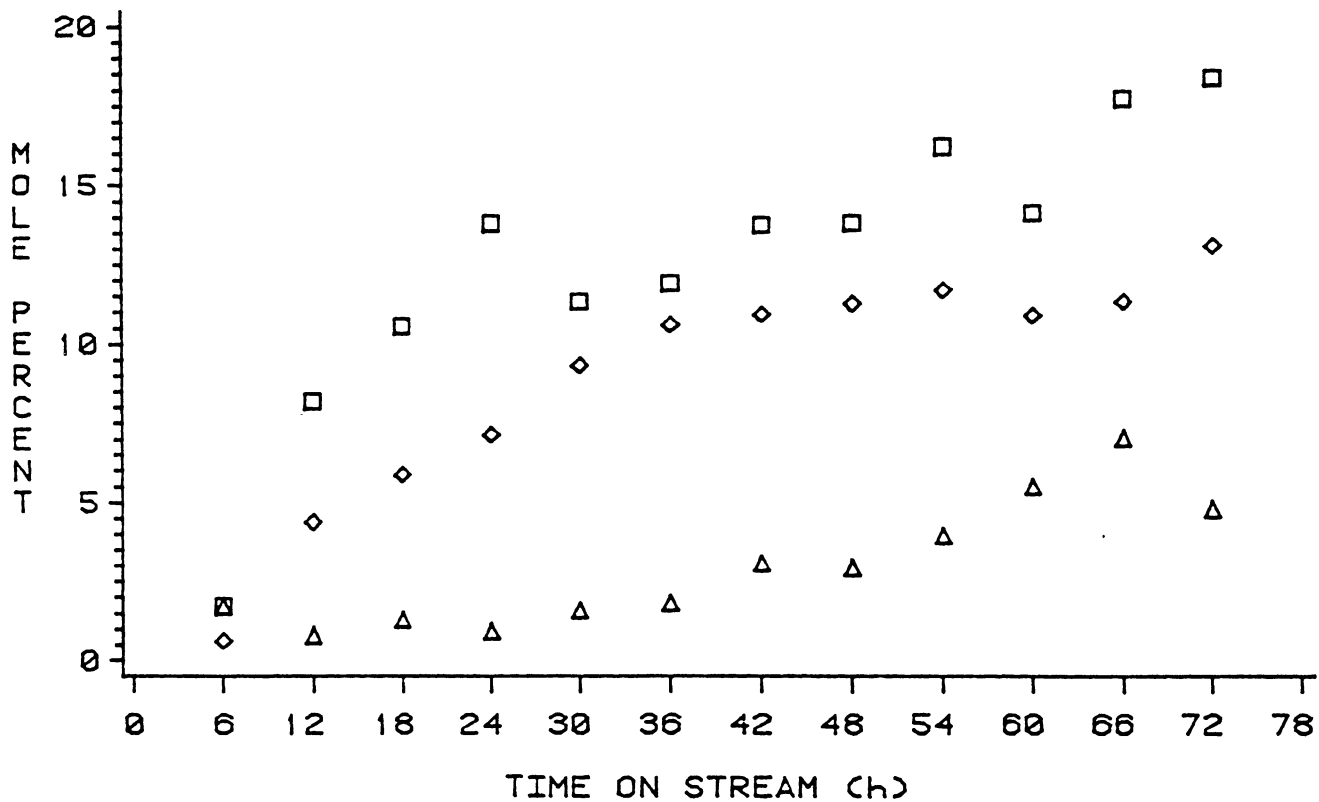
sulfides during the run itself, because the feed contained no sulfur species. This effect was expected to be reproducible from run to run.

Different concentrations of quinoline in the feedstock also affects the product distribution in liquid samples. The mole percentage of propylcyclohexane (Figure 14) decreases with increasing feedstock quinoline, but that of 1,2,3,4-THQ (Figure 15) and DHQ (Figure 16) increases. There are little changes in 5,6,7,8-THQ (Figure 17), OPA (Figure 18), and propylbenzene (Figure 19). Apparently the reaction steps $1,2,3,4\text{-THQ} \rightarrow \text{OPA}$ and $\text{DHQ} \rightarrow \text{PCH}$ are inhibited by increasing quinoline concentration in the feed mixture. To explain these phenomena, a simple acid-base mechanism has to be considered. As a result of interaction between a nitrogen base and acid sites on the catalyst, the unit number of acid sites (total number of acid sites per mole of nitrogen base) that are available for reaction decreased as the nitrogen poisoning increased in the feed (it should be noted that this interaction need not be an irreversible adsorption) and hence increased the concentrations of some major intermediates. In considering the relative changes of intermediates, quinoline HDN reaction generally follows the trends of feedstock quinoline through the route $1,2,3,4\text{-THQ} \rightarrow \text{DHQ} \rightarrow \text{PCH}$ at the established operating conditions (350°C and 12.4MPa).



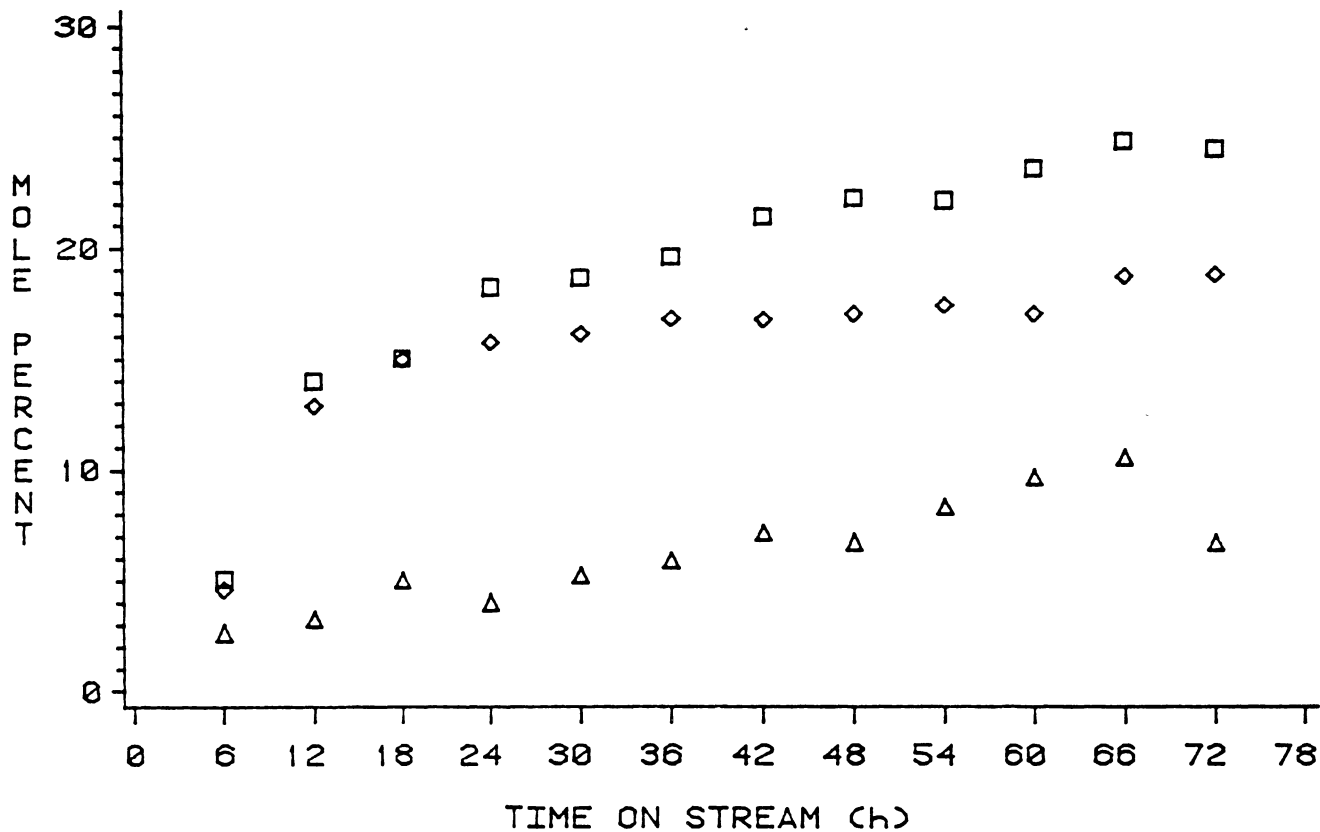
NOTATION □ □ □ PDD(30%Q) ◇ ◇ ◇ PDE(20%Q) △ △ △ PDF(10%Q)

Figure 14. Concentration of Propylcyclohexane, Run PDD(30%Q), PDE(20%Q), and PDF(10%Q)

