

THE DESIGN, CONSTRUCTION AND OPERATIONS OF A
GRADIENTLESS CSTR REACTOR SYSTEM USED FOR
HYDROGENATION OF TETRALIN

By

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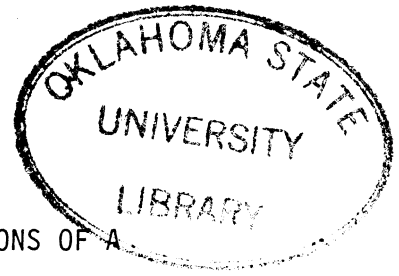
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ABSTRACT

In the hydrogenation of coal liquids or liquids derived from coal, kinetic data is needed for commercial application, however, the kinetic data is masked by heat and mass transfer effects. To obtain kinetic data free of transport effects, a gradientless reactor can be used. There are several designs of gradientless reactors available such as the Robinson-Amoco, Carberry and the Berty. The reactor used for this study was the Berty design.

This study mainly dealt with the design, construction and operation of a gradientless reactor system with the Berty design as the heart of the system. The system has proved to be sound and functional. The stirrer speed of 1500 RPM greatly reduced or eliminated the transfer effects so true kinetic data can be studied. The catalyst analysis was inconclusive. The preliminary results indicate that titanocene dichloride does increase the hydrogenation of tetralin, however, it does not increase the hydrogenation of tetralin in a tetralin/phenanthrene mixture.

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CHAPTER I

INTRODUCTION

Different reactor systems have been used to study the hydrogenation of coal liquids. The problem of most reactor systems is the heat and mass transfer effects on the reaction. To alleviate the problem of heat and mass transfer effects, a gradientless reactor system was designed and constructed using a Bertly reactor. Several gradientless reactor designs were considered including the Robinson-Amoco and the Carberry. The Bertly reactor was chosen mainly because the temperature of the catalyst bed can be directly measured.

The project has two objectives. The first is to determine the stirrer speed which will reduce or eliminate the effects of heat and mass transfer. The second objective is to run a series of experimental runs to determine the effects of titanocene dichloride addition on the hydrogenation of Tetralin and a mixture of Tetralin and phenanthrene. Also, the effect of titanocene dichloride on the catalyst will be investigated.

Chan (1) investigated the effect on the activity when adding titanocene dichloride to an SRC-II coal liquid using a trickle bed reactor. He found the activity to increase. Tscheikuna (29) found similar results using a trickle bed reactor and a feedstock of Tetralin.

In this work, the experimental runs with titanocene dichloride were compared with the experimental runs without titanocene dichloride.

The hydrocarbon samples were compared to determine any increase or decrease in the hydrogenation. The catalyst samples were compared to determine any effect on the coking of the catalyst.

CHAPTER II

LITERATURE REVIEW

The literature review will cover the following subjects:

1. Catalytic Reactors
2. Reactions of Tetralin and Phenanthrene
3. Catalyst Deactivation
4. Titanocene Dichloride

Catalytic Reactors

Most catalytic studies are conducted in flow systems that more closely resemble commercial processes such as fixed bed, fluid bed and CSTR reactors (2). Although such studies are conducted in commercially similar processes, what is needed are kinetic data free from mass and heat transfer effects. The kinetic data are essential to the development of rate equations for the design of chemical reactors not only for hydrotreating crude oil but also for coal liquids. These studies can be conducted in gradientless reactors which produce kinetic data that are greatly reduced or free from heat and mass effects.

There are currently three types of gradientless reactors: the Robinson-Amoco, Carberry and Berty. These reactors are designed to operate as a gradientless reactor except each reactor has its own characteristics.

The Robinson-Amoco is a spinning basket gradientless reactor. The

catalyst is held in place by wire mesh in an annular space inside the basket with internal baffles between the catalyst space and the center support shaft. The basket is also surrounded by a baffle system which directs the fluid flow and prevents liquid vortexing.

The reactor operates with the spinning catalyst basket submerged in the highly turbulent gas-liquid mass which ensures good mixing or in the gradientless regime. Mahoney et. al. (3) operated their Robinson-Amoco reactor in the gradientless regime by using a magne drive speed of 750 rpm.

The Carberry reactor has the same design as the Robinson-Amoco reactor in that the catalyst basket is a spinning basket, however; instead of being an annular spinning basket, the catalyst basket consists of four paddles which holds the catalyst (4). The paddles can be of cylindrical or rectangle design with preference on the latter.

There are some disadvantages inherent in both the Robinson-Amoco and the Carberry type of gradientless reactors. One of the greatest disadvantages is the temperature of the surface of the catalyst can not be measured, which is important in kinetic studies. Doraiswamy and Tabjl (5) discussed the disadvantage of the spinning basket reactor which is the actual temperature at the surface of the catalyst, or even in the field immediately external to the catalyst can not be directly measured since the basket with its catalyst-fluid system constitutes the moving part. Therefore, the temperature measured is that of the fluid in the pot and hence one is forced to accept predict catalyst temperatures. Some of the other disadvantages are the recycle ratio can not be calculated due to the previous disadvantage and there is some question whether all the catalyst "sees" the fluid uniformly.

The Berty reactor is a stationary catalyst basket gradientless reactor. The catalyst is held by wire mesh in the basket, which is

suspended centrally in the autoclave. The stirrer which consists of the magne-drive and the impeller is mounted through the bottom of the autoclave. Baffles or vains are mounted on the outside of the catalyst basket and force the fluid to rise from the bottom of the autoclave reactor to the top where the cap or top of the autoclave is concave downwards and forces the fluid through the catalyst basket. Temperature measurements can be made of the catalyst surface and of the recycling fluid by two thermocouples. The reactants are fed from the bottom of the reactor and the products are taken from the recycling fluid or top of the reactor.

Advantages of all three of the reactors are that different designs of the basket configuration can be implored (5) and that one can eliminate temperature and mass transfer gradients (3). The Berty reactor has advantages beyond these mentioned. Probably the most important is the temperature at the surface of the catalyst can be measured directly. By measuring the temperature of the catalyst surface and the recycling fluid, the recycle ratio can be calculated. Berty (6) reported recycle ratios over 20 will approximate the performance of a continuous stirred tank reactor. Also in the Berty reactor any form, size or even a single catalyst pellet can be tested.

Reactions of Tetralin and Phenanthrene

Tetralin

Tetralin is considered to be a hydrogen donor solvent and is widely used in the hydrogenation of coal.

Hooper et. al. (7) reported the thermal dissociation of tetralin between 300°C (572°F) and 450°C (842°F). They showed that at a

temperature of 350°C (662°F) the formation of naphthalene is accomplished from an initial concentration of 2 g/kg of Tetralin to 4 g/kg. However, between 350°C (662°F) and 450°C (842°F), the formation of 1-methyl indan increased and at 420°C (788°F) it becomes the predominant reaction product. Some of the other products were ethyl benzene, propyl benzene, indan, butyl benzene, trans-decalin, cis-decalin and naphthalene.

Potgieter and Liebenberg (8) studied the uncatalyzed hydrogenation of coal in Tetralin at 160 - 180 bars (2320 psia - 2610 psia) and 380 - 440°C (716 - 824°F) and split the sample into three portions: an insoluble portion in benzene, a soluble portion in benzene but not soluble in hexane and a soluble portion in both benzene and hexane. The third portion contained the unreacted Tetralin and products formed from Tetralin, mainly naphthalene.

Dziewiecki et. al. (9) investigated Ni-Mo catalysts that exhibited a higher activity in dehydrogenation of Tetralin or decalin, they were also found to be more active in the hydrogenation of coal extract solution.

Neavel (10) studied the liquefaction of coal in hydrogen-donor and non-donor vehicles. He found when Tetralin was heated to 400°C (752°F) for 30 minutes with charcoal the centrifuge clarified liquid contained naphthalene, dihydronaphthalene, tetralin and decahydronaphthalene. He also detected small amounts of alkyl benzene, indane or indenenes.

Phenanthrene

Wiser (11) suggests that phenanthrene, a three membered condensed aromatic ring molecule, may serve as an excellent model as one of the principle structures found in coal. Shabtai et. al. (12) hydrogenated phenanthrene using a Ni-Mo/Al₂O₃ catalyst at 10.4 MPa (1500 psig) and

341°C (646°F). They found the products to be perhydrophenanthrene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene, 1,2,3,4,9,10,11,12-octahydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene and isomeric mixtures of decahydrophenanthrene and dodecahydrophenanthrene.

Friedman (13) investigated the hydrogenation of phenanthrene using alkali metals, alkali metal alloys and alkali metal-alkali metal salts combinations as catalyst at a hydrogen pressure of 9.7 MPa (1400 psig) and at temperatures in the range of 180 - 250°C (324 - 482°F). The principle products were 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene and octahydrophenanthrene. Skowronski and Recht (14) hydrogenated phenanthrene at a hydrogen pressure of 20.7 MPa (3000 psia) and at a temperature of 480°C (896°F) using a molten hydroxide-carbonate catalyst. They found the products to be 6-butyl-1,2,3,4-tetrahydronaphthalene, 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene.

Penninger and Slotboom (15) investigated the uncatalyzed thermal high-pressure hydrogenolysis of phenanthrene at a hydrogen pressure of 8.3 MPa (1200 psia) and at temperatures of 475°C (887°F) and 495°C (923°F). They found the products to be 1,2,3,4-tetrahydrophenanthrene and 9,10-Dihydrophenanthrene.

Huang et. al. (16) using a Co-Mo/Al₂O₃ catalyst found the main products of the hydrocracking to be perhydrophenanthrene isomers. Sullivan et. al. (17) hydrocracked phenanthrene using NiS/Al₂O₃ catalyst at 293°C (559°F) with the major products being Tetralin and methylcyclohexane.

Catalyst Deactivation

The purpose of catalyst is to promote a chemical reaction and ideally

not to deactivate from different mechanisms. The cause of deactivation is poisoning or metal deposition, coking (18). The latter cause is generally not a factor in catalytic processes and will not be discussed.

Poisoning a catalyst is the strong chemisorption of reactants, products or impurities on the catalyst active sites (19). However, what may be a poison for one catalyst may not be a poison for another. Poisons for hydrogenation catalyst are metals such as Mercury, Vanadium and Arsenic (18). Wei (20) stated that the metals vanadium and nickel which are removed from the oil by hydrodemetallation reactions deposit on the catalyst and eventually deactivate it by blocking the active sites and plugging the catalyst pores. The metals in the oil can be organometallic or inorganic compounds. Chiou and Olson (21) found that most metals deposit on the surface where organometallics can penetrate into the catalyst. Wei and Wei (20) also found that in hydrometallation an intermediate is formed which can penetrate into the catalyst.

Another cause of deactivation is fouling or coking. Coke is considered to be a carbonaceous material that deposits on the surface of the catalyst and causes deactivation by decreasing the surface area (22).

The formation of coke is complex and the structure can range from high molecular weight hydrocarbons to carbon such as graphite (18). Gates et. al. (23) suggested that coke is the result of cracked coke precursors that have been catalyzed by the acid sites. Benzenes that react with Bronsted acids form carbonium ions, then condense with other benzenes into multi-ring compounds such as anthracenes. Since the aromatic carbonium ions are so stable, this process can continue until very large compounds are built up. Beuther et. al. (24) found that aromatics concentrate and condense into clusters and then into crystals. This crystalline

"mesophase" formed after a long time at high temperatures is hardened coke that results in severe deactivation of the catalyst.

Appelby et. al. (25) found a similar coking process. They concluded that aromatics adsorbed on the catalyst and reacted to form ions by condensation and hydrogen elimination.

Ramser and Hill (26) noted that coke deposition caused a decrease in catalyst activity due to a decrease in the active surface area. However, the catalyst can be regenerated by burning the coke.

Titanocene Dichloride

In the hydrogenation of coal liquids, trace metals, especially titanium compounds, effect the catalyst, by metal deposition which cause catalyst deactivation. However, even under severe conditions of liquefaction, these metal complexes survive. McGinnis (27) found in coal liquids that titanium complexes exist in the form of organic complexes.

Chan (1) hydrotreated a SRC oil doctored with titanocene dichloride, Bis(cyclopentadienyl) titanium dichloride, and found a decrease in the coke content. The catalyst activity improvement was also found to be dependent upon the titanium concentration.

Titanocene dichloride hydrolyzes in water to form $(C_5H_5)_2Ti(OH)Cl$. It is soluble in dilute acids, moderately soluble in toluene, chloroform, alcohol and other hydroxide solvents and sparingly soluble in benzene, carbon tetrachloride and water (28).

CHAPTER III

EXPERIMENTAL APPARATUS AND ANALYSIS TECHNIQUE

Experimental Apparatus

A process flow diagram of the CSTR hydrogenation unit is shown in Figure 1 and the Berty Reactor internals is shown in Figure 2. The system was designed, built and operated at Oklahoma State University by this investigator.