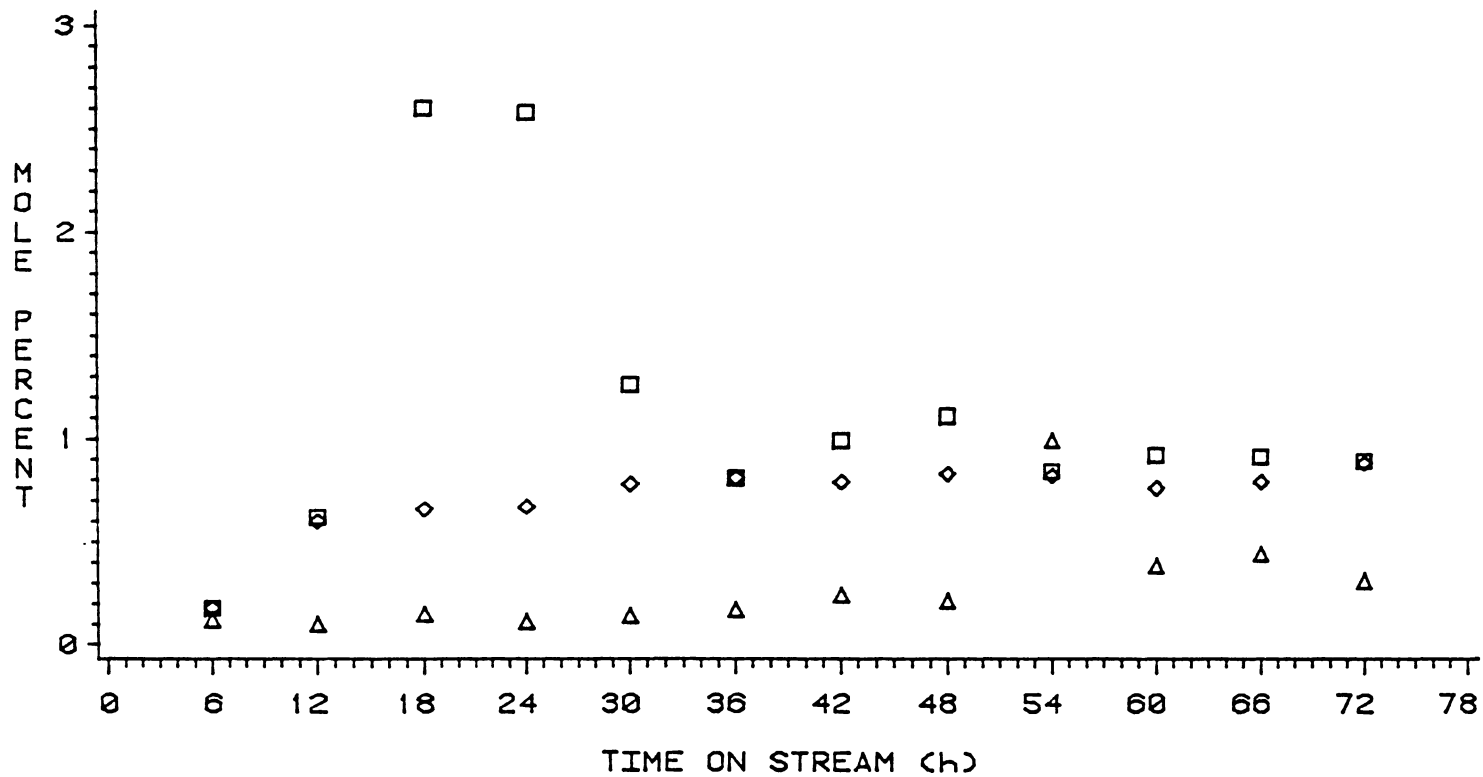


NOTATION □ □ □ PDD(30%Q) ◇ ◇ ◇ PDE(20%Q) △ △ △ PDF(10%Q)

Figure 15. Concentration of 1,2,3,4-Tetrahydroquinoline, Run PDD(30%Q), PDE(20%Q), and PDF(10%Q)

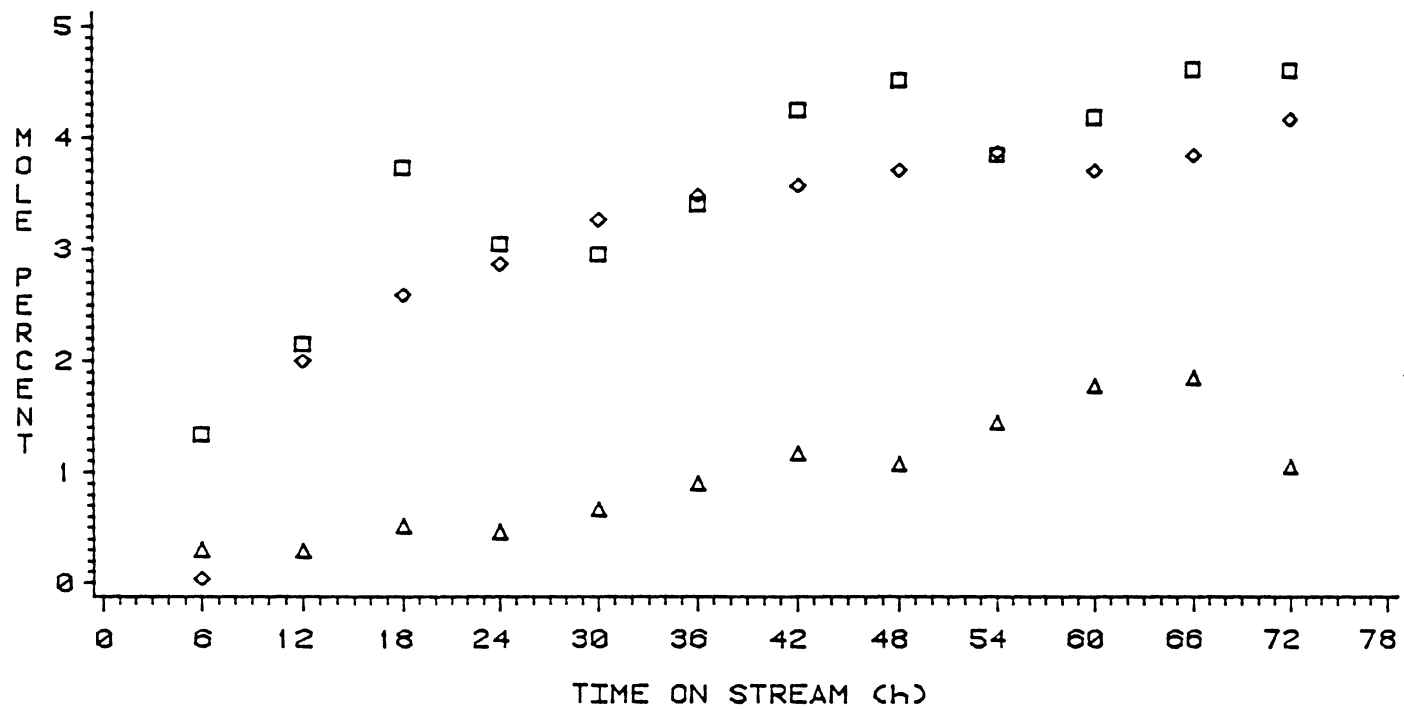


NOTATION □ □ □ PDD(30%Q) ◇ ◇ ◇ PDE(20%Q) △ △ △ PDF(10%Q)
 Figure 16. Concentration of Decahydroquinoline, Run PDD(30%Q), PDE(20%Q), and PDF(10%Q)



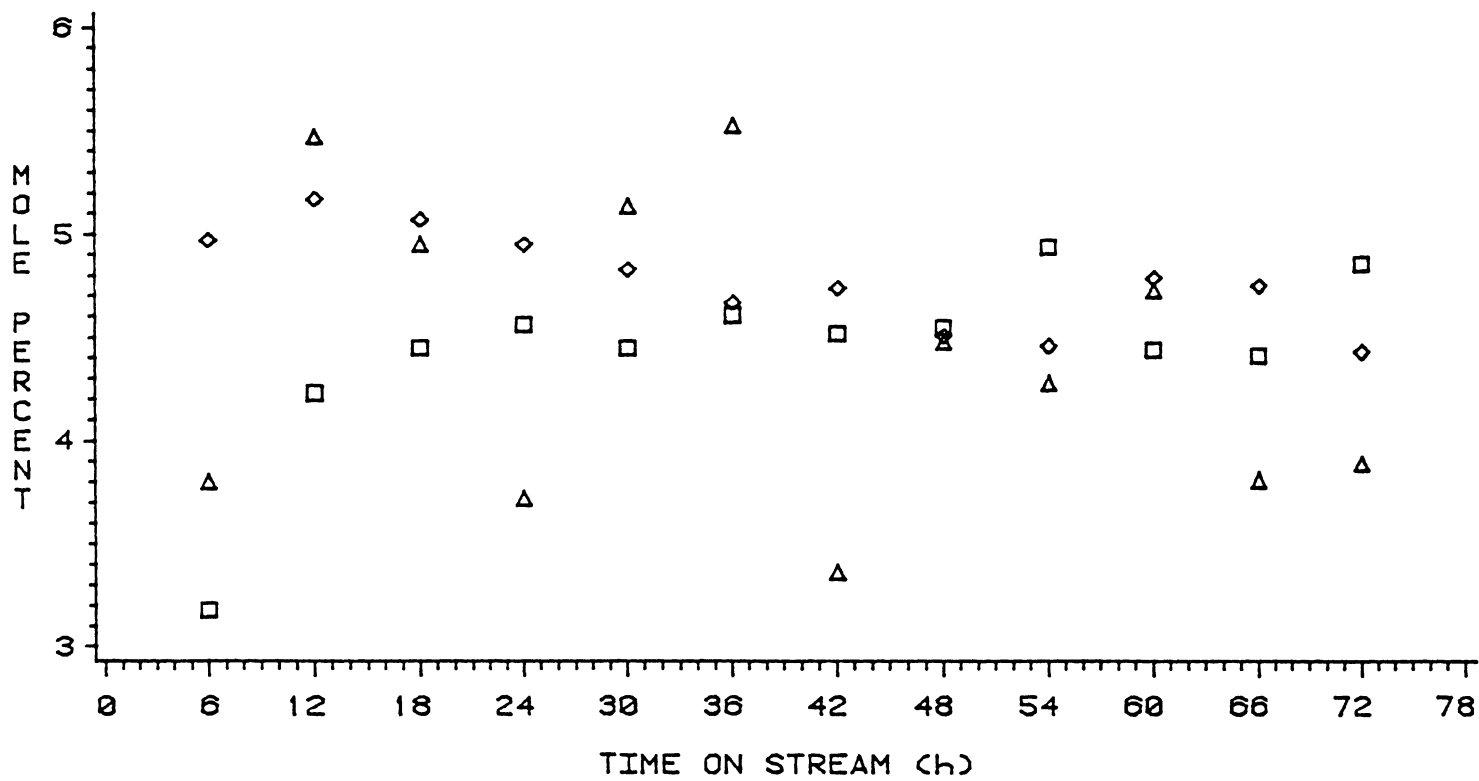
NOTATION □ □ □ PDD(30%Q) ◇ ◇ ◇ PDE(20%Q) △ △ △ PDF(10%Q)

Figure 17. Concentration of 5,6,7,8-Tetrahydroquinoline, Run PDD(30%Q), PDE(20%Q), and PDF(10%Q)



NOTATION □ □ □ PDD(30%Q) ◇ ◇ ◇ PDE(20%Q) △ △ △ PDF(10%Q)

Figure 18. Concentration of Propylaniline, Run PDD(30%Q), PDE(20%Q), and PDF(10%Q)



NOTATION □ □ □ PDD(30%Q) ◇ ◇ ◇ PDE(20%Q) △ △ △ PDF(10%Q)

Figure 19. Concentration of Propylbenzene, Run PDD(30%Q), PDE(20%Q), and PDF(10%Q)

Catalyst Analysis

The coke contents in spent catalysts were affected by quinoline concentration in feed. Increase in quinoline concentration resulted in coke content increase in the spent catalysts. More detail results are given in Appendix E. Table IV presents the properties of spent and regenerated catalysts. There were substantial losses in both surface area (23-30%) and pore volume (31-38%) for spent catalysts; however, these properties recovered 92-98% of their original values after regeneration. No evidence shows that quinoline concentration affected these properties.

A relationship of coke content in catalysts and quinoline concentration is presented in Figure 20. Run PDD had the largest coke content in spent catalyst due to its large quinoline concentration (30%) in feed. Liquid volume hourly space time (LVHST) also affects coke formation. The average coke content increased from 8.25% to 10.58% as space time decreased from 2.3h (run PDA) to 1h (run PDB). These phenomena were attributed to larger amounts of quinoline (higher liquid flow rate) used in run PDB.

Reproducibility

All experimental runs in this study have been conducted at 12.4MPa(1800psi). Less than 0.3MPa(40psi) deviation was observed during normal operation. Sooter (1977) reported that an increase in pressure beyond 7.0MPa(1000psi) had no significant effect on the heteroatom removal from coal

TABLE IV
 PROPERTIES OF SPENT AND REGENERATED
 CATALYSTS (Spent/Regenerated)

	Coke(wt%)	SA($\times 10^3 \text{ m}^2/\text{kg}$)*	PV($\times 10^{-3} \text{ m}^3/\text{kg}$)*	MP(nm)*
PDA	7.27 \pm 0.85	230/245	0.44/0.55	7.9/9.4
PDB	9.60 \pm 1.52	185/241	0.37/0.54	7.8/9.2
PDC	8.45 \pm 0.69	194/244	0.37/0.54	7.8/9.1
PDD	10.59 \pm 0.96	193/240	0.37/0.55	7.6/9.2
PDE	9.84 \pm 0.59	192/238	0.38/0.54	7.8/9.4
PDF	8.86 \pm 0.90	190/237	0.38/0.54	8.2/9.2
PDG	8.82 \pm 0.74	190/235	0.39/0.55	8.0/9.0

* Fresh catalyst was $253 \times 10^3 \text{ m}^2/\text{kg}$, $0.57 \times 10^{-3} \text{ m}^3/\text{kg}$, and 9.8nm respectively

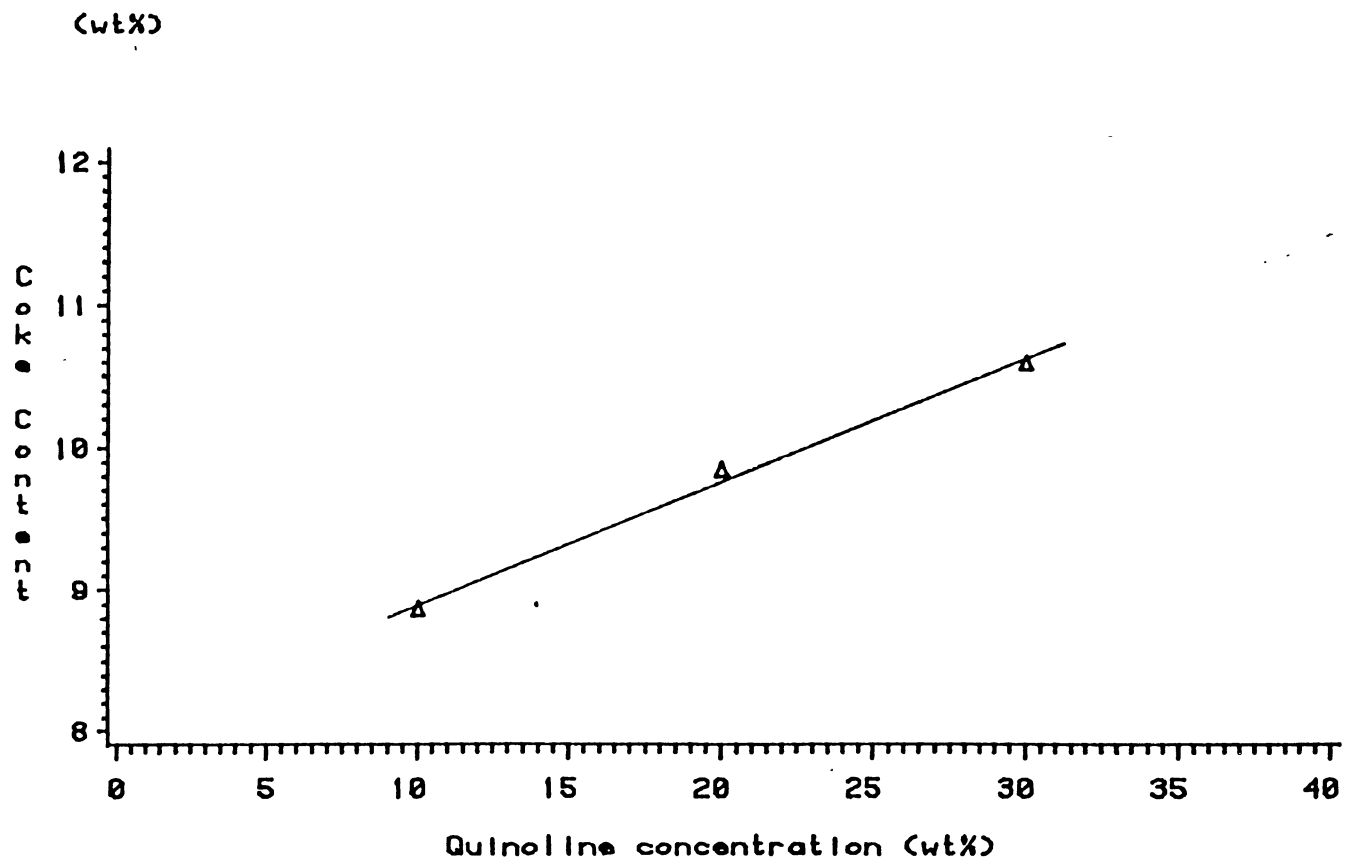


Figure 20. Coke Content on Catalyst as A Function of Quinoline Concentration

liquids. The effect of these small fluctuations in this study was, therefore, not expected to be significant.

Under normal operation, the gas flow rate was essentially stable. Liquid feed was delivered by a metering pump at a constant flow rate. The operating temperature was controlled by a temperature control. Temperature distributions along the outer wall were excellent. The variations with both time and position were only 2.5°C. Less than 4°C in temperature differential across reactor tube wall was reported by Chang (1982). This differential was expected to be reproducible from run to run in this study.