Liquid hydrocarbons are continuously pumped from the feed tank to the reactor by a Milton Roy positive displacement pump. The pump pressure is monitored by pressure gauge P4. Back flow from the reactor is prevented by a check valve. The hydrogen pressure is monitored by P1 and is regulated by two pressure regulators. The first is a Victor 2-stage regulator and the second is a Mighty-Mite regulator to regulate the pressure more accurately. A cold trap is in the line to prevent any hydrocarbons from diffusing back into the hydrogen line. Both the liquid and gas feeds are fed into the bottom of the reactor. The product fluids are taken off from the top of the reactor and flow into the first separation cylinder where the liquid and gas separates. Any entrained liquid in the gas stream is separated in the second separation cylinder. The gases from the second separation cylinder are throttled to approximately 20 psig and any liquid is condensed and collected in the third separation cylinder. The exit gas flow rate is measured by a rotameter and then scrubbed with a

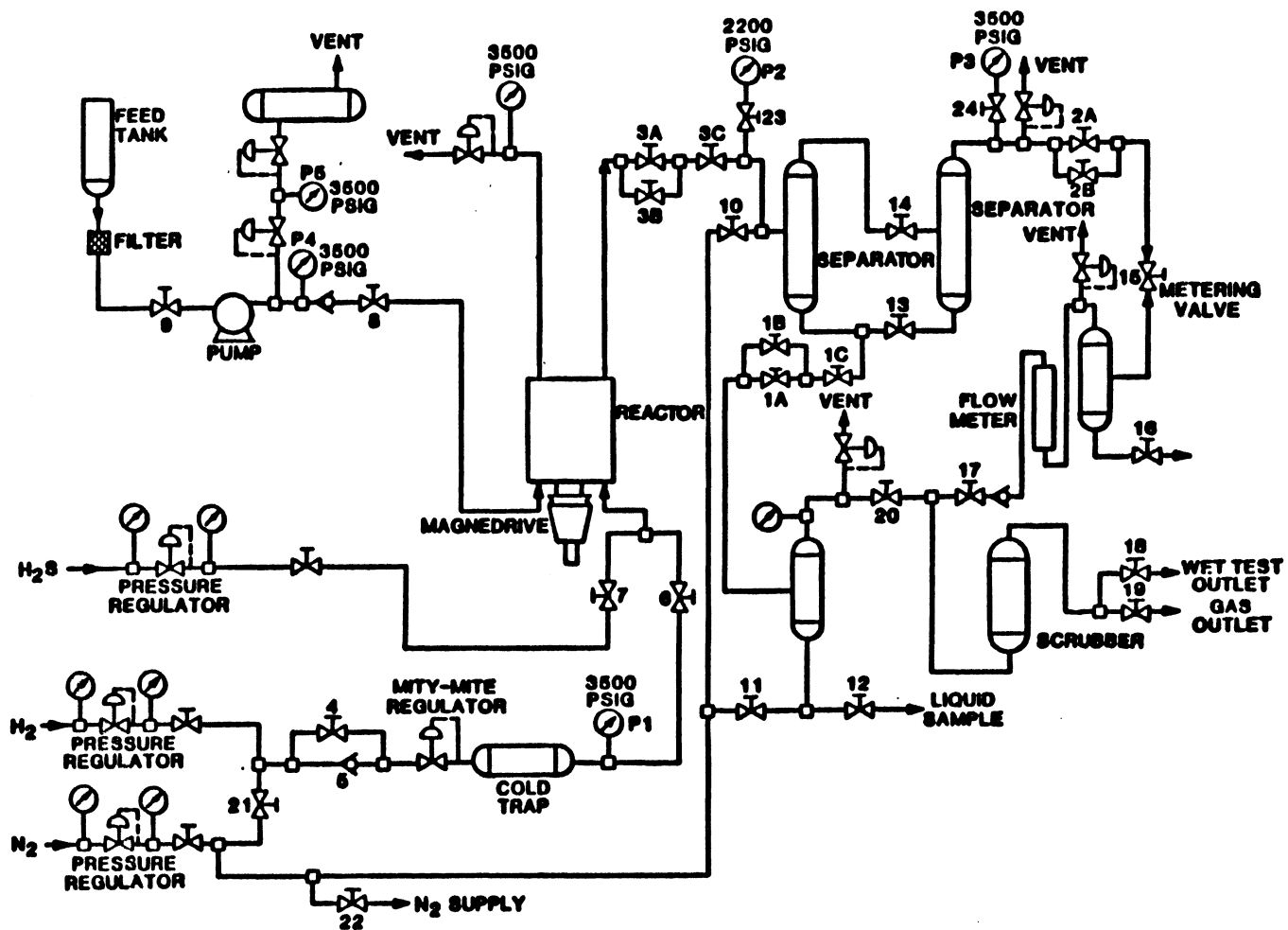


Figure 1. Process Flow Diagram of Reactor System

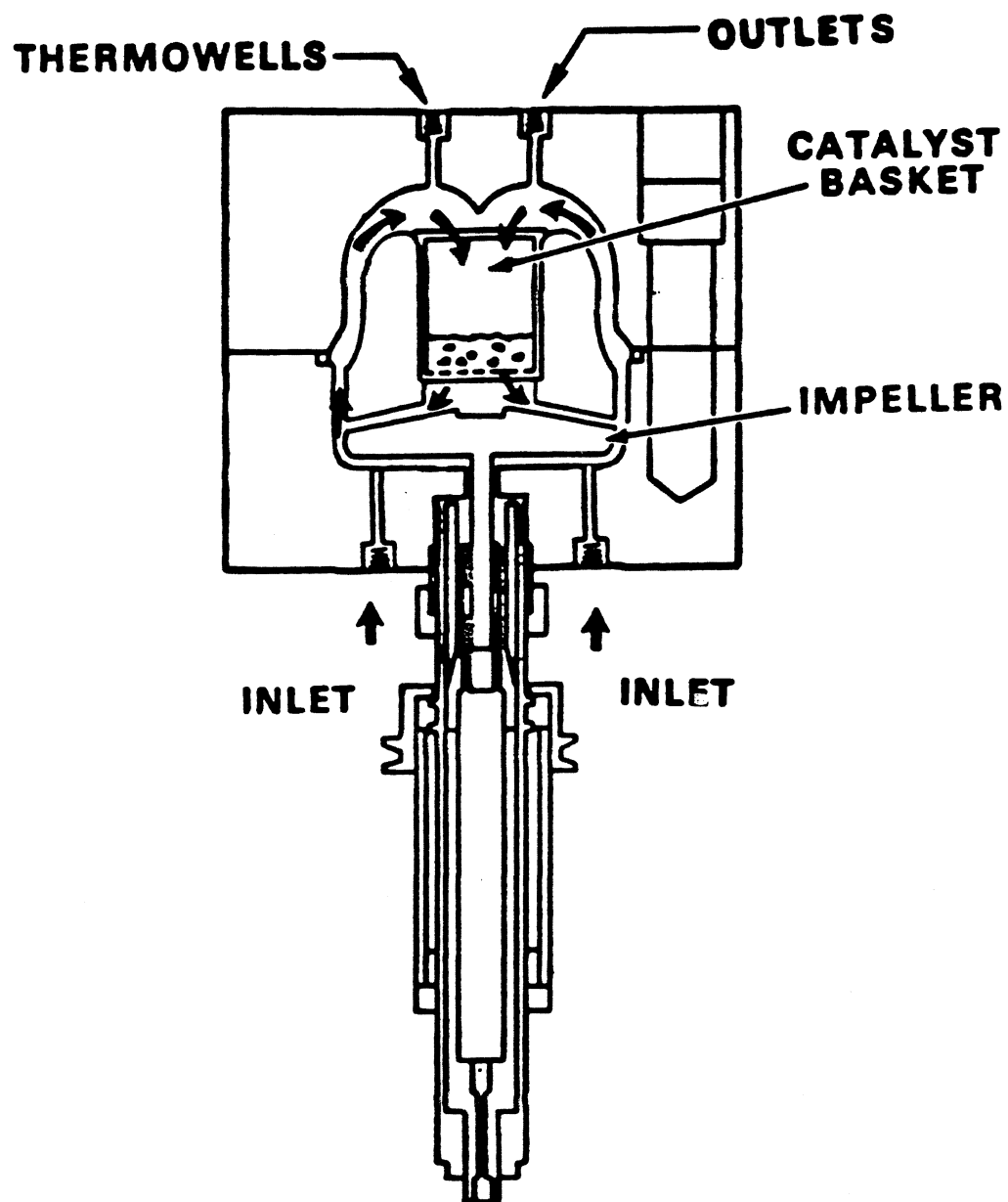


Figure 2. Bertly Reactor Internals and flow of Homogenous Mixture

sodium hydroxide solution. The gas is either vented to the atmosphere or the flow rate is measured by a wet test meter.

The liquids from the first and second separation cylinders are transferred to another cylinder when a sample is desired. The sampling can be accomplished remotely by using three solenoid valves. If desired, the sample can be scrubbed to remove any dissolved gases when sulfur and nitrogen containing compounds are present in the feed.

The temperature is controlled by an Autoclave Engineers temperature controller. The stirrer speed is controlled by an Autoclave Engineers speed controller. A more detailed description of the reactor system is given in Appendix A and the experimental procedures are described in Appendix B.

Analyses

Liquid product samples were taken every two hours with an experimental run duration of twelve hours. The liquid samples were analyzed for hydrogen and carbon content by two different methods and the conversion of 1,2,3,4 tetrahydronaphthalene and phenanthrene was measured. After each experimental run, the catalyst was removed, extracted with tetrahydrofuran and labeled. The catalyst samples were analyzed for coke content, titanium content and its distribution. The pore volume, surface area and most frequent pore diameter before and after regeneration were also measured.

Liquid Product Analyses

Gas Chromatographic Analysis

A Varian Model 3740 Gas Chromatograph equipped with an Analabs

25 meter capillary column Model GB-5 was used to analyze the liquid product for 1,2,3,4 tetrahydronaphthalene, phenanthrene and their hydrogenated products. Sample Chromatograms are shown in Appendix D. A 1 microliter sample is injected into the gas chromatograph where the sample is vaporized at 225°C (437°F) with nitrogen which is used as the carrier gas. The mixture is split and only a fraction of the sample is separated by the column. At the end of the column, the separated sample is mixed again with nitrogen as a make up gas. The stream is then burned by a hydrogen flame and ions and free electrons enter a cylindrical collector in which an electrical potential is imposed. As the ions and free electrons pass through the collector, a current flows which is measured and recorded by a Hewlett-Packard Integrator Model 3390A.

The liquid samples were also analyzed using a Perkin Elmer Elemental Analyzer Model 240B to determine the hydrogen to carbon atomic ratio. The analyzer consists of two furnaces and the detector. In the first, the combustion furnace, the sample is burned at 950°C in pure oxygen with a silver tungstate and magnesium oxide catalyst. The combustion gases are carried through the furnace by pure helium. Any halogens or sulfur oxides are removed by silver vanadate, silver oxide and silver tungstate. Any nitrogen oxides are reduced to nitrogen by the reduction tube. The remaining gases, nitrogen, water vapor, carbon dioxide and helium are transferred to a mixing volume until equilibrium is achieved then they flow through a series of traps and the detector. The thermal conductivity of the gaseous mixture is measured and the water vapor is removed by magnesium perchlorate. The thermal conductivity is measured again and the difference constitutes the hydrogen content. The carbon dioxide is removed by

colorcarb and the difference from the thermal conductivity before and after removal of the carbon dioxide gives the carbon content. The thermal conductivity of the remaining gases is measured and compared with that of the pure helium stream which gives the nitrogen content.

Catalyst Analysis

The catalyst from each run is extracted in a Soxhlet with tetrahydrofuran for 60 hours. The samples were then air dried for 48 hours.

Surface Area, Pore Volume and Most Frequent Pore Diameter

The surface area, pore volume and most frequent pore diameter are measured on each catalyst sample both before and after regeneration. Regeneration is conducted the same way as the coke measurements. Each catalyst sample is ran three times and the average is used. The equipment used to analyze the catalyst is an Autoscan 60 Porosimeter and a Series 200 Omnigraph X-Y recorder.

The Autoscan 60 Porosimeter consists of an Autoscan Porosimeter Micro-Computer Data Acquisition and Reduction system and the filling apparatus. The system consists of signal conditioning and buffering on input and output, two 13 bit analog to digital converter for data acquisition. A complete Z80 micro-computer with control program in ROM and RAM for data storage, and two 12 bit digital to analog converter for output. The filling apparatus consists of a sample cell, a vacuum pump and a stainless steel sheath.

The catalyst sample is pressured up to 416 MPa and the change in volume is recorded and stored by the computer. 470 data points are taken in each run. By relating the change in volume to pressure,

the surface area, pore volume, and most frequent pore diameter are calculated and plotted by the X-Y recorder.

Coke Analysis

The catalyst samples are weighted at room temperature and the carbonaceous material is burned off by heating the sample to 550°C (1022°F) for 60 hours. The catalyst samples are cooled to room temperature and reweighed. The difference in the weights is considered as the amount of coke. The following equation is used.

$$\% \text{ Coke} = \frac{\text{Spent Weight} - \text{Burned Off Weight}}{(\text{Burned Off Weight})} \times 100$$

Titanium Distribution

The titanium distribution is measured by a Jeol Model JFM-35 Electron Scanning Microscope equipped with an Energy Dispersive X-Ray Analyzer. The sample is bombarded with electrons of different energies and the X-Rays emitted are measured. Different metals emit X-Rays when excited with electrons at a specific energy. The catalyst samples are analyzed at six different points from the center to the edge.

CHAPTER IV

RESULTS

The results of the twelve experimental runs conducted in the Berty autoclave reactor will be presented in this chapter.

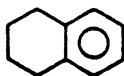
The twelve experimental runs were divided into two sets of six experimental runs. The first set of experimental runs was to investigate the effect of the stirrer speed on the conversion of Tetralin to its hydrogenated products. The second set was to study the effect of Bis (cyclopentadienyl) titanium dichloride (titanocene dichloride) and temperature on the hydrogenation of 1,2,3,4 tetrahydronaphthalene (Tetralin) and phenanthrene. The physical properties of Tetralin, phenanthrene and Titanocene dichloride are presented in Tables I, II and III. In all of the experimental runs, a pressure of 10.4 MPa (1500 psig) and a temperature of 350°C (662°F) was used except for Run 8 which was at a temperature of 375°C (707°F). A hydrogen to oil ratio of 800 $\text{m}^3 \text{H}_2/\text{m}^3 \text{oil}$ (5620 SCF/Bbl) was used. Tables IV and V give the experimental conditions. Each run used 20 grams of Shell 324 catalyst with the properties reported in Table VI.

The liquid samples were analyzed by gas chromatography and by an elemental analyzer. The gas chromatograph gave the conversion of Tetralin and phenanthrene to their hydrogenated products. The elemental analyzer gave the H/C atomic ratio which is an indication of the extent of hydrogenation. By knowing all or the major peaks

TABLE I
PROPERTIES OF 1,2,3,4 TETRAHYDRONAPHTHALENE (30)
(TETRALIN)

Formula: $-C_6H_4CH_2(CH_2)_2CH_2-$

Structure



Physical Properties:

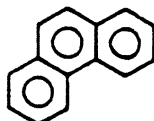
Molecular Weight	132.21
State	Liquid
Color	Water Clear
Melting Point	-35.8°C (-32°F)
Normal Boiling Point	207.6°C (405°F)
Specific Gravity	0.9702
Solubility	Insoluble in Water Soluble in Alcohol and Ether
Purity	99%

Supplier Aldrich Chemical Company

TABLE II
PROPERTIES OF PHENANTHRENE (30)

Formula: $(C_6H_4CH)_2$

Structure:



Physical Properties:

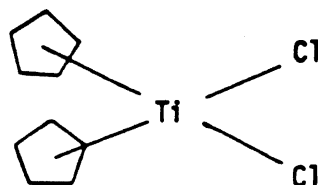
Molecular Weight	178.24
State	Solid
Color	White
Melting Point	101°C (214°F)
Boiling Point	340°C (644°F)
Specific Gravity	0.9800
Solubility	Insoluble in Water Soluble in Ether
Purity	98% (By Supplier)

Supplier Aldrich Chemical Company

TABLE III
 PROPERTIES OF BIS(CYCLOPENTADIENYL)TITANIUM DICHLORIDE (30)
 (TITANOCENE DICHLORIDE)

Formula $(C_5H_5)_2TiCl_2$

Structure:



Physical Properties:

Molecular Weight	249.0
State	Crystalline Solid
Color	Red
Melting Point	289 - 291°C (522°F - 556°F) (With Decomposition)
Titanium Content	19.24 wt.%
Chloride Content	28.48 wt.%
Solubility	Moderately soluble in toluene and chloroform and in alcohol and other hydroxlic solvents. Sparingly soluble in ether, benzene, carbon disulfide, carbon tetrachloride, petroleum ether, and water.

Supplier Alpha Products

TABLE IV
EXPERIMENTAL CONDITIONS

Feedstock: 1,2,3,4 Tetrahydronaphthalene (Tetralin)

Operating Conditions:

Pressure:	10.4 MPa (1500 psig)
Temperature:	350°C (662°F)
Hydrogen Flowrate:	24 l/h (400 cm ³ /minute)
Feedstock Flowrate:	1.8 l/h (30 cm ³ /hour)
Sampling:	Every 2 hours
Length of Run:	12 hours

<u>Run</u>	<u>Magnedrive Speed</u>
#	(RPM)
1	500
2	1000
3	1500
4	2000
5	1750
6	1250

TABLE V
EXPERIMENTAL CONDITIONS

<u>Run</u>	<u>Feedstock</u>
#	
7	1,2,3,4 Tetrahydronaphthalene (Reference Run)
8	1,2,3,4 Tetrahydronaphthalene, 375°C, (707°F)
9	1,2,3,4 Tetrahydronaphthalene (Duplicate Run)
10	1,2,3,4 Tetrahydronaphthalene + 5 Wt% Phenanthrene
11	1,2,3,4 Tetrahydronaphthalene + 5 Wt% Phenanthrene + 100 ppm Titanium as Bis(cyclopentadienyl)titanium dichloride
12	1,2,3,4 Tetrahydronaphthalene + 100 ppm Titanium as Bis(cyclopentadienyl)titanium dichloride

Operating Conditions:

Pressure:	10.4 MPa (1500 psig)
Temperature:	350°C (662°F), except run #8
Hydrogen Flowrate:	24 l/h (400 cm ³ /minute)
Feedstock Flowrate:	1.8 l/h (30 cm ³ /hour)
Sampling:	Every 2 hours
Length of Run:	12 hours
Magnedrive Speed:	1500 RPM

TABLE VI
 PROPERTIES OF SHELL 324 CATALYST*

Chemical Composition, wt.%

NiO 3.4

MoO₃ 19.3

Physical Properties:

Physical Arrangement 1.6mm (1/16 in) Extrudate

Surface Area, m²/kg 146 x 10³

Pore Volume, m³/kg 4.2 x 10⁻⁴

Most Frequent Pore Diameter 11.8 nm

Pore Distribution

% Pore Volume in Pore

Diameter, nm	%
3.5 - 7.0	12
7.0 - 10.0	21
10.0 - 15.0	57
15.0 - 20.0	2
20.0 - 40.0	1
40.0 - 60.0	1
60.0	<u>6</u>
Total	100

*From Shell

of the gas chromatographic analysis, an atomic ratio can be calculated. This procedure provided a check for the elemental analyzer; however, due to malfunctions in the elemental analyzer, the data presented will be from the gas chromatograph analysis. See Appendix C for details of the calculations. The conversion of Tetralin and phenanthrene to their hydrogenated products is presented in Tables VII, VIII, IX and X and in Figures 3 through 14.

There are two catalyst samples for each run. One is the spent catalyst sample which has been extracted with tetrahydrofuran for 60 hours. The other sample, regenerated sample, has also been extracted and the coke has been burned off at 550°C (1022°F) for 60 hours. The samples were analyzed using the Autoscan 60 Porosimeter for pore volume, surface area and the most frequent pore diameter with the data presented in Figures 15, 16 and 17. The results of coke analysis are presented in Table XI and in Figure 18.

Each point in the figures represents the average of three points except for the coke analysis which is the average of six points. The vertical line above and below the points represents the range of values. If there is not a vertical line, the range is within the symbol. The horizontal line represents the overall average of all the points in the Figures.

The distribution of Titanium in the catalyst samples for Runs 10 and 12 is presented in Figures 19 and 20. The percent titanium is the percent of titanium counts of the total metal counts from the Electron Scanning Microscope. It indicates a relative concentration and does not present a true weight percent of titanium in the catalyst.

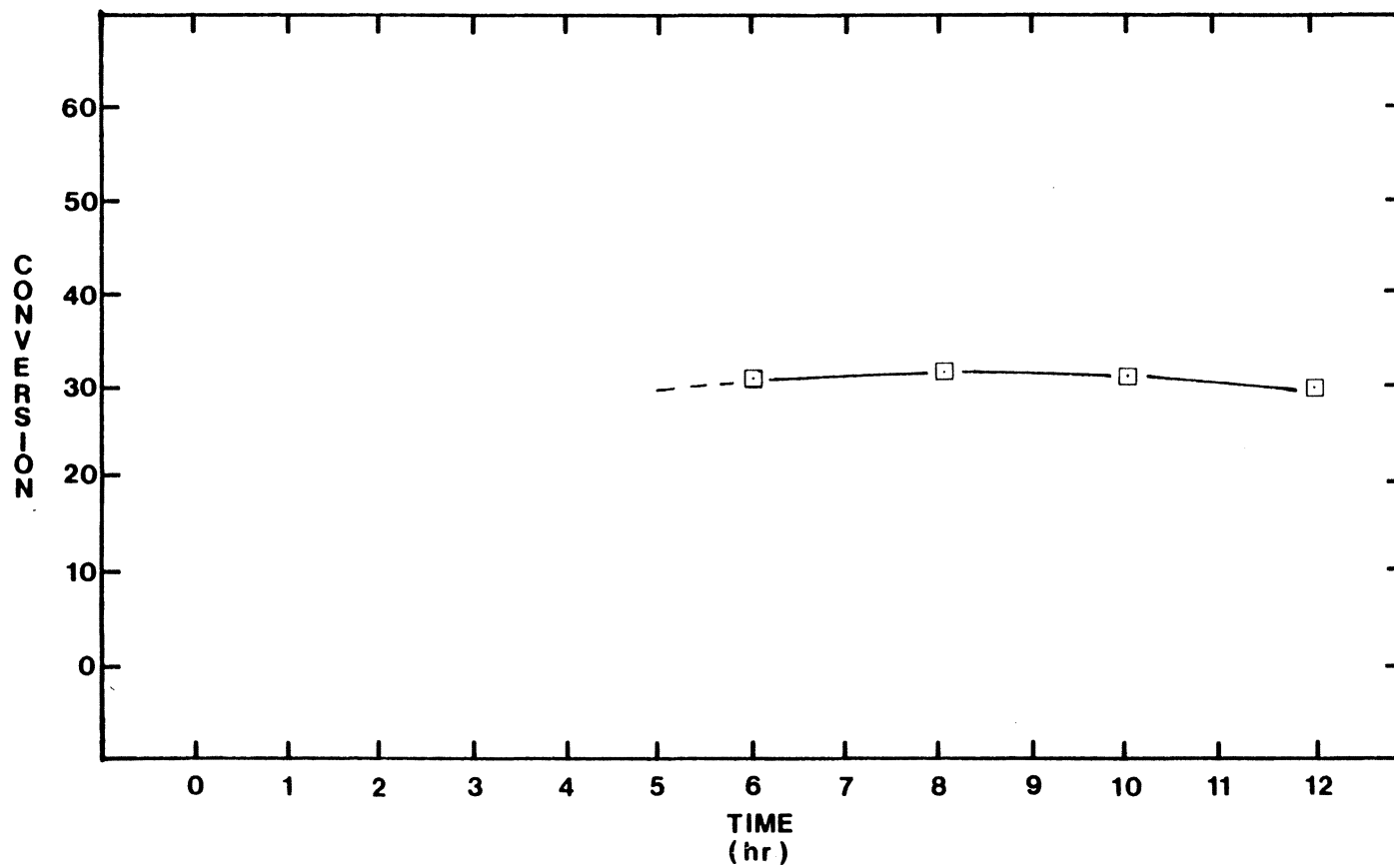


Figure 3. Conversion of Tetralin as a Function of Time with a Stirrer Speed of 500 RPM for Run #1

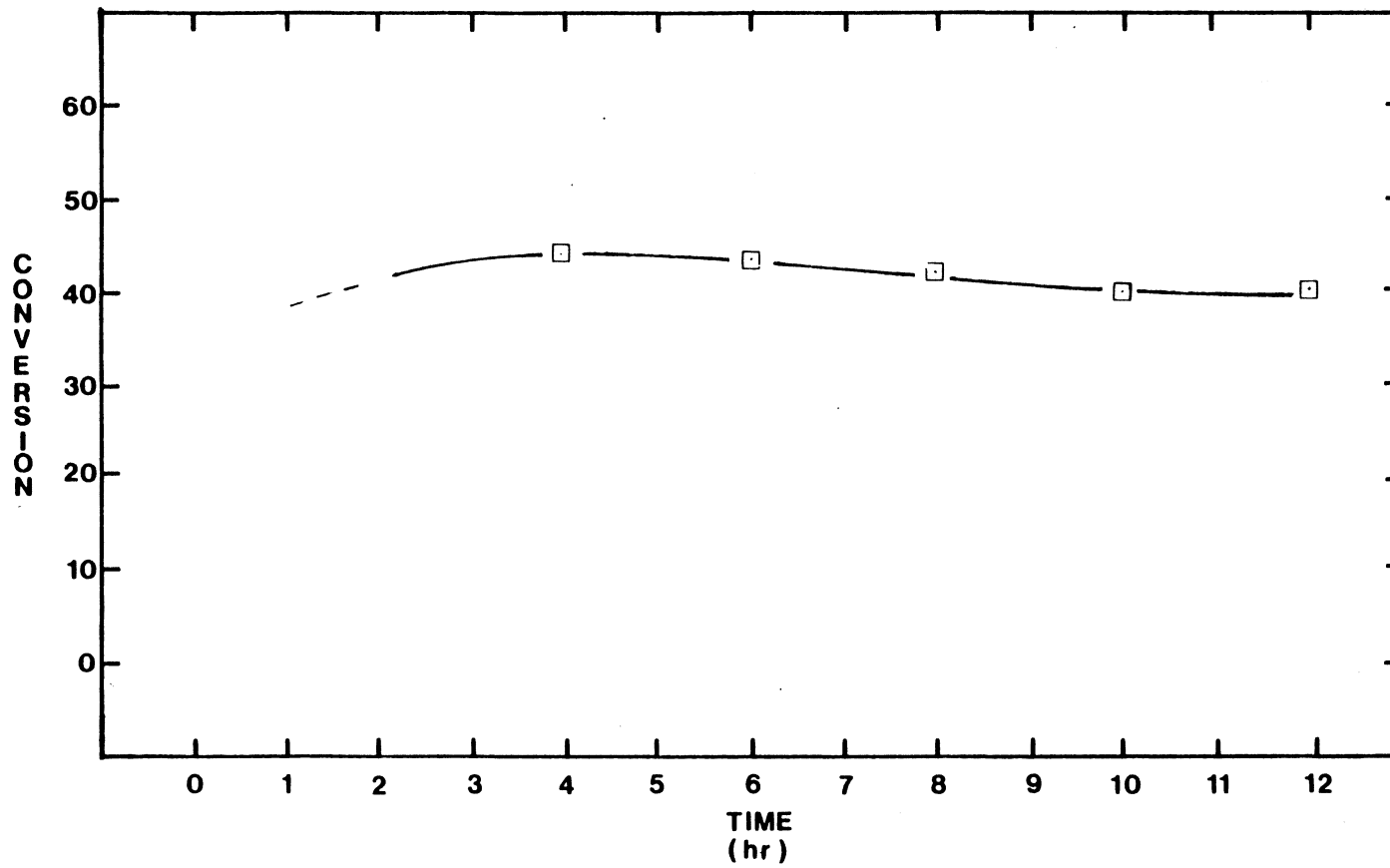


Figure 4. Conversion of Tetralin as a Function of Time with a Stirrer Speed of 1000 RPM for Run #2