A nitrogen mass balance was made for each sample by use of the following equation:

$$\text{Percent Difference} = \frac{N_f - (N_l + N_g)}{N_f} \times 100\%$$

Where, N_f = nitrogen in feed

N_l = nitrogen in liquid sample calculated from nitrogen compounds

N_g = nitrogen in effluent gas calculated from hydrocarbons in liquid sample

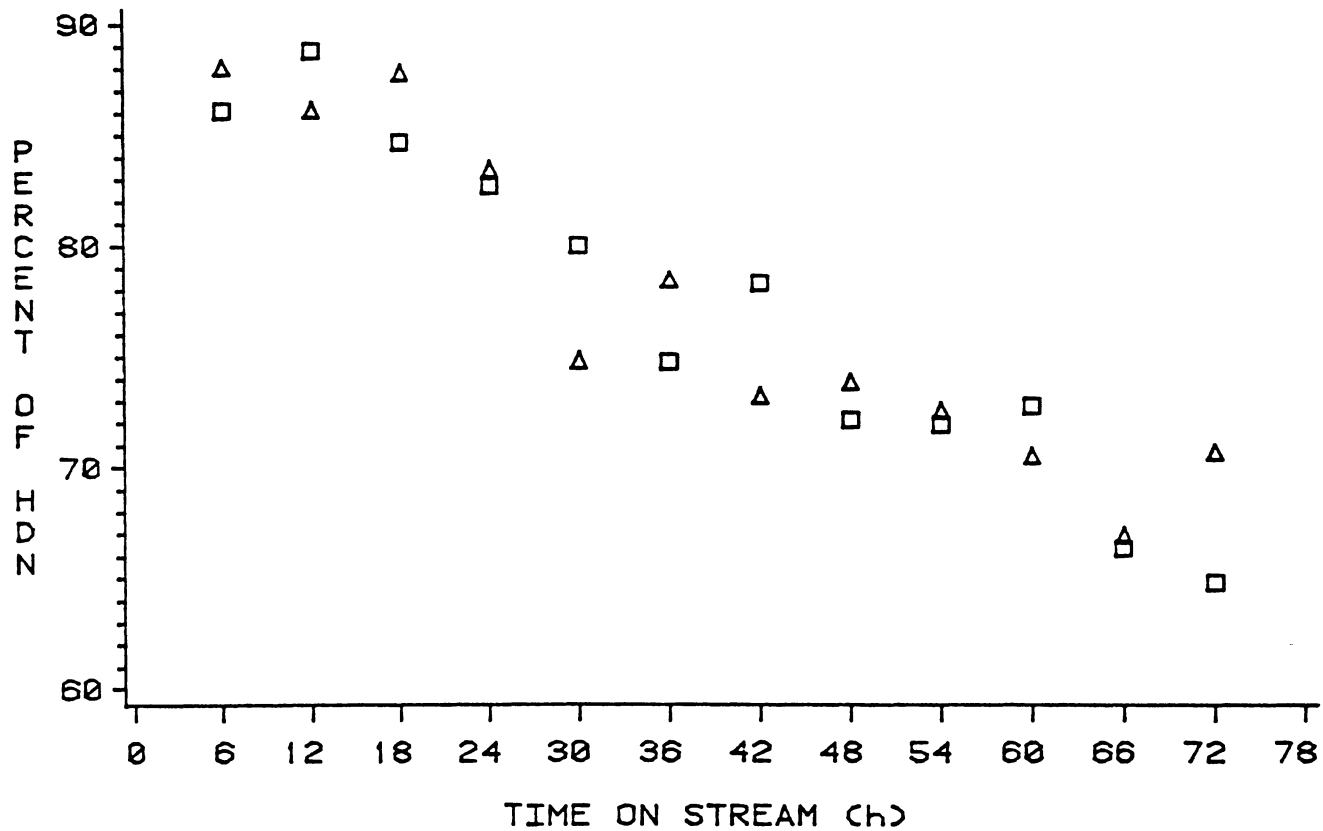
Appendix F also gives an example of this calculation. Table V presents the results from runs PDD to PDF. Two reasons for these differences were considered: (1) catalyst cracking ability decomposed nitrogen compound into gaseous components, and (2) under the operating conditions the volatility of reactants and reaction intermediates distributed

TABLE V
PERCENT DIFFERENCE OF NITROGEN MASS
BALANCE

TIME	PDD(30%Q)	PDE(20%Q)	PDF(10%Q)
6	62.1	54.7	26.7
12	42.7	43.1	31.1
18	21.0	29.7	29.4
24	33.2	35.1	22.2
30	14.0	24.4	22.2
36	19.2	36.5	15.8
42	32.7	27.3	26.4
48	18.2	25.0	15.3
54	12.4	32.7	20.2
60	8.5	24.4	24.9
66	17.3	30.3	17.7
72	12.4	37.1	7.3

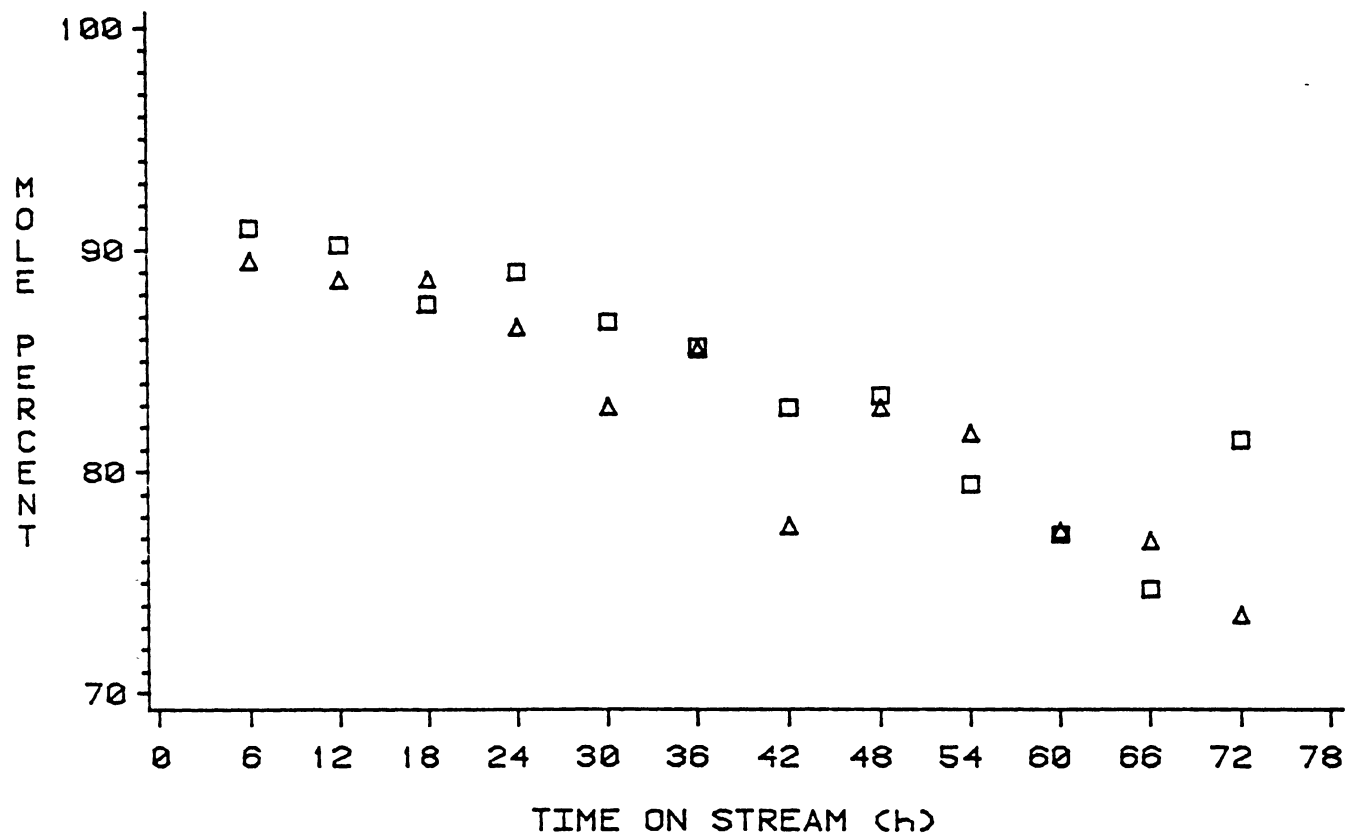
themselves between liquid and vapor phases. Those nitrogen compounds in the vapor phase flowed out with the effluent gas (Smith and Satterfield, 1986). Under these conditions a mass balance over a system to indicate the validity of experimental results was impossible, so it was necessary to rely on the good reproducibility of the results as an indication of their validity. Therefore, run PDG was made to repeat the conditions of run PDF.

The HDN ability of runs PDF and PDG is presented in Figure 21. The data show errors within 10% in major species propylcyclohexane (Figure 22), DHQ (Figure 23), and 1,2,3,4-THQ (Figure 24). Large deviation in minor products was a result of the analytical technique. Excellent agreement was found in the properties of both spent and regenerated catalysts. Acceptable error in major compounds and excellent agreement in solid catalyst samples indicate that reproducibility is acceptable.