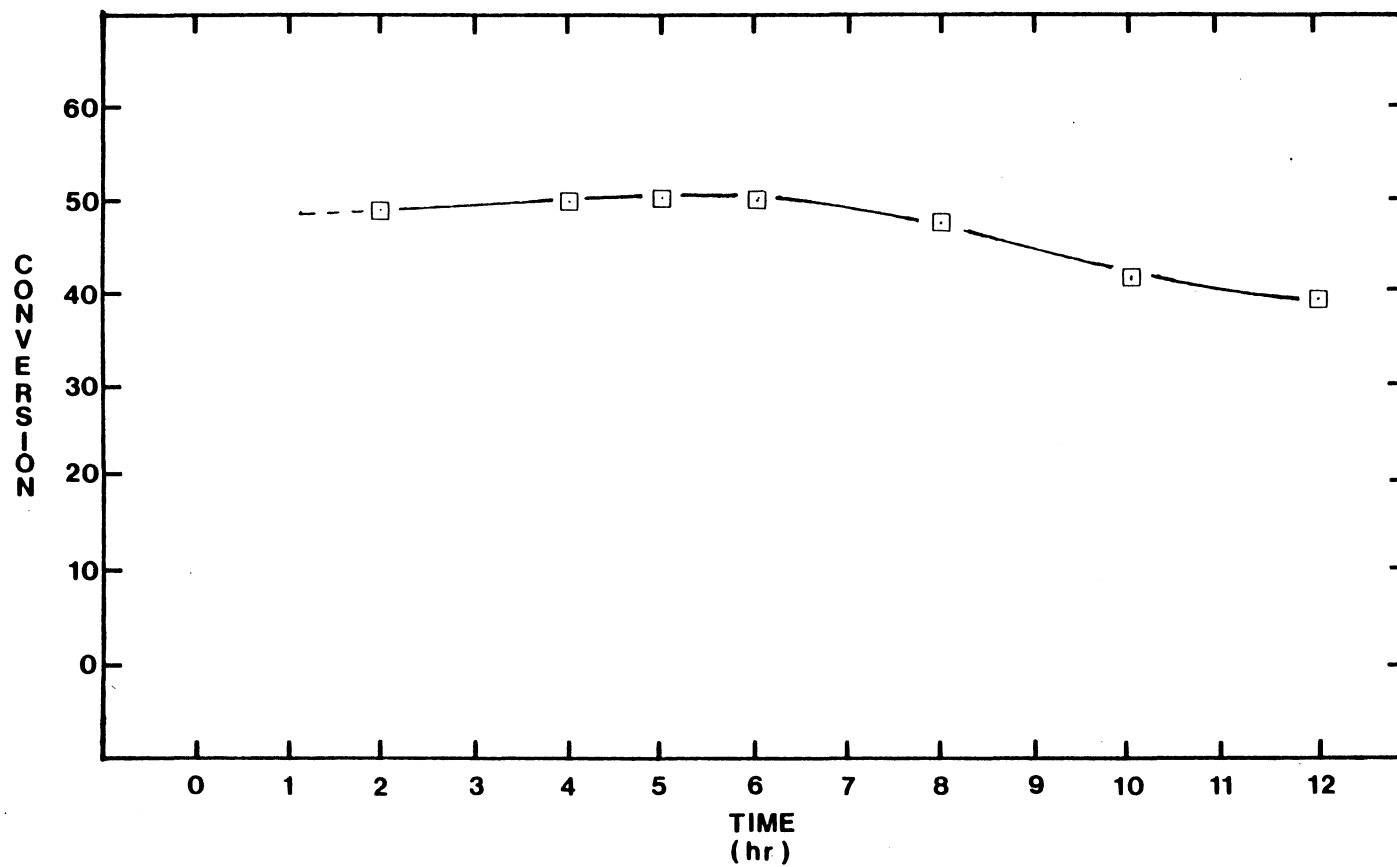


Figure 5. Conversion of Tetralin as a Function of Time with a Stirrer Speed of 1500 RPM for Run #3

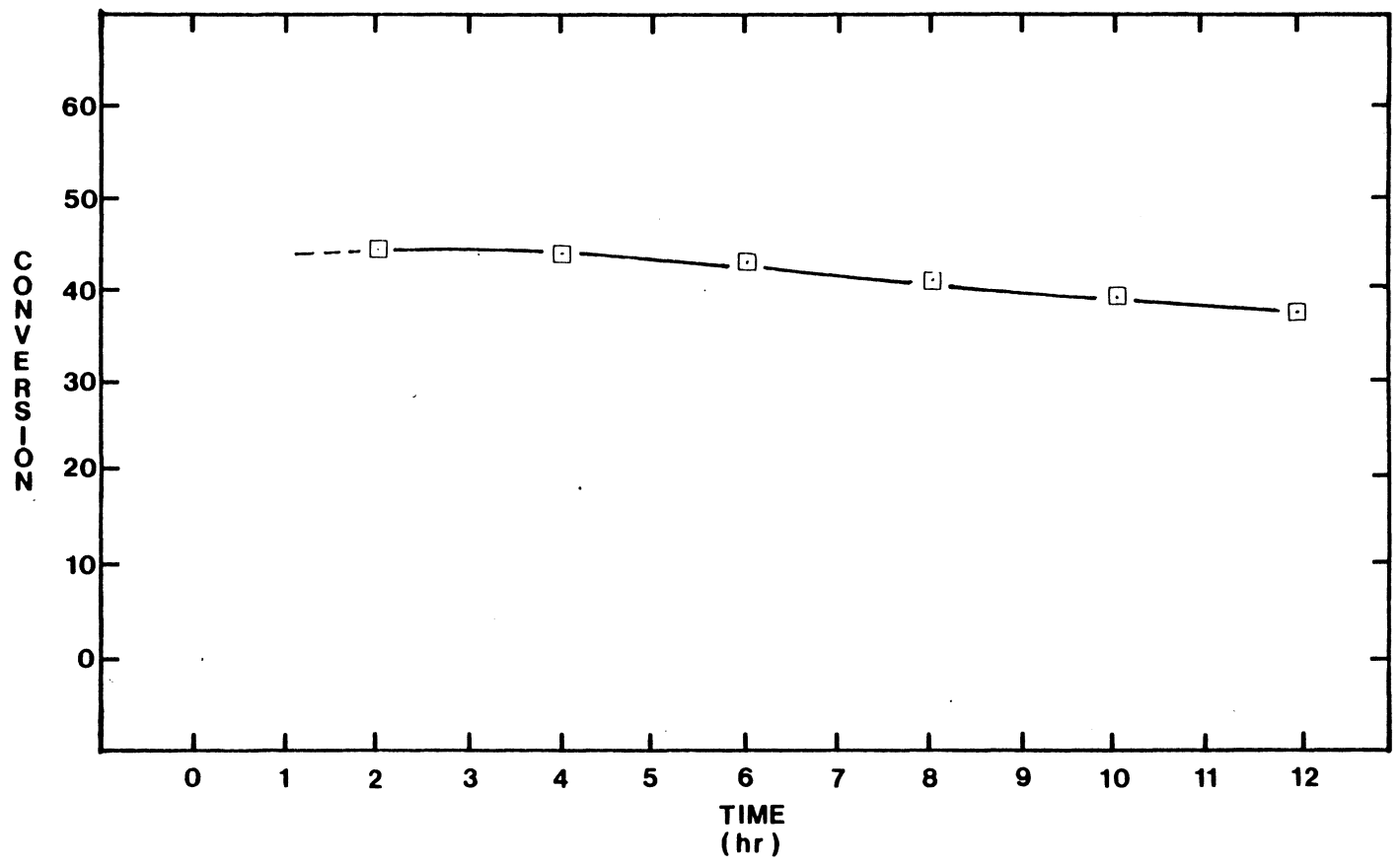


Figure 6. Conversion of Tetralin as a Function of Time with a Stirrer Speed of 2000 RPM for Run #4

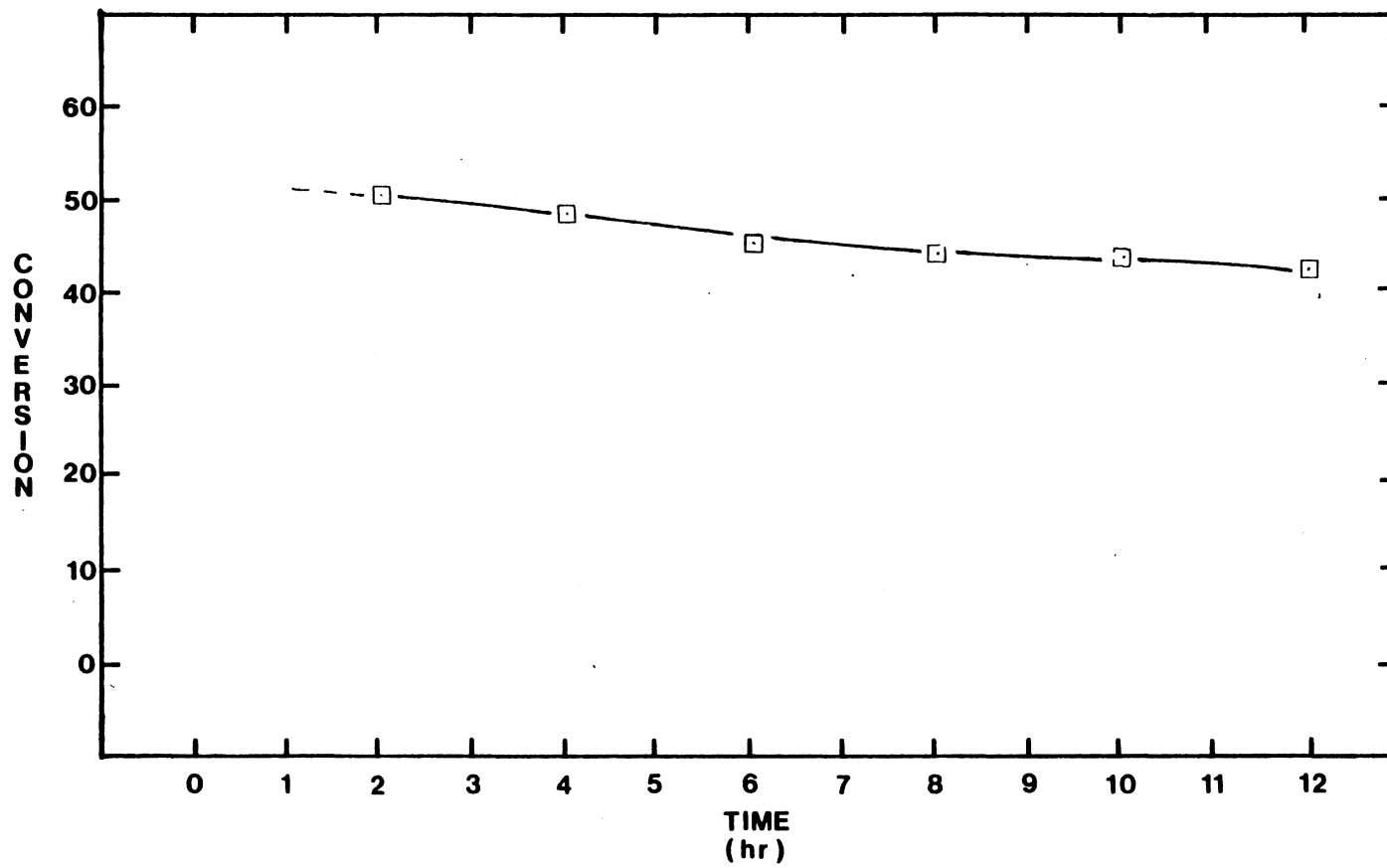


Figure 7. Conversion of Tetralin as a Function of Time with a Stirrer Speed of 1250 RPM for Run #5

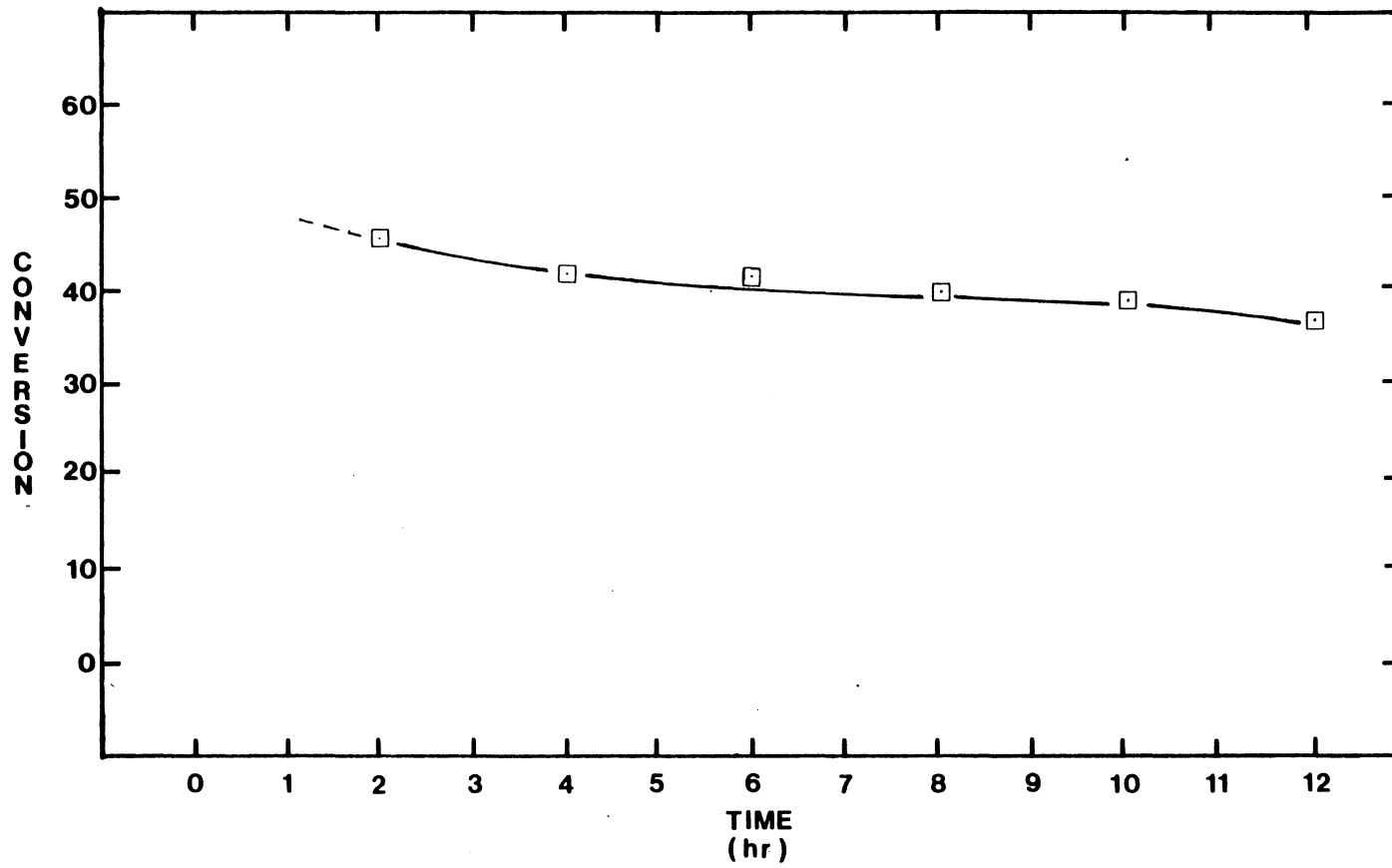


Figure 8. Conversion of Tetralin as a Function of Time with a Stirrer Speed of 1750 RPM for Run #6

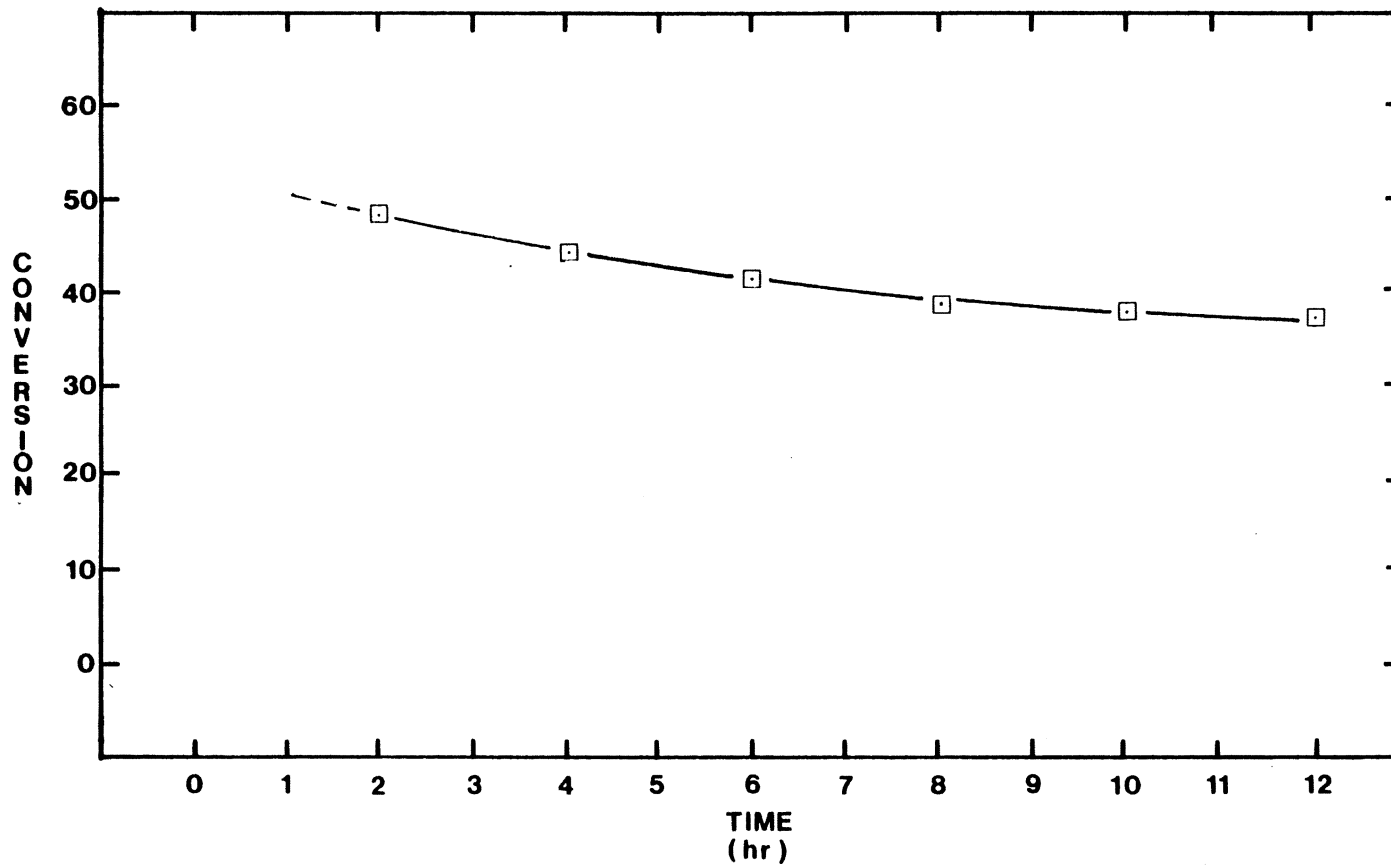


Figure 9. Conversion of Tetralin as a Function of Time at 350°C for Run #7

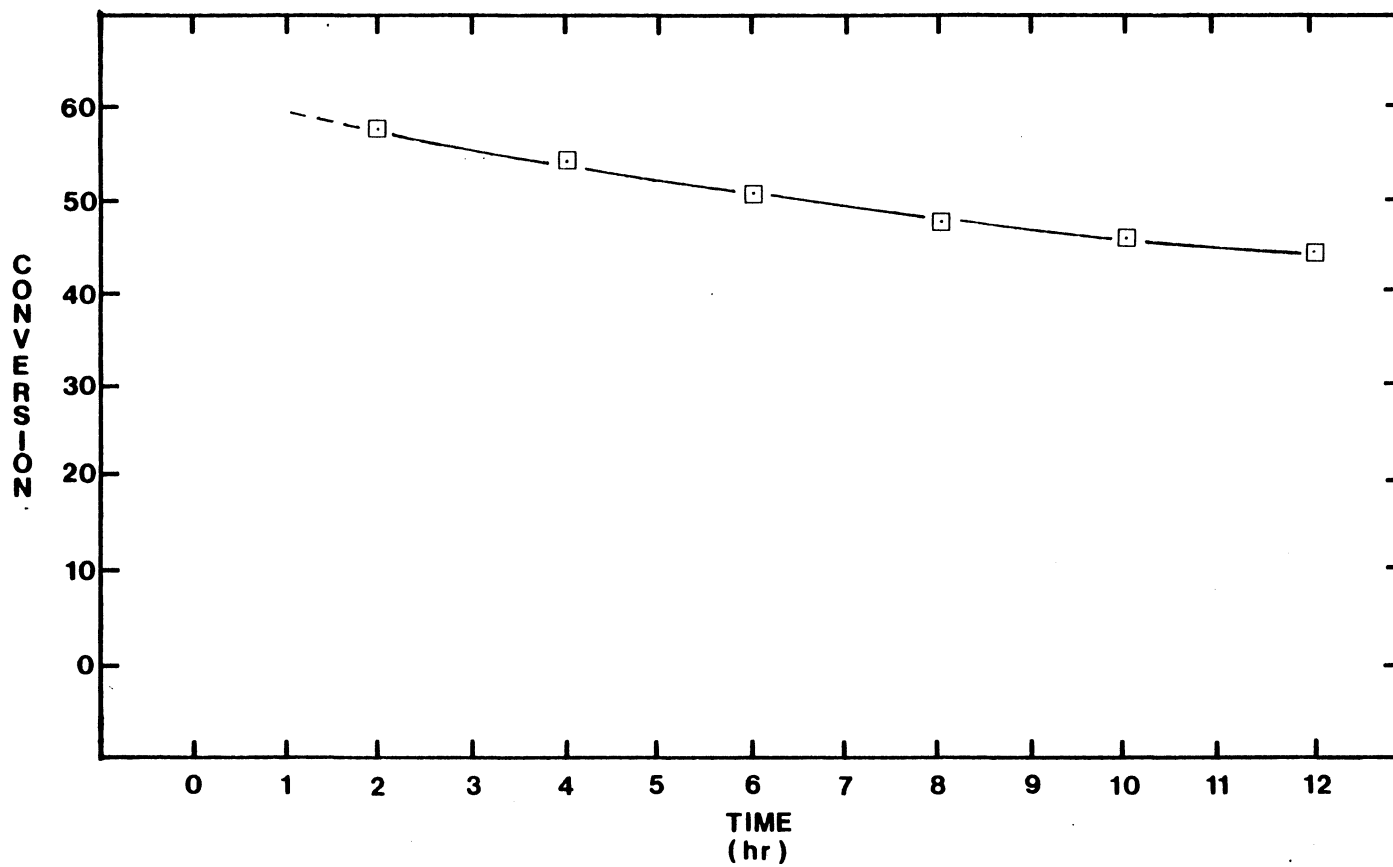


Figure 10. Conversion of Tetralin as a Function of Time at 375°C for Run #8

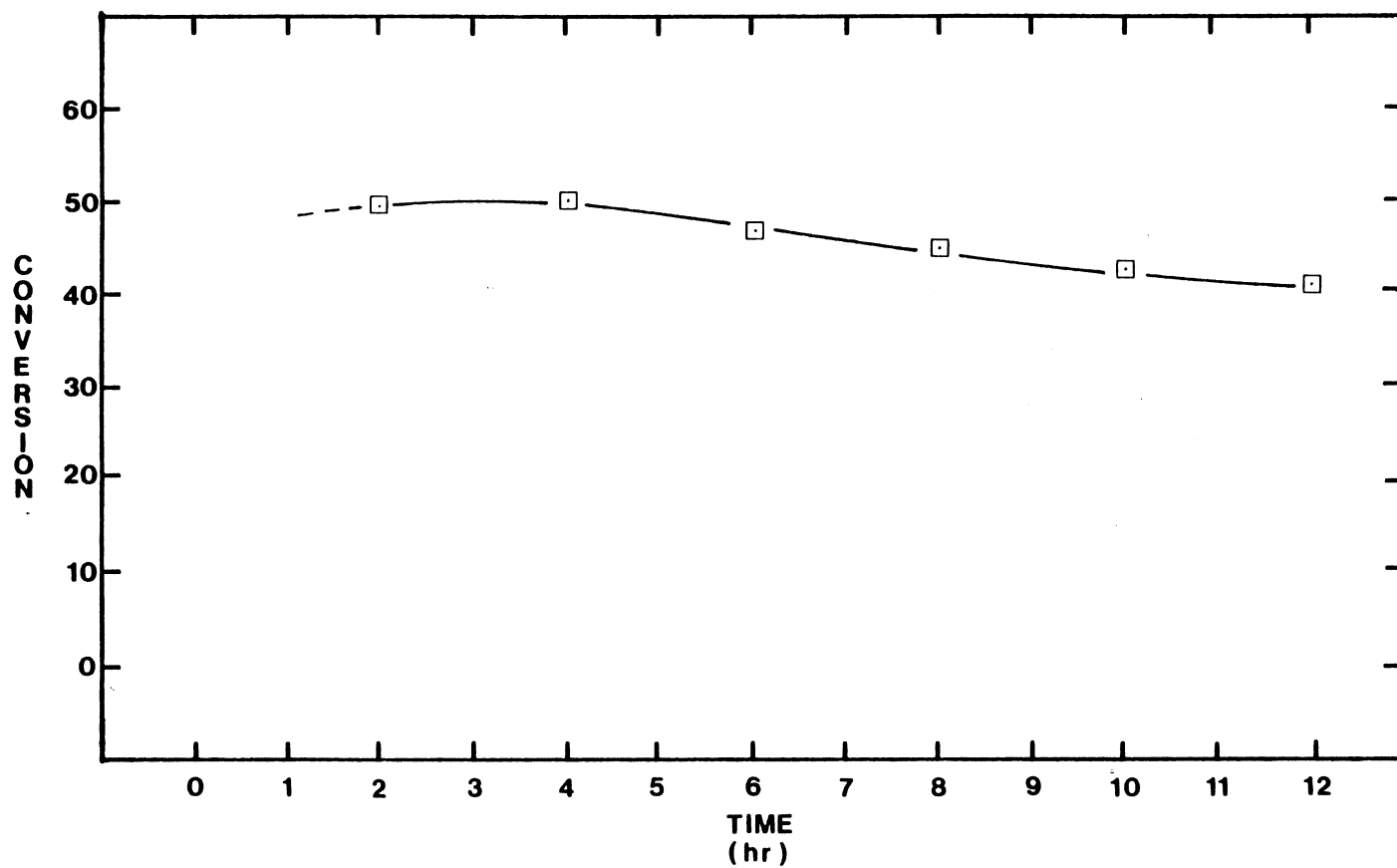


Figure 11. Conversion of Tetralin as a Function of Time at 350°C for Run #9
(Duplicate of Run #7)