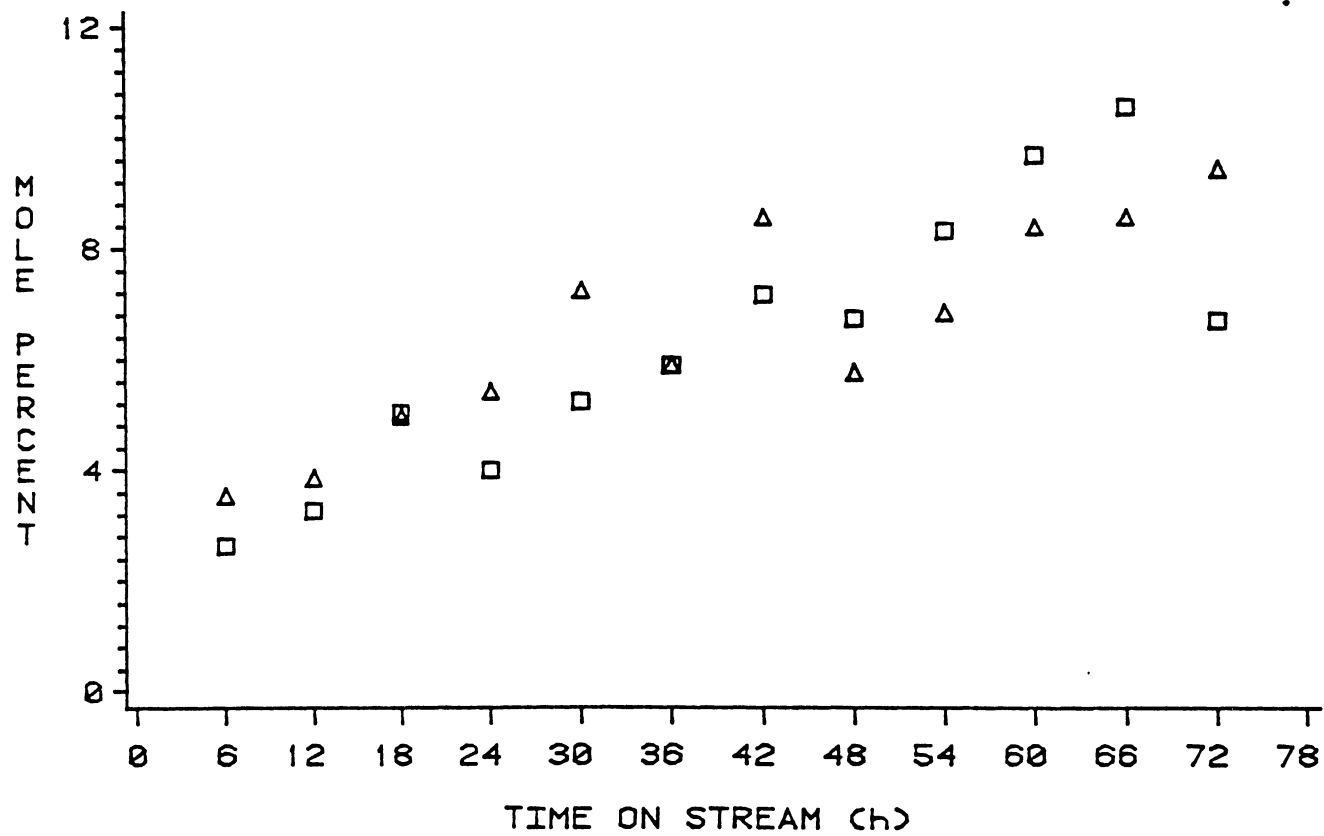
NOTATION □ □ □ PDF △ △ △ PDG

Figure 21. Percent of HDN from Runs PDF and PDG



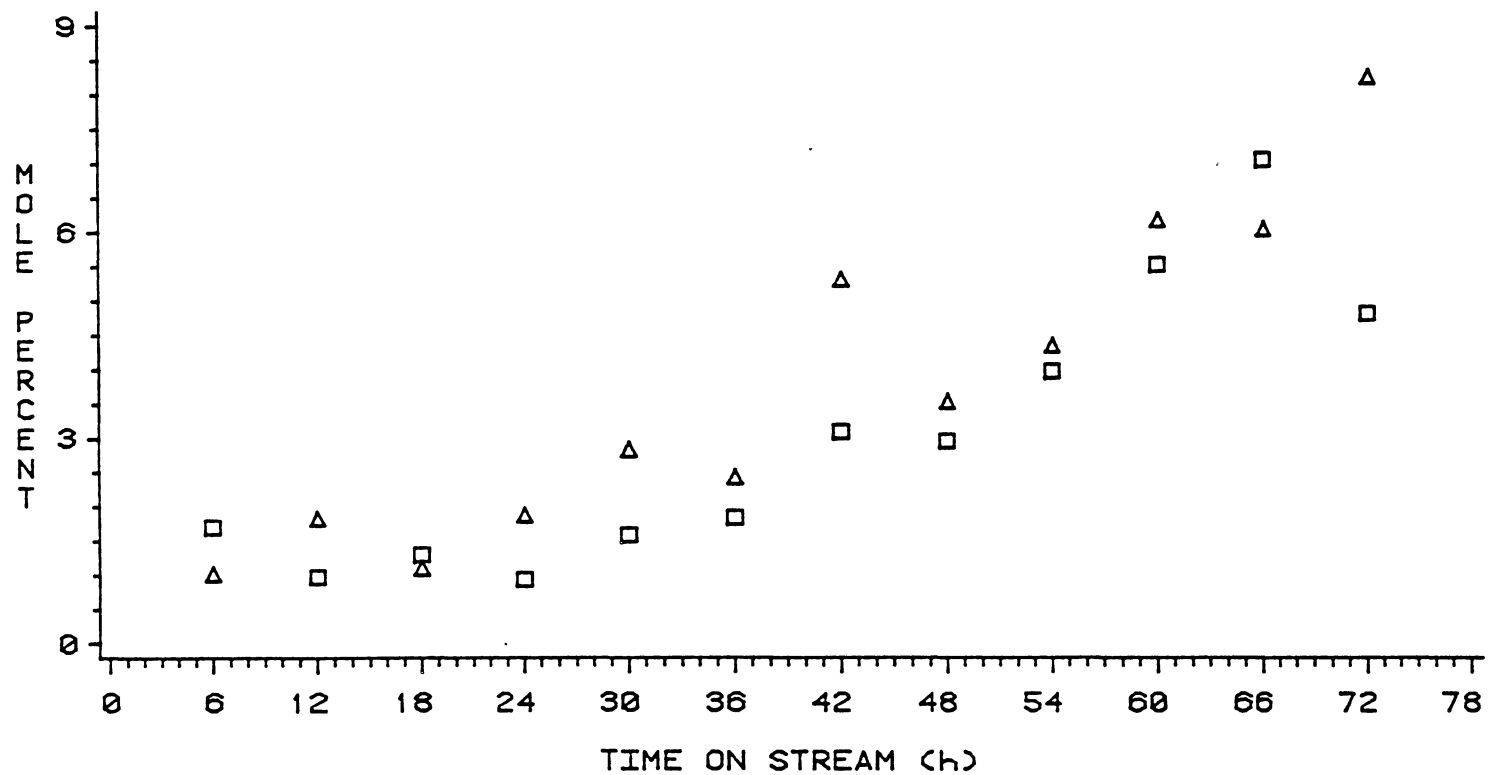
NOTATION □ □ □ PDF △ △ △ PDG

Figure 22. Concentration of Propylcyclohexane, Runs PDF and PDG



NOTATION □ □ □ PDF △ △ △ PDG

Figure 23. Concentration of Decahydroquinoline, Runs PDF and PDG



NOTATION □ □ □ PDF △ △ △ PDG

Figure 24. Concentration of 1,2,3,4-Tetrahydroquinoline, Runs PDF and PDG

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusion

The conclusions of this study can be drawn as follows:

1. The HDN ability of a catalyst strongly depends on the level of nitrogen-poisoning in the feedstock. This study shows that the HDN ability of a catalyst decreases more than 50% as quinoline concentration increases from 10% to 30%.

2. The adsorption of basic nitrogen compounds on the acid sites contributes to the catalyst decay during the early portion of the run. Afterward, deactivation occurs due to coking.

3. Increased quinoline concentration in the feed mixture inhibits reaction steps $1,2,3,4\text{-THQ} \rightarrow \text{OPA}$ and $\text{DHQ} \rightarrow \text{PCH}$. The reaction route tends to $1,2,3,4\text{-THQ} \rightarrow \text{DHQ} \rightarrow \text{PCH}$ at 350°C and 12.4MPa .

4. Coke content on the catalyst is increased with increasing quinoline concentration in the feed.

Recommendations

Through this study, a better understanding of the quinoline HDN reaction and the effects on HDN catalysts has

been provided. However, there are still some questions which need to be answered. To address these questions, the following recommendations are made:

1. Though a reaction network has been proposed; However, some intermediates still can not be confirmed due to their unavailability. A GC/MS instrument should be used to confirm the presence of these compounds in quinoline HDN reaction network.

2. Reaction route is probably affected by temperature; therefore, a set of experimental runs should be made by varying the temperature from 300 to 350°C.

3. A study with different compounds should be further investigated, especially with multi-ring nitrogen compounds, e.g., acridine, carbazole.

4. In order to provide a better understanding of the existence of two types of active sites on HDN catalysts, a study of simultaneous hydrogenation and hydrodenitrogenation of model compounds has to be made. The reactions should be performed in two ways: with and without the presence of H_2S . With the use of this procedure, one might conclude that H_2S improves hydrogenolysis but inhibits hydrogenation.

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APPENDICES

APPENDIX A

LIST OF CHEMICALS

TABLE VI
LIST OF CHEMICALS

Chemicals	Purity	Vendor
Quinoline	99%	Alfa
1,2,3,4-Tetrahydro-quinoline	97%	Aldrich
5,6,7,8-Tetrahydro-quinoline	97%	Aldrich
Decahydro-quinoline	99%	Alfa
O-propylaniline	97%	Aldrich
Tiludiene	99%	Aldrich
Ethylaniline	98%	Aldrich
Aniline	99.5%	Aldrich
Propylbenzene	98%	Aldrich
Propylcyclohexane	97%	Alfa
n-hexadecane	99%	Alfa
Hydrogen	99.5%	Sooner Supply
Nitrogen	99.5%	Sooner Supply

* Vendor specification

APPENDIX B
EXPERIMENTAL DATA

TABLE VII
MOLE PERCENT OF PRODUCTS IN LIQUID SAMPLE, RUN PDA

Time(h)	Benzene	Cyclohexane	Ethyl- Cyclohexane	Propyl- Cyclohexane	Propyl- Benzene	Propyl- Aniline	Deca- Hydroquinoline	5,6,7,8-Tetra Hydroquinoline	quinoline	1,2,3,4-Tetra Hydroquinoline
6	0.22	0.00	0.64	94.45	2.52	1.67	0.00	0.50	0.00	0.00
12	0.00	0.00	1.73	91.24	1.44	0.58	4.84	0.17	0.00	0.00
18	0.00	0.67	0.00	92.82	5.61	0.89	0.00	0.00	0.00	0.00
24	0.00	0.80	1.44	91.05	4.11	0.85	1.63	0.12	0.00	0.00
30	0.00	1.27	1.67	85.88	5.60	1.02	2.09	0.15	2.32	0.00
36	0.35	1.20	0.71	76.68	9.89	0.71	4.02	0.00	2.65	3.79
42	0.00	0.00	0.00	74.91	12.15	2.50	3.91	0.00	1.36	5.17
48	0.20	0.67	0.77	74.11	13.77	0.16	3.94	0.00	1.29	5.09
60	0.00	0.51	0.00	84.22	10.19	0.37	3.40	0.00	0.99	0.32
72	1.30	0.59	0.98	83.24	12.19	1.04	0.00	0.00	0.13	0.52
84	1.93	0.66	0.14	65.90	10.99	0.76	3.07	2.78	0.04	13.73
96	0.49	0.18	0.09	35.55	8.03	16.63	1.87	7.38	0.06	29.73
108	1.77	0.48	0.20	36.93	7.19	22.11	0.00	5.92	0.11	25.27
120	0.62	1.47	0.60	14.29	3.34	48.44	2.10	4.77	0.15	24.22

TABLE VIII

MOLE PERCENT OF PRODUCTS IN LIQUID SAMPLE, RUN PDB

Time(h)	Benzene	Cyclohexane	Ethyl- Cyclohexane	Propyl- Cyclohexane	Propyl- Benzene	Propyl- Aniline	Deca- Hydroquinoline	5,6,7,8-Tetra Hydroquinoline	quinoline	1,2,3,4-Tetra Hydroquinoline
6	0.00	0.33	2.49	92.03	0.42	0.00	1.09	2.78	0.80	0.05
12	0.00	0.41	2.20	96.32	0.59	0.00	0.45	0.00	0.03	0.00
18	0.00	0.50	1.79	94.61	0.97	0.15	0.65	0.00	0.02	1.32
24	0.00	0.43	1.57	93.39	1.27	0.23	2.53	0.00	0.00	0.59
30	0.00	0.53	1.44	93.04	1.90	0.14	2.19	0.00	0.00	0.76
36	0.00	0.60	1.34	93.95	2.57	0.07	1.14	0.00	0.00	0.34
42	0.00	0.60	1.13	91.62	2.82	0.25	3.22	0.01	0.04	0.31
48	0.07	1.24	1.31	89.08	4.95	0.25	2.73	0.19	0.00	0.19
60	0.04	0.92	1.15	88.47	4.08	0.28	4.16	0.37	0.11	0.41
72	0.23	1.20	1.00	69.22	3.41	0.98	3.48	1.96	16.77	1.75
84	0.24	1.03	1.15	31.09	3.36	1.31	3.73	5.52	40.84	11.73
96	0.06	0.83	1.07	87.13	4.84	0.31	2.47	0.05	0.56	2.68
108	0.28	1.86	1.22	75.90	5.70	1.54	0.76	3.07	8.56	1.11
120	0.16	1.58	1.30	72.28	5.44	0.94	1.48	2.48	10.46	3.87

TABLE IX

MOLE PERCENT OF PRODUCTS IN LIQUID SAMPLE, RUN PDC

Time(h)	Benzene	Cyclohexane	Ethyl- Cyclohexane	Propyl- Cyclohexane	Propyl- Benzene	Propyl- Aniline	Deca- Hydroquinoline	5,6,7,8-Tetra Hydroquinoline	quinoline	1,2,3,4-Tetra Hydroquinoline
6	13.12	0.00	0.42	52.59	3.02	2.20	1.30	12.42	7.33	5.77
12	1.45	0.64	0.58	83.19	4.81	0.45	4.80	0.54	0.28	3.20
18	1.04	0.26	0.53	56.25	4.20	2.05	6.44	11.81	8.26	7.05
24	0.84	0.71	0.37	22.94	2.32	1.48	4.28	14.48	40.63	9.61
30	0.59	0.56	0.54	68.63	4.90	1.15	11.26	0.91	6.41	4.98
36	1.62	0.79	0.36	43.06	3.43	2.44	7.39	13.28	14.08	11.36
42	0.44	0.69	0.55	42.22	3.66	2.07	8.42	13.49	13.01	13.37
48	0.73	0.60	0.30	16.69	1.85	0.00	3.49	17.34	41.81	14.66
60	0.47	0.35	0.25	18.99	1.95	0.00	4.70	9.57	51.59	10.83
72	0.57	0.16	0.15	8.36	1.03	0.00	2.25	9.29	69.83	6.98
84	2.77	0.40	0.22	9.56	1.61	0.00	2.46	1.86	67.02	13.15
96	6.02	0.08	0.25	13.22	1.41	0.00	1.48	4.44	58.29	13.45
108	2.18	0.29	0.19	12.84	0.58	0.00	5.30	4.98	62.31	10.17
120	0.87	0.31	0.22	12.67	0.66	0.00	3.64	9.96	59.03	11.45

TABLE X

MOLE PERCENT OF PRODUCTS IN LIQUID SAMPLE, RUN PDD

Time(h)	Benzene	Cyclohexane	Ethyl- Cyclohexane	Propyl- Cyclohexane	Propyl- Benzene	Propyl- Aniline	Deca- Hydroquinoline	5,6,7,8-Tetra Hydroquinoline	quinoline	1,2,3,4-Tetra Hydroquinoline
6	0.26	0.91	1.14	85.45	3.80	1.34	5.08	0.18	0.11	1.73
12	0.10	1.25	1.12	67.08	5.47	2.15	14.01	0.62	0.00	8.19
18	0.85	1.27	0.83	56.23	4.95	3.73	15.04	2.60	3.92	10.57
24	0.86	1.22	0.74	51.99	3.72	3.05	18.22	2.58	3.82	13.81
30	0.49	1.18	0.75	53.17	5.14	2.96	18.66	1.26	5.05	11.35
36	0.12	0.89	0.58	56.78	5.53	3.41	19.64	0.81	0.33	11.93
42	0.20	1.03	0.55	54.26	3.36	4.26	21.43	0.99	0.16	13.76
48	0.10	1.23	0.63	51.74	4.48	4.53	22.24	1.11	0.13	13.82
54	0.49	0.59	0.46	50.93	4.28	3.86	22.14	0.84	0.16	16.24
60	0.15	1.09	0.53	50.51	4.73	4.19	23.58	0.92	0.14	14.16
66	0.06	0.88	0.44	46.61	3.81	4.62	24.79	0.91	0.15	17.74
72	0.08	0.85	0.41	46.21	3.89	4.61	24.48	0.89	0.15	18.42

TABLE XI

MOLE PERCENT OF PRODUCTS IN LIQUID SAMPLE, RUN PDE

Time(h)	Benzene	Cyclohexane	Ethyl- Cyclohexane	Propyl- Cyclohexane	Propyl- Benzene	Propyl- Aniline	Deca- Hydroquinoline	5,6,7,8-Tetra Hydroquinoline	quinoline	1,2,3,4-Tetra Hydroquinoline
6	0.05	0.65	0.78	88.10	4.97	0.04	4.60	0.18	0.00	0.62
12	0.08	0.88	0.63	73.32	5.17	2.00	12.88	0.60	0.07	4.38
18	0.07	0.82	0.56	69.40	5.07	2.59	14.95	0.66	0.00	5.88
24	0.06	0.85	0.50	67.22	4.95	2.87	15.73	0.67	0.00	7.14
30	0.04	0.77	0.45	64.28	4.83	3.27	16.14	0.78	0.11	9.33
36	0.06	0.82	0.43	62.20	4.67	3.49	16.81	0.81	0.11	10.60
42	0.07	0.84	0.42	61.76	4.74	3.58	16.75	0.79	0.12	10.93
48	0.08	0.90	0.40	61.14	4.51	3.72	17.01	0.83	0.13	11.27
54	0.03	0.84	0.38	60.33	4.46	3.88	17.42	0.82	0.13	11.70
60	0.06	0.84	0.41	61.41	4.79	3.71	17.01	0.76	0.12	10.90
66	0.03	0.71	0.35	59.35	4.75	3.85	18.70	0.79	0.12	11.34
72	0.06	0.79	0.38	57.24	4.43	4.17	18.77	0.88	0.13	13.13

TABLE XII

MOLE PERCENT OF PRODUCTS IN LIQUID SAMPLE, RUN PDF

Time(h)	Benzene	Cyclohexane	Ethyl- Cyclohexane	Propyl- Cyclohexane	Propyl- Benzene	Propyl- Aniline	Deca- Hydroquinoline	5,6,7,8-Tetra Hydroquinoline	quinoline	1,2,3,4-Tetra Hydroquinoline
6	0.54	0.25	0.46	90.70	3.18	1.70	2.64	0.12	0.10	1.70
12	0.00	0.45	0.64	90.23	4.23	0.79	3.27	0.10	0.00	0.79
18	0.08	0.39	0.51	87.57	4.45	1.30	5.04	0.15	0.00	1.30
24	0.00	0.40	0.51	89.02	4.56	0.94	4.01	0.11	0.00	0.94
30	0.20	0.48	0.47	86.76	4.45	1.59	5.23	0.14	0.00	1.59
36	0.00	0.49	0.46	85.65	4.61	1.83	5.89	0.17	0.00	1.83
42	0.00	0.48	0.43	82.88	4.52	3.09	7.16	0.24	0.03	3.09
48	0.07	0.53	0.44	83.42	4.55	2.95	6.72	0.21	0.04	2.95
54	0.04	0.48	0.37	79.41	4.94	3.96	8.31	0.99	0.04	3.96
60	0.00	0.54	0.43	77.18	4.44	5.51	9.67	0.38	0.06	5.51
66	0.05	0.52	0.38	74.70	4.41	7.04	10.54	0.44	0.08	7.04
72	0.00	0.37	0.36	81.43	4.86	4.80	6.69	0.31	0.13	4.80