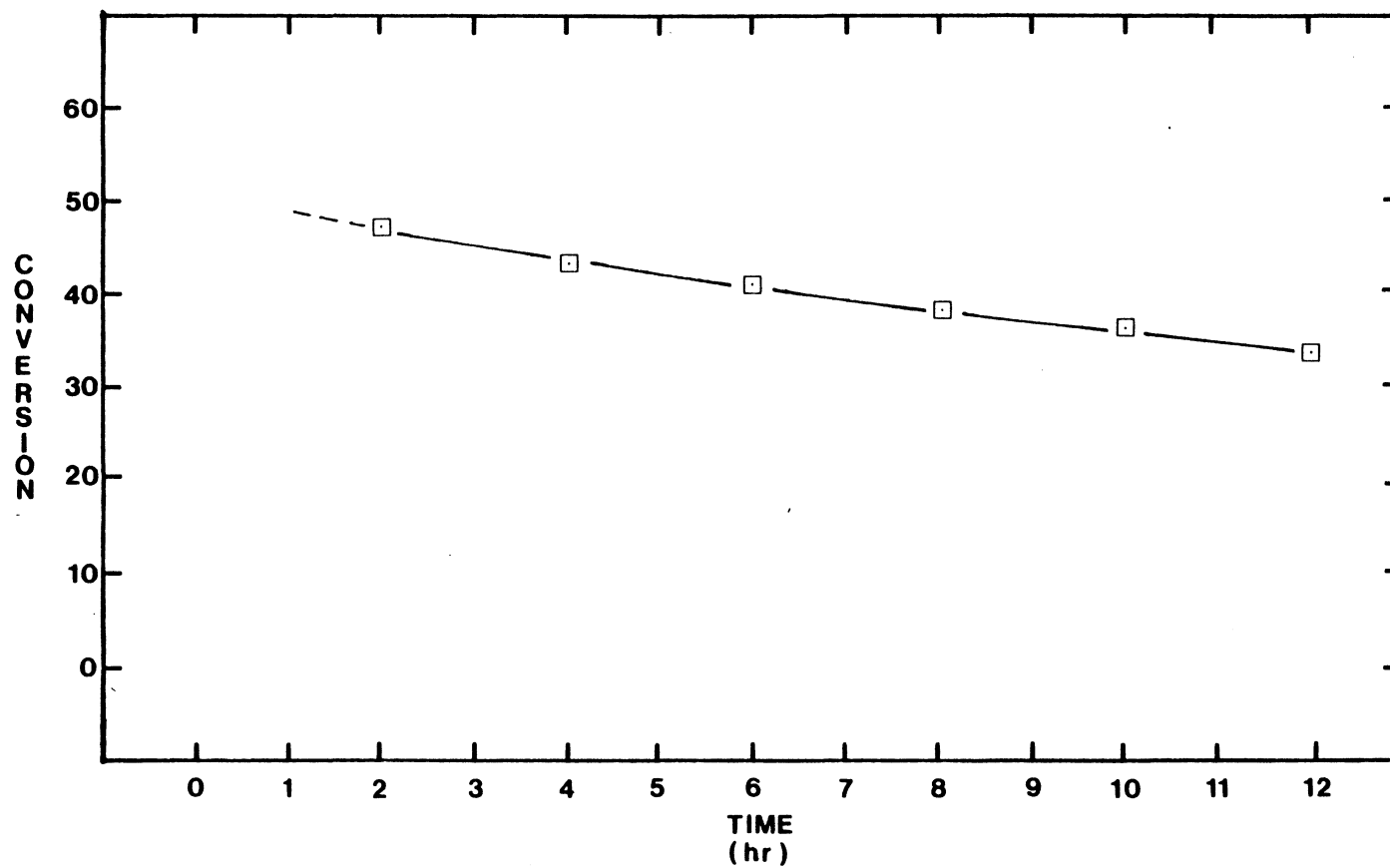


Figure 12. Conversion of Tetralin as a Function of Time with a 5 wt% Phenanthrene for Run #10

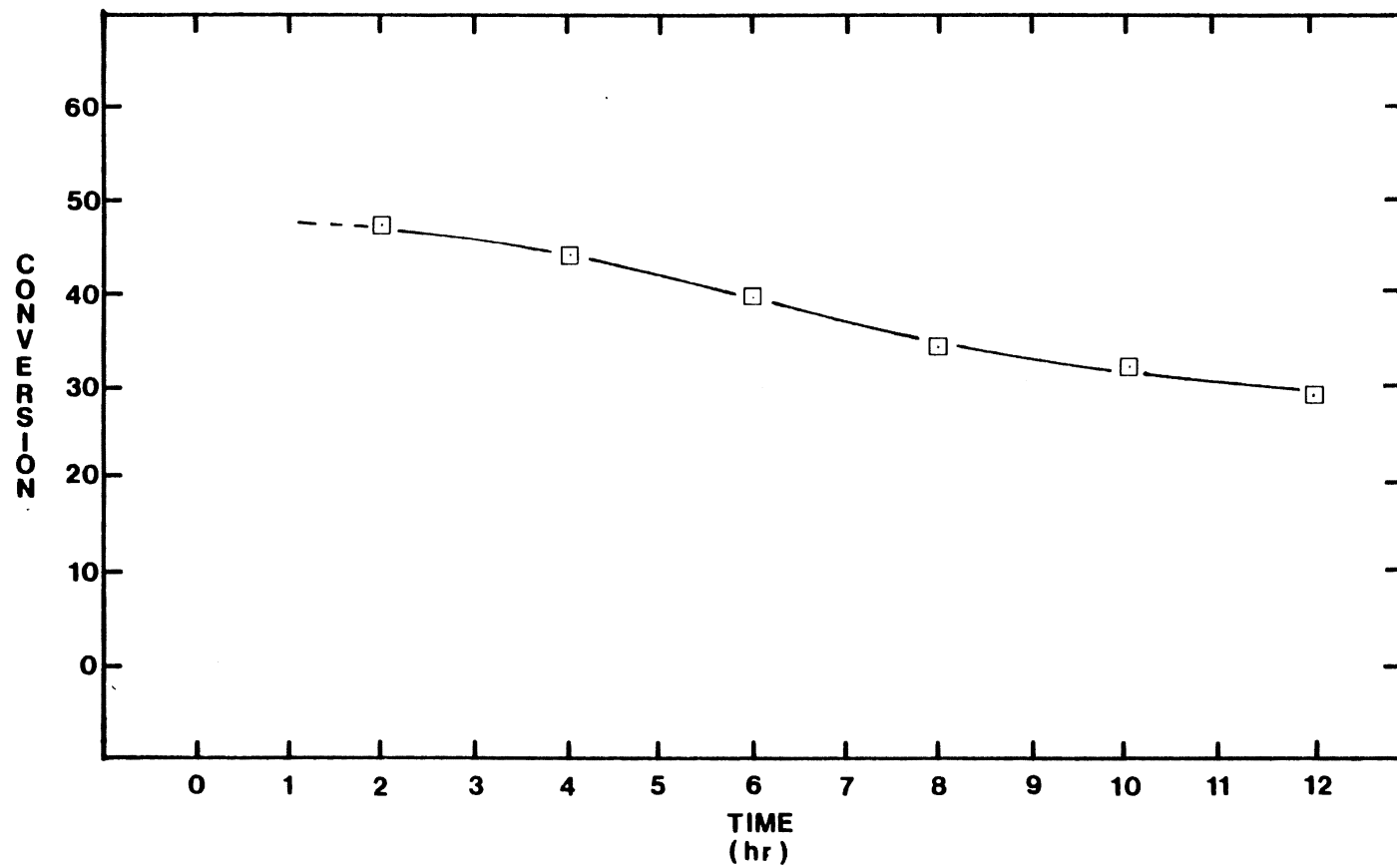


Figure 13. Conversion of Tetralin as a Function of Time with 5 wt% Phenanthrene and 100 PPM Titanium for Run #11

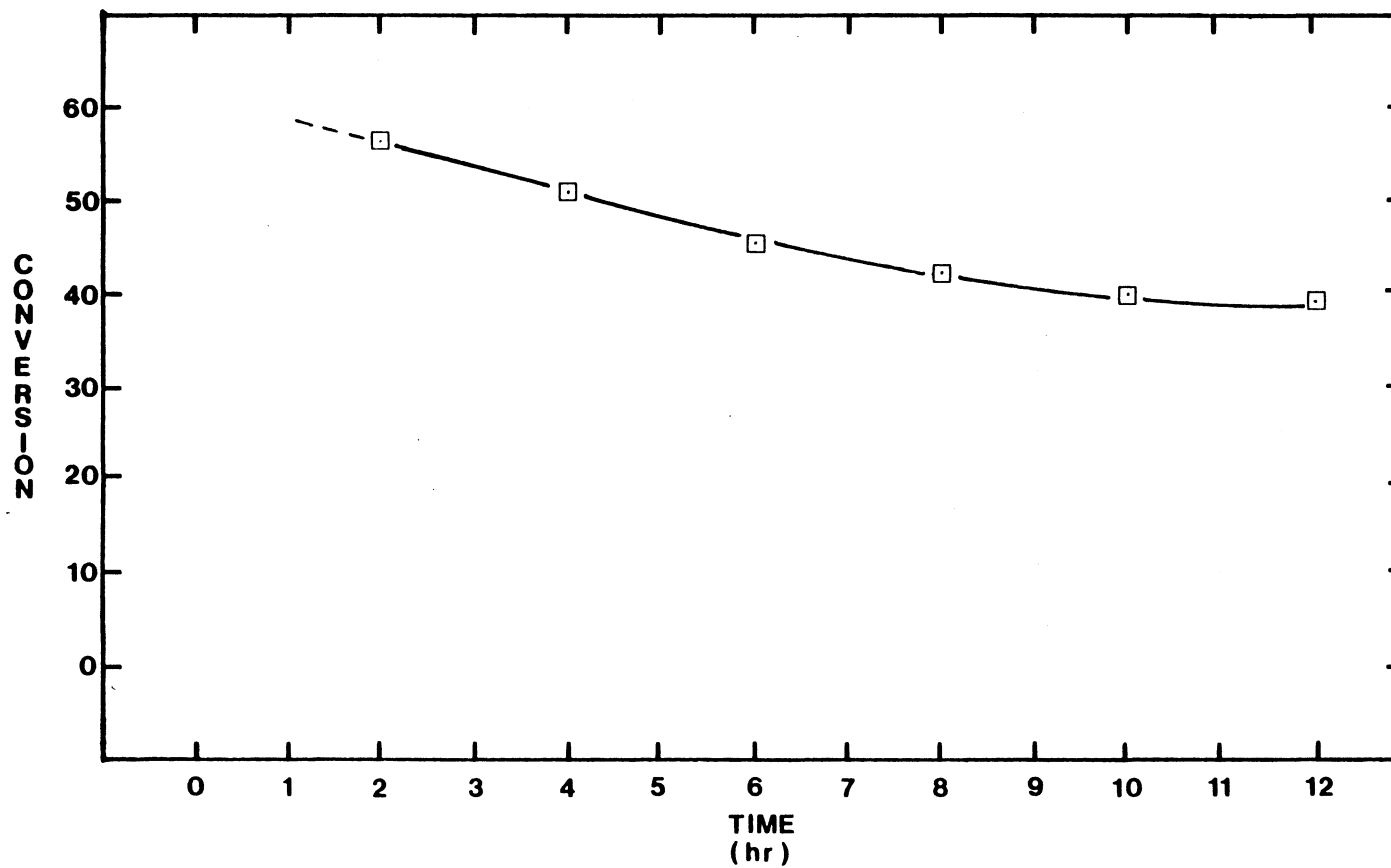


Figure 14. Conversion of Tetralin as a Function of Time with 100 PPM Titanium for Run #12

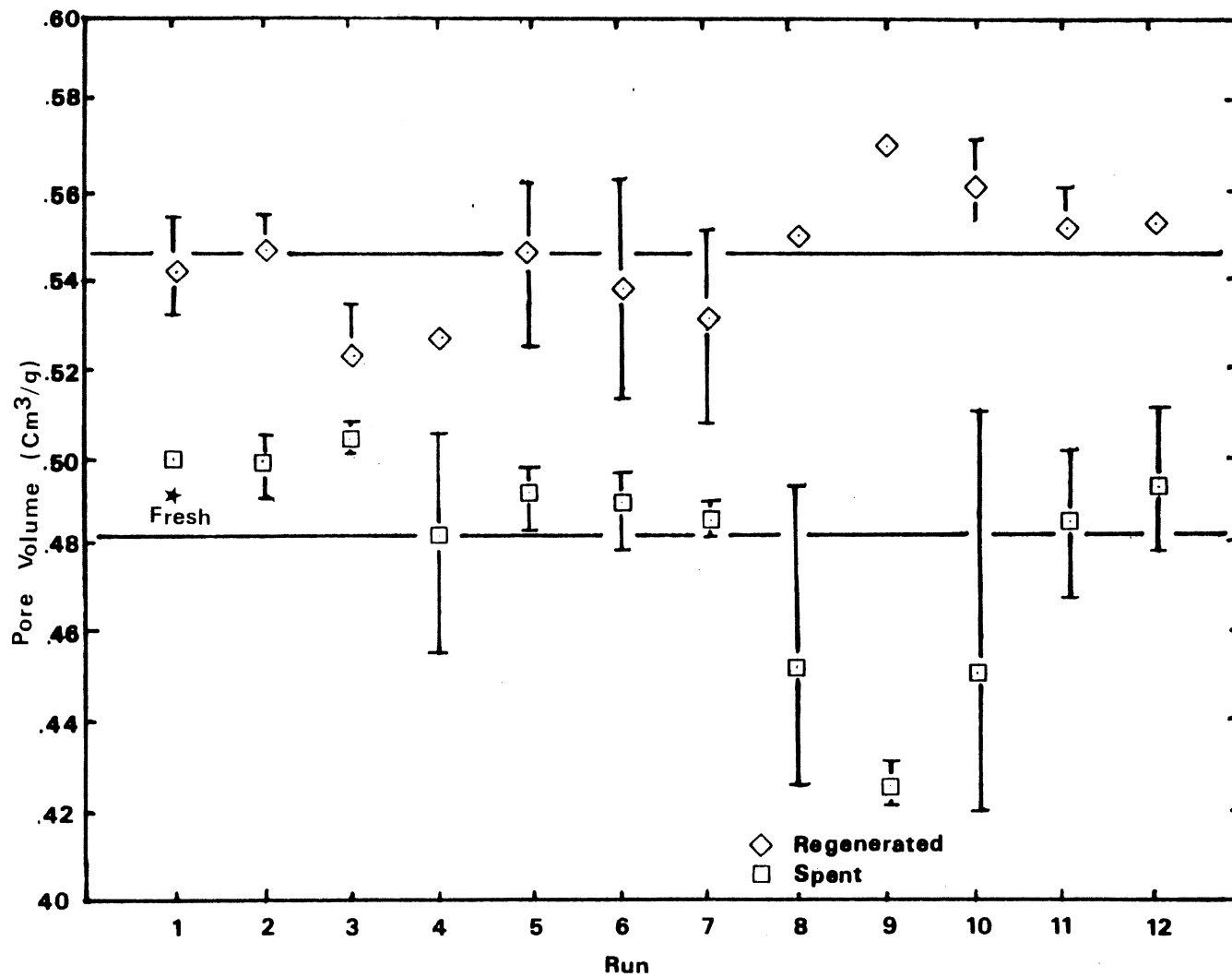


Figure 15. Comparison of Pore Volume of Regenerated and Spent Catalyst Samples

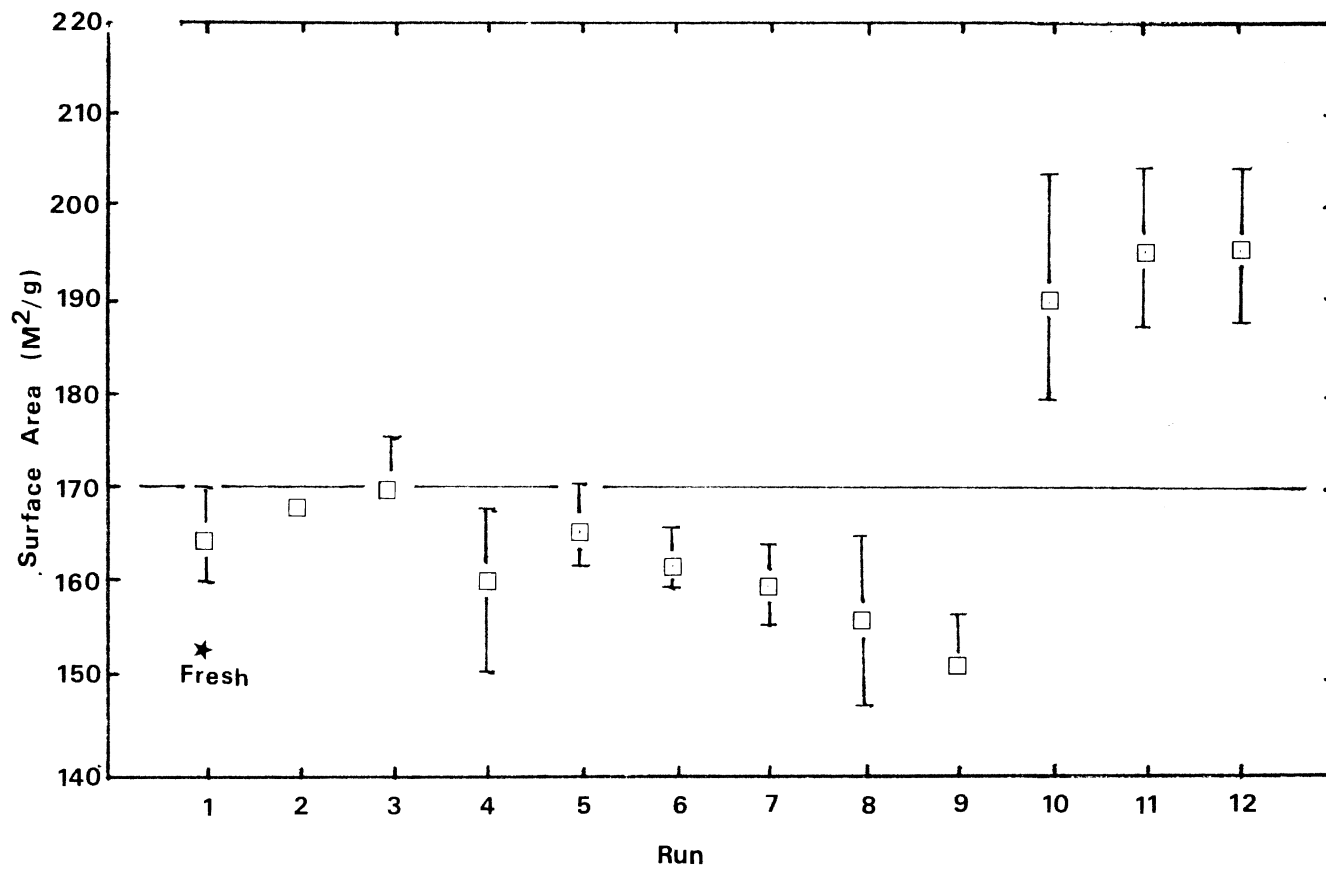


Figure 16. Comparison of Surface Area of Spent Catalyst Samples

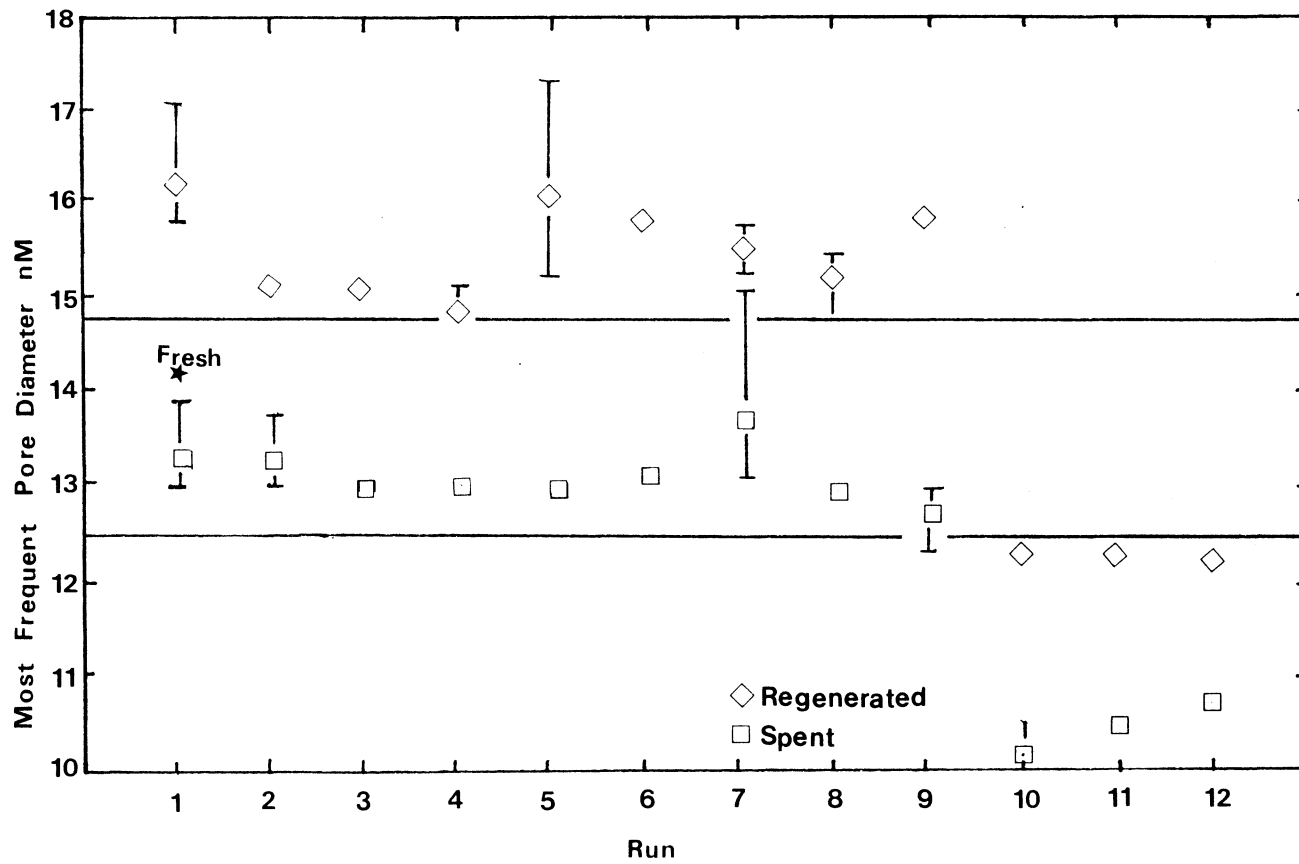


Figure 17. Comparison of Most Frequent Pore Diameter of Spent and Regenerated Catalyst Samples

TABLE VII
CONVERSION OF TETRALIN

Run #	Sample #	Time (Hour)	Speed (RPM)	Gas Chromatography Analysis				
				% Conversion Tetralin	wt.% Tetralin	Trans-Decalin	Cis-Decalin	Naphthalene
1	1	2	500	-	-	-	-	-
1	2	4	500	-	-	-	-	-
1	3	6	500	31.8	68.3	20.7	8.5	1.2
1	4	8	1,000	32.2	67.8	21.5	8.5	1.1
1	5	10	1,000	32.0	68.0	20.9	8.6	1.2
1	6	12	1,000	30.7	69.3	20.7	8.2	1.0
2	1	2	1,000	42.0	58.0	28.8	10.3	1.4
2	2	4	1,000	44.8	55.2	30.0	12.2	0.6
2	3	6	1,000	44.4	55.6	29.7	11.9	0.8
2	4	8	1,000	42.7	57.3	28.6	11.6	0.7
2	5	10	1,000	41.1	58.9	27.8	11.2	0.7
2	6	12	1,000	41.0	59.0	27.6	11.2	0.7
3	1	2	1,500	49.8	50.2	33.4	13.3	0.8
3	2	4	1,500	50.6	49.4	34.5	13.6	0.5
3	3	5	1,500	50.6	49.4	34.0	13.5	0.6
3	4	6	1,500	50.8	49.2	35.0	13.5	0.5
3	5	8	1,500	48.3	51.7	32.4	12.7	0.7
3	6	10	1,500	42.6	57.4	28.7	11.4	0.7
3	7	12	1,500	40.2	59.8	27.3	10.9	0.7

- No Sample Available

TABLE VII (continued)

Run #	Sample #	Time (Hour)	Speed (RPM)	Gas Chromatography Analysis				
				% Conversion Tetralin	Tetralin	wt.% Trans-Decalin	Cis-Decalin	Naphthalene
4	1	2	2,000	44.6	55.4	30.0	12.1	0.8
4	2	4	2,000	44.2	55.8	29.7	12.1	0.7
4	3	6	2,000	43.3	56.7	29.5	11.7	0.7
4	4	8	2,000	41.5	58.5	28.2	11.3	0.6
4	5	10	2,000	39.8	60.2	27.0	11.0	0.6
4	6	12	2,000	38.6	61.4	26.1	10.7	0.6
5	1	2	1,750	50.2	49.8	33.8	13.7	0.6
5	2	4	1,750	48.8	51.1	33.5	13.2	0.4
5	3	6	1,750	45.9	53.6	31.7	12.0	0.4
5	4	8	1,750	44.7	55.2	30.8	12.1	0.4
5	5	10	1,750	44.1	56.0	29.8	11.8	0.5
5	6	12	1,750	42.3	57.7	28.6	11.5	0.5
6	1	2	1,250	45.8	54.2	30.7	12.3	1.3
6	2	4	1,250	42.3	57.7	29.2	11.5	0.4
6	3	6	1,250	41.8	58.2	28.8	11.2	0.4
6	4	8	1,250	40.2	59.8	27.9	10.8	0.3
6	5	10	1,250	39.5	60.5	27.0	10.6	0.5
6	6	12	1,250	37.2	62.8	25.7	10.2	0.4

TABLE VII (continued)

Run #	Sample #	Time (Hour)	Speed (RPM)	Gas Chromatography Analysis				
				% Conversion Tetralin	Tetralin	wt.% Trans-Decalin	Cis-Decalin	Naphthalene
7	1	2	1,500	48.4	51.6	33.2	12.8	0.6
7	2	4	1,500	44.6	55.5	30.8	12.2	0.2
7	3	6	1,500	42.0	58.0	29.3	11.5	0.2
7	4	8	1,500	39.6	60.4	27.6	10.9	0.2
7	5	10	1,500	38.7	61.3	26.9	10.6	0.3
7	6	12	1,500	38.2	61.8	26.3	10.5	0.3
8	1	2	1,500	57.7	42.3	38.7	13.7	1.4
8	2	4	1,500	54.4	45.6	36.6	12.9	1.1
8	3	6	1,500	51.1	48.9	34.3	12.1	1.3
8	4	8	1,500	48.2	51.9	33.0	11.4	1.3
8	5	10	1,500	46.3	53.7	30.8	11.0	1.6
8	6	12	1,500	45.1	54.9	30.1	10.8	1.6
9	1	2	1,500	49.5	50.5	33.2	13.6	0.8
9	1	2	1,500	50.2	49.8	34.1	13.4	0.5
9	3	6	1,500	47.2	52.9	31.8	12.7	0.6
9	4	8	1,500	45.2	54.8	30.3	12.3	0.6
9	5	10	1,500	43.3	56.7	29.0	11.8	0.6
9	6	12	1,500	41.5	58.6	28.1	11.4	0.5