TABLE XIII

MOLE PERCENT OF PRODUCTS IN LIQUID SAMPLE, RUN PDG

Time(h)	Benzene	Cyclohexane	Ethyl- Cyclohexane	Propyl- Cyclohexane	Propyl- Benzene	Propyl- Aniline	Deca- Hydroquinoline	5,6,7,8-Tetra Hydroquinoline	quinoline	1,2,3,4-Tetra Hydroquinoline
6	0.13	0.10	0.36	90.74	3.65	0.35	3.59	0.07	0.00	1.02
12	0.19	0.31	0.50	88.45	4.23	0.50	3.85	0.15	0.00	1.82
18	0.03	0.24	0.52	87.62	4.94	0.54	4.91	0.11	0.00	1.09
24	0.00	0.37	0.68	86.50	4.54	0.48	5.42	0.15	0.00	1.87
30	0.00	0.48	0.63	82.93	4.82	0.83	7.23	0.26	0.00	2.83
36	0.00	0.48	0.42	84.70	4.83	1.15	5.82	0.19	0.00	2.40
42	0.04	0.71	0.78	78.47	4.60	0.91	8.65	0.49	0.00	5.37
48	0.01	0.35	0.50	83.24	4.91	1.30	5.78	0.18	0.18	3.54
54	0.00	0.37	0.38	81.70	4.83	1.36	6.83	0.13	0.05	4.34
60	0.00	0.58	0.38	77.35	4.68	1.91	8.37	0.48	0.08	6.16
66	0.00	0.39	0.51	77.72	4.66	1.72	8.66	0.18	0.06	6.10
72	0.00	0.37	0.51	74.62	4.51	1.85	9.57	0.17	0.05	8.37

APPENDIX C
PUMP CALIBRATION

Pump Calibration

The pump was calibrated at the operating pressure (12.4MPa) before experimental runs. The fluid used for calibration was n-hexadecane. The average of three values was used to determine the volume flow rate at each gear setting. The calibration curve is given in Figure 25.

$1 \times 10^{-3} / h$

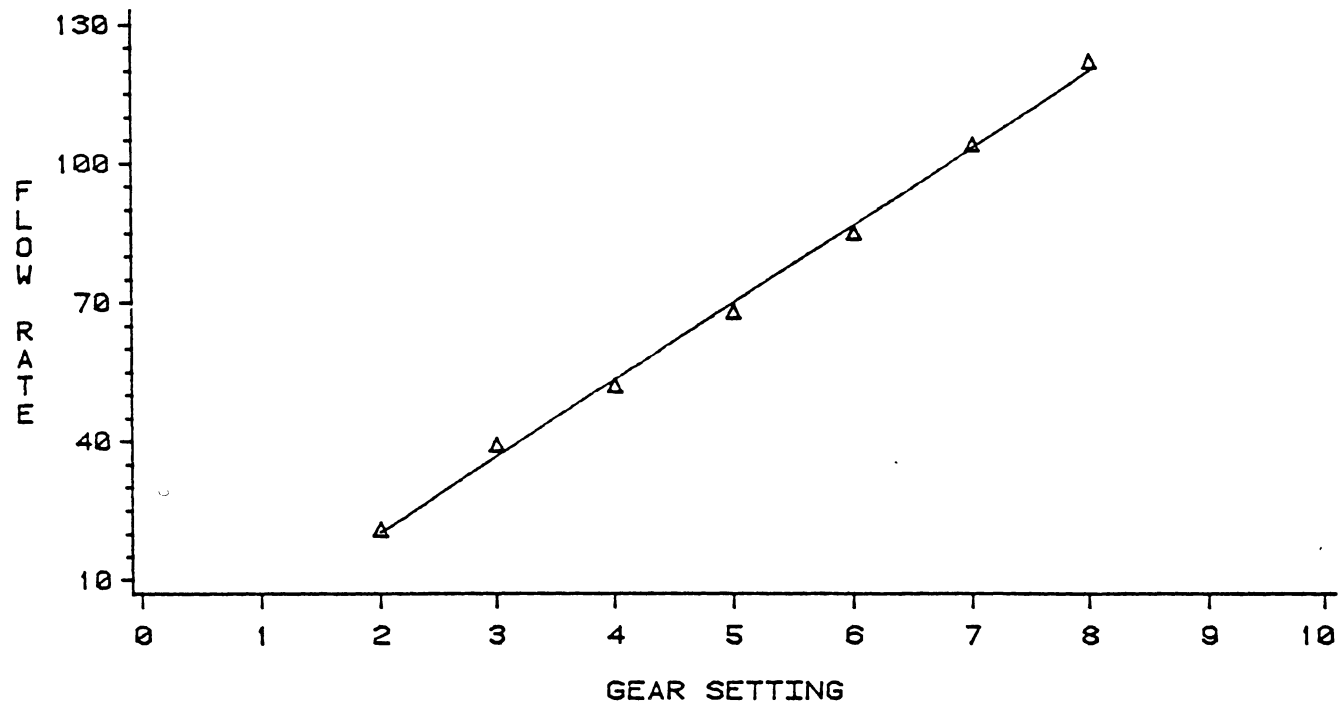


Figure 25. Calibration Curve of Lewa FL-3 Pump

APPENDIX D

GAS CHROMATOGRAPH CALIBRATION

Gas Chromatograph Calibration

Analysis of liquid samples were performed in a Hewlett Packard 5890 gas chromatograph equipped with a thermal conductivity detector and a 60m capillary column Model DB-1, supplied by J and W Inc. For the thermal conductivity detector, the carrier gas (He) flow rate was $0.0018 \text{ m}^3/\text{h}$. The temperature program employed for the column was: initial temperature 60°C , initial time 2 min, program rate $8^\circ\text{C}/\text{min}$, final temperature 200°C , and final time 30 min. A standard solution was used to determine the retention time of liquid products. Table XIV presents these data.

TABLE XIV
RETENTION TIME OF PRODUCTS

Compounds*	Retention time(min)
Benzene	4.90
Cyclohexane	5.10
Ethylcyclohexane	8.80
Propylcyclohexane	11.21
Propylbenzene	11.46
O-propylaniline	17.68
Decahydroquinoline	16.06
1,2,3,4-Tetrahydroquinoline	19.52
5,6,7,8-Tetrahydroquinoline	17.58
Quinoline	17.70

* Note that aniline, toludine, and ethylaniline are not listed.

APPENDIX E

CATALYST ANALYSIS

Catalyst Analysis

In this study, spent catalysts were separated into four reactor sections, 6.13cm (2.5in) each, except those of runs PDA and PDB which were separated into eight sections. From each section randomly selected were six catalyst pellets to analyze for coke content. Table XV presents these data. Section number increases with catalyst bed length. Figure 26 shows the coke content profile along the catalyst bed for run PDA. Results reveal that the coke content in the catalyst bed decrease somewhat with increasing bed length. Properties of spent and regenerated catalysts of each section from run PAD are presented in Table XVI. Results show that these properties have no significant change among sections. Presumably, similar results could be found in runs PDB to PDG; therefore, only top sections of these runs were analyzed. Data were presented in Table IV.

TABLE XV
PERCENT OF COKE CONTENT

	1	2	3	4	5	6	Avg.	Std.
Run PDA								
1	8.22	7.23	7.64	8.36	8.59	8.75	8.13	0.58
2	8.55	8.69	9.29	8.82	9.13	8.98	8.91	0.28
3	7.50	6.94	7.08	7.10	7.15	7.39	7.19	0.21
4	7.64	7.12	7.27	6.92	7.49	7.23	7.28	0.26
5	6.71	7.03	7.07	7.27	6.83	7.01	6.99	0.20
6	6.51	6.85	6.26	6.19	6.42	7.08	6.55	0.35
7	6.11	6.33	6.65	6.59	6.50	6.41	6.43	0.20
8	6.23	6.91	6.37	6.70	7.04	6.56	6.64	0.31
							<u>7.27</u>	<u>0.85</u>
Run PDB								
1	11.39	9.95	9.97	10.15	10.73	9.92	10.26	0.70
2	11.58	10.94	11.81	11.13	11.91	11.27	11.44	0.39
3	10.66	10.15	10.18	10.22	10.25	10.54	10.33	0.21
4	10.18	10.41	9.82	10.50	9.93	9.43	10.05	0.40
5	9.52	10.23	9.26	9.63	9.30	10.53	9.74	0.52
6	9.94	10.29	10.86	9.20	10.09	9.88	9.87	0.89
7	8.83	8.35	8.27	8.76	8.78	8.90	8.65	0.27
8	6.40	5.41	6.15	7.54	6.38	6.38	6.38	0.68
							<u>9.60</u>	<u>1.52</u>
Run PDC								
1	9.83	9.28	9.56	8.99	8.99	8.98	9.27	0.36
2	8.40	8.12	7.92	7.91	7.91	9.26	8.40	0.53
3	8.28	7.89	8.38	7.43	7.43	7.82	8.03	0.38
4	7.05	8.91	8.50	8.03	8.03	8.65	8.14	0.70
							<u>8.457</u>	<u>0.69</u>

TABLE XV (Continue)

	1	2	3	4	5	6	Avg.	Std.
Run PDD								
1	11.78	10.98	11.84	11.42	11.12	11.29	11.41	0.35
2	10.47	10.77	11.30	11.18	12.25	11.20	11.20	0.61
3	10.26	8.94	9.61	11.01	9.04	9.06	9.65	0.83
4	9.68	11.11	9.55	9.47	9.84	10.67	10.05	0.67
							<u>10.59</u>	<u>0.96</u>
Run PDE								
1	10.58	9.97	9.62	9.65	9.46	9.82	9.85	0.40
2	10.60	10.64	10.32	10.44	10.61	10.19	10.40	0.20
3	10.56	9.52	10.13	9.44	9.47	8.54	9.61	0.69
4	9.97	8.93	9.73	9.47	8.67	10.34	9.52	0.63
							<u>9.84</u>	<u>0.59</u>
Run PDF								
1	9.13	8.95	9.44	9.87	9.77	8.53	9.28	0.51
2	9.60	8.73	10.13	9.10	9.23	9.62	9.40	0.48
3	9.48	9.08	9.06	9.67	8.48	8.75	9.08	0.44
4	7.27	7.28	6.75	8.69	8.87	7.21	8.67	0.88
							<u>8.86</u>	<u>0.90</u>
Run PDG								
1	8.65	10.22	10.22	9.76	9.70	9.31	9.64	0.60
2	8.92	8.54	9.16	8.77	9.25	8.02	8.77	0.45
3	8.82	9.30	8.62	8.90	8.65	8.44	8.79	0.30
4	8.69	7.38	8.70	8.15	7.47	7.94	8.05	0.59
							<u>8.82</u>	<u>0.74</u>

TABLE XVI
 PROPERTIES OF SPENT AND REGENERATED
 CATALYSTS FROM RUN PDA
 (Spent/Regenerated)

Section	SA($\times 10^3 \text{ m}^2/\text{kg}$)*	PV($\times 10^{-3} \text{ m}^3/\text{kg}$)*	MP(nm)*
1(Top)**	234/245	0.435/0.549	8.0/9.6
2	235/248	0.455/0.553	8.2/9.6
3	235/246	0.455/0.552	8.3/9.6
4	219/235	0.415/0.536	7.8/9.2
5	229/240	0.430/0.542	7.8/9.2
6	231/241	0.435/0.543	7.8/9.2
7	229/240	0.430/0.541	7.8/9.2
8(Bottom)	231/240	0.430/0.542	7.8/9.2

- * Fresh catalyst was $253 \times 10^3 \text{ m}^2/\text{kg}$,
 $0.57 \times 10^{-3} \text{ m}^3/\text{kg}$, and 9.8nm, respectively,
 ** Each section is 6.13cm (2.5in) long.

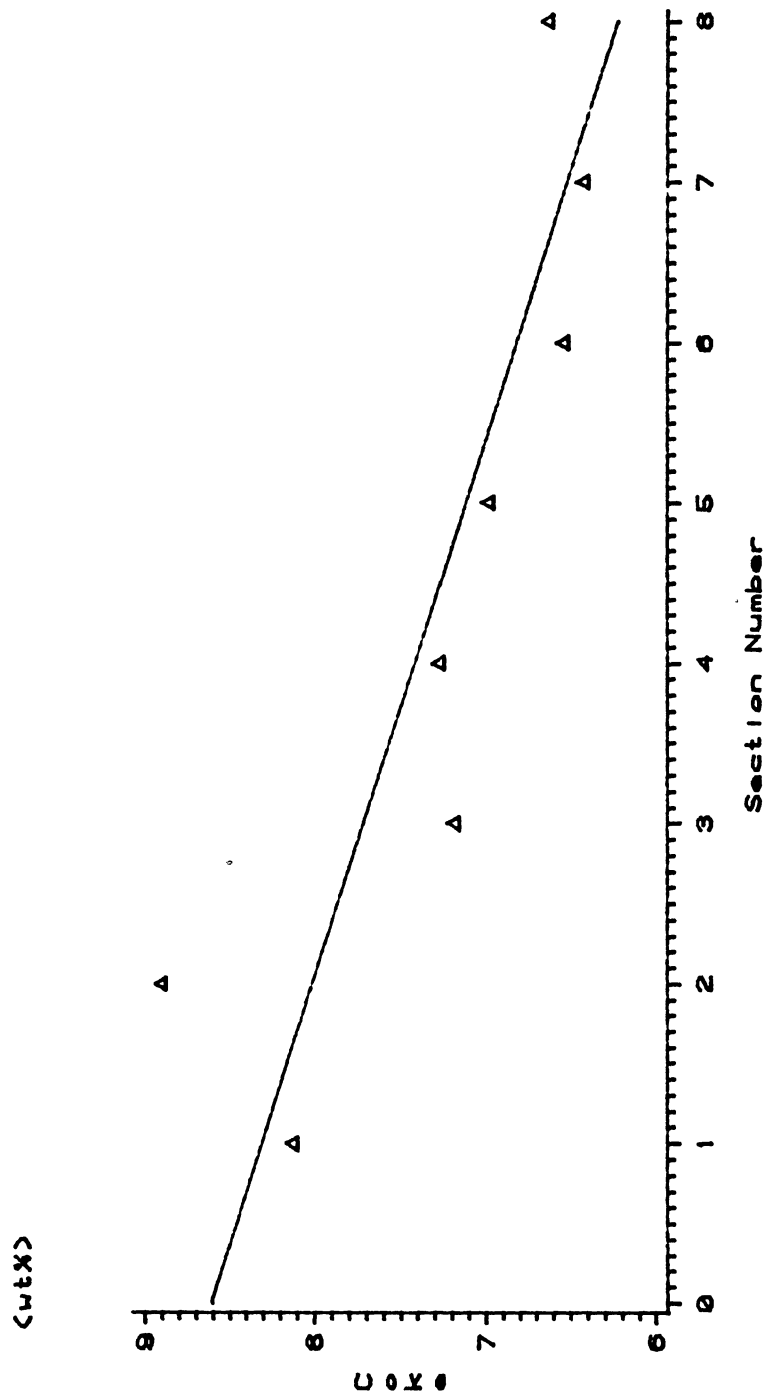


Figure 26. Coke Content Profile, Run PDA

APPENDIX F

EXAMPLE OF CALCULATIONS FOR PERCENT OF
HDN AND NITROGEN MASS BALANCES

APPENDIX F

EXAMPLE OF CALCULATIONS FOR PERCENT OF
HDN AND NITROGEN MASS BALANCES

Example of Calculations for Percent of
HDN and Nitrogen Mass Balances

In order to let readers have a better understanding of percent of HDN and nitrogen mass balance calculation, a step by step calculation is presented in this Appendix.

A feedstock contains 20wt% of quinoline and its liquid products (100g) are:

Compound	wt%
Benzene	0.005
Cyclohexane	0.050
Ethylcyclohexane	0.050
Propylcyclohexane	12.000
Propylbenzene	0.500
Propylaniline	0.500
Decahydroquinoline	2.000
1,2,3,4-tetrahydroquinoline	1.500
5,6,7,8-tetrahydroquinoline	0.005
Quinoline	0.005

Calculate mole percent of quinoline HDN product in liquid sample, percent of HDN, and nitrogen mass balance. Note that nitrogen content in effluent gases is calculated from hydrocarbons which are reconized in liquid samples, and assume that feedstock and liquid product are of the same quantity on weight basis.

Compounds	M.W. (g/mol.)	Weight(g)	Mol.	Mol. %	N in liq. (g)	N in eff. gas(g)
Benzene	78.12	0.005	6.40×10^{-5}	0.05	0.	8.96×10^{-4}
Cyclohexane	84.16	0.050	5.94×10^{-4}	0.46	0.	8.32×10^{-3}
Ethylcyclohexane	112.22	0.050	4.46×10^{-4}	0.36	0.	6.24×10^{-3}
Propylcyclohexane	126.24	12.000	0.095	73.64	0.	1.33
Propylbenzene	120.20	0.500	4.16×10^{-3}	3.22	0.	0.058
Propylaniline	135.21	0.500	3.70×10^{-3}	2.87	0.052	0.
Decahydroquinoline	139.24	2.000	0.014	10.85	0.201	0.
1,2,3,4-tetrahydroquinoline	133.20	1.500	0.011	8.53	0.158	0.
5,6,7,8-tetrahydroquinoline	133.20	0.005	3.75×10^{-5}	0.03	5.26×10^{-4}	0.
Quinoline	129.16	0.005	3.87×10^{-5}	0.03	5.42×10^{-4}	0.
Total			0.129	100.04	0.412	1.403

Nitrogen content in feed = $N_f = 2.16(\text{g})$

Nitrogen content in liquid sample = $N_l = 0.412(\text{g})$

Nitrogen content in effluent gases = $N_g = 1.403(\text{g})$

$$\begin{aligned} \% \text{ of HDN} &= \frac{N_f - N_l}{N_f} \times 100\% \\ &= \frac{2.16 - 0.412}{2.16} \times 100\% \\ &= 80.93\% \end{aligned}$$

Percent difference in nitrogen balance

$$\begin{aligned} &= \frac{N_f - (N_l + N_g)}{N_f} \times 100\% \\ &= \frac{2.16 - (0.412 + 1.403)}{2.16} \times 100\% \\ &= 15.97\% \end{aligned}$$

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