TABLE VIII
 CONVERSION OF TETRALIN AND PHENANTHRENE

Run #	Sample #	Time (Hour)	Speed (RPM)	Gas Chromatography Analysis					
				% Conversion Tetralin	Tetralin	wt.% Trans-Decalin	Cis-Decalin	Naphthalene	Phenanthrene
10	1	2	1,500	47.3	49.3	34.2	13.5	0.7	0.0
10	2	4	1,500	43.6	52.9	31.5	12.3	0.3	0.0
10	3	6	1,500	41.6	54.6	29.0	11.5	0.6	0.0
10	4	8	1,500	38.9	57.2	27.4	10.8	0.7	0.0
10	5	10	1,500	36.9	59.1	25.9	10.3	0.5	0.0
10	6	12	1,500	34.2	61.6	24.7	9.9	0.4	0.0
11	1	2	1,500	47.5	49.2	34.3	13.2	0.6	0.0
11	2	4	1,500	44.8	52.0	30.6	12.3	0.6	0.0
11	3	6	1,500	40.0	56.2	26.9	11.1	0.7	0.0
11	4	8	1,500	35.1	60.8	24.9	10.1	0.5	0.0
11	5	10	1,500	32.9	62.9	22.1	9.4	0.9	0.0
11	6	12	1,500	30.1	65.5	20.9	9.0	0.6	0.0
12	1	2	1,500	56.3	43.7	39.6	15.0	0.5	-
12	2	4	1,500	50.9	49.1	35.1	14.1	0.4	-
12	3	6	1,500	45.8	54.2	31.6	13.0	0.4	-
12	4	8	1,500	42.6	57.4	29.2	12.2	0.4	-
12	5	10	1,500	40.5	59.4	27.9	11.4	0.4	-
12	6	12	1,500	39.7	60.3	26.4	11.1	0.8	-

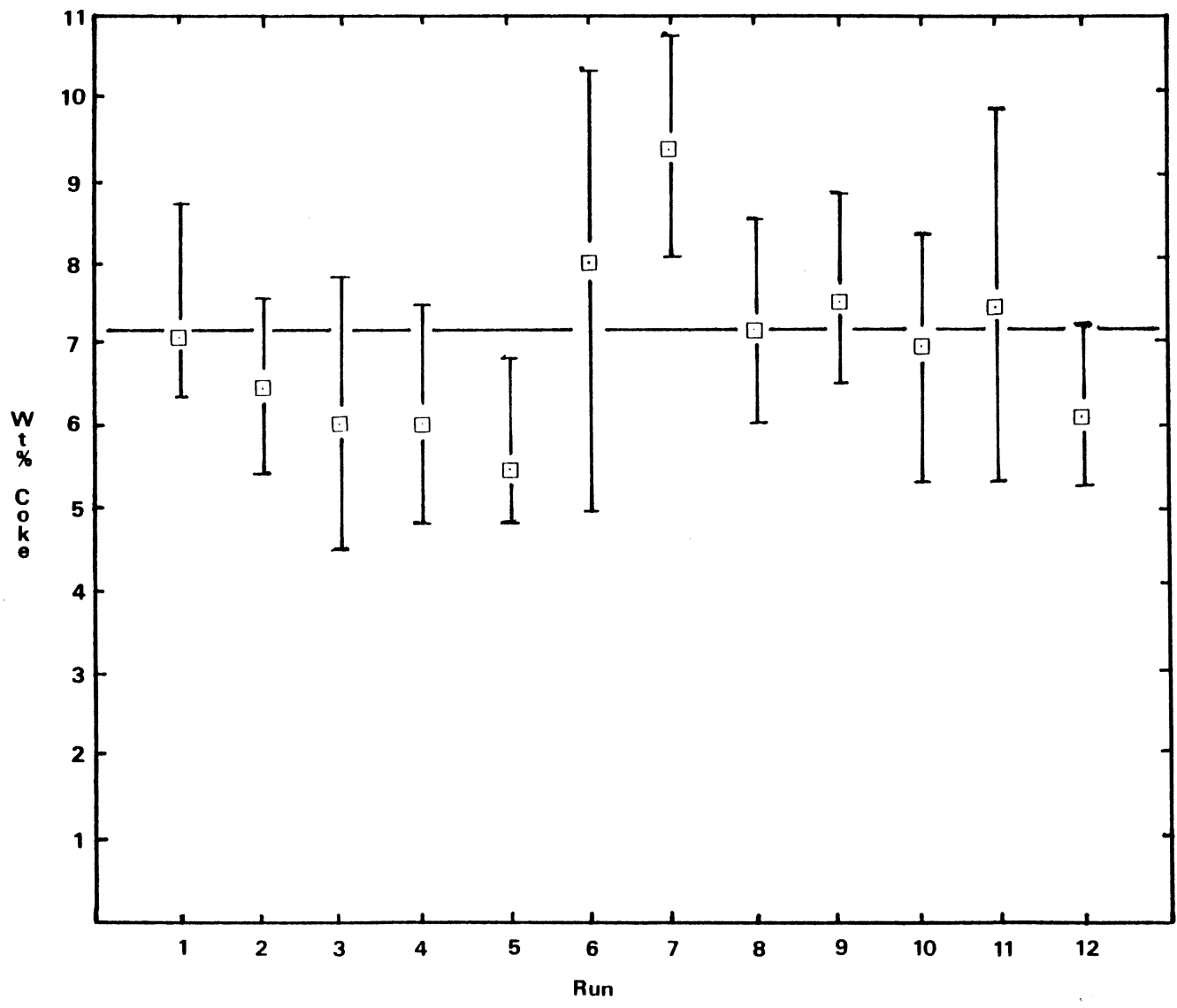


Figure 18. Comparison of Weight Percent of Coke on Catalyst Sample

TABLE IX
 CATALYST COKING ANALYSIS
 WT. % COKE

Run No.	Sample Number						Average	Standard Devia- tion
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>		
1	6.47	7.02	6.32	8.88	7.02	7.24	7.16	0.835
2	5.45	6.20	5.62	7.30	7.61	6.95	6.52	0.820
3	5.21	5.11	4.52	7.01	7.75	6.79	6.07	1.175
4	5.15	4.99	4.80	7.45	6.83	7.36	6.10	1.138
5	4.88	5.11	4.76	6.13	4.77	6.76	5.40	0.768
6	10.16	9.17	9.32	7.18	7.18	4.98	8.00	1.744
7	10.72	10.23	9.98	8.66	8.11	8.63	9.49	0.964
8	8.50	8.07	7.58	6.34	6.09	6.44	7.17	0.925
9	8.82	7.58	8.55	6.53	6.67	7.44	7.60	0.859
10	6.61	5.95	5.23	8.01	8.30	8.61	7.12	1.265
11	5.67	5.52	5.24	9.81	9.51	10.11	7.64	2.177
12	5.29	5.80	5.37	7.01	7.11	7.05	6.27	0.801

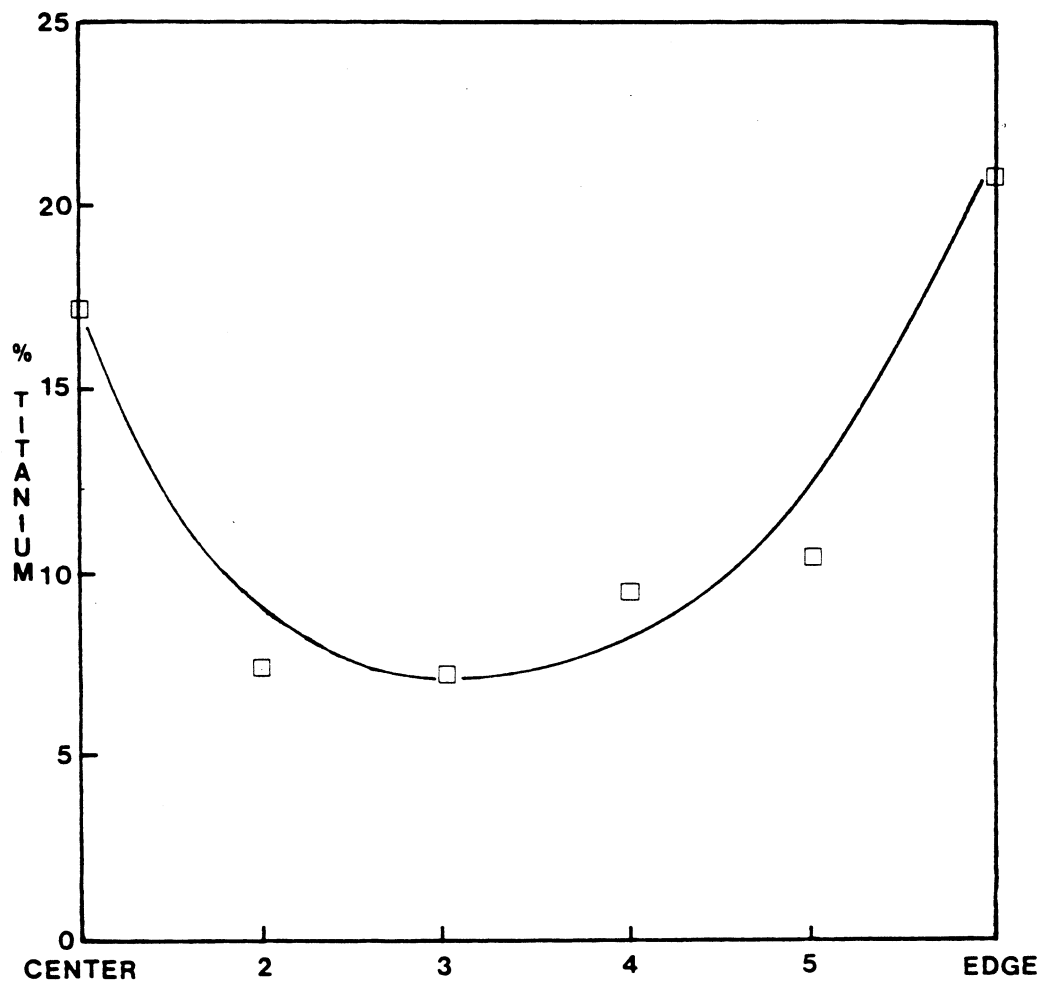


Figure 19. Percent of Titanium Counts as a Function of the Catalyst Profile Using an Electron Scanning Microscope of Run #10

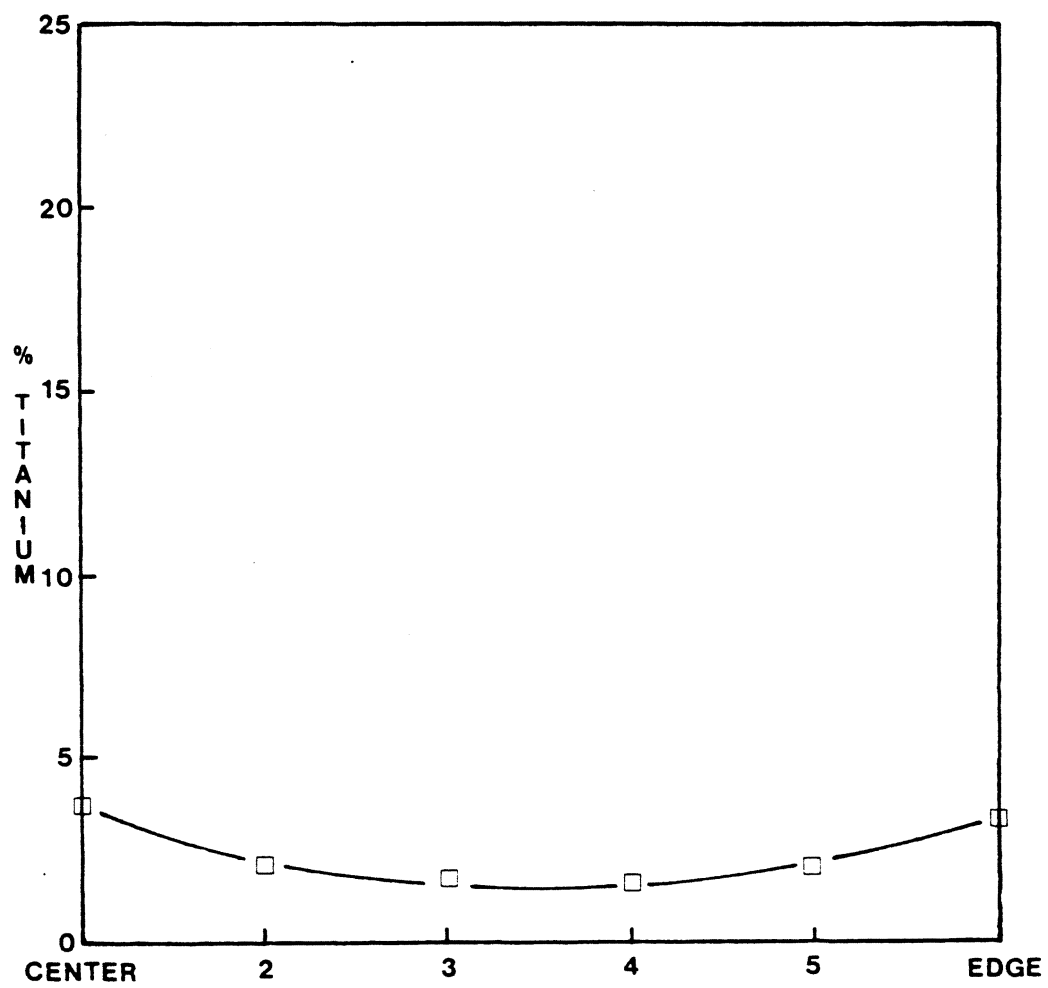


Figure 20. Percent of Titanium Counts as a Function of the Catalyst Profile Using an Electron Scanning Microscope of Run #12

CHAPTER V

DISCUSSION

Liquid Analysis

Experimental Runs 1 through 6

Mahoney et. al. (3) used the procedure of finding the minimum stirring speed needed to eliminate mass and heat transfer effects by varying the magne-drive stirrer speed to achieve the maximum conversion. This procedure was used to determine the stirrer speed that would eliminate the mass and heat transfer effects in the hydrogenation of the model compounds. Figure 21 shows the effect of the magne-drive stirrer speed on the conversion of the first sample taken from the first six experimental runs. As indicated by the graph, a magne-drive stirrer speed of 1500 rpm resulted in the maximum conversion of Tetralin and the elimination of heat and mass transfer effects. The first sample of each experimental run was used for the comparison instead of the other samples taken because of mechanical and operator sampling problems. The latter samples would not give an indication correct indication of the effects of the stirrer speed on the conversion because of the differences in catalyst coking and deactivation.

Experimental Run 7 and Run 9

Run 7 is the reference run to study the effects of phenanthrene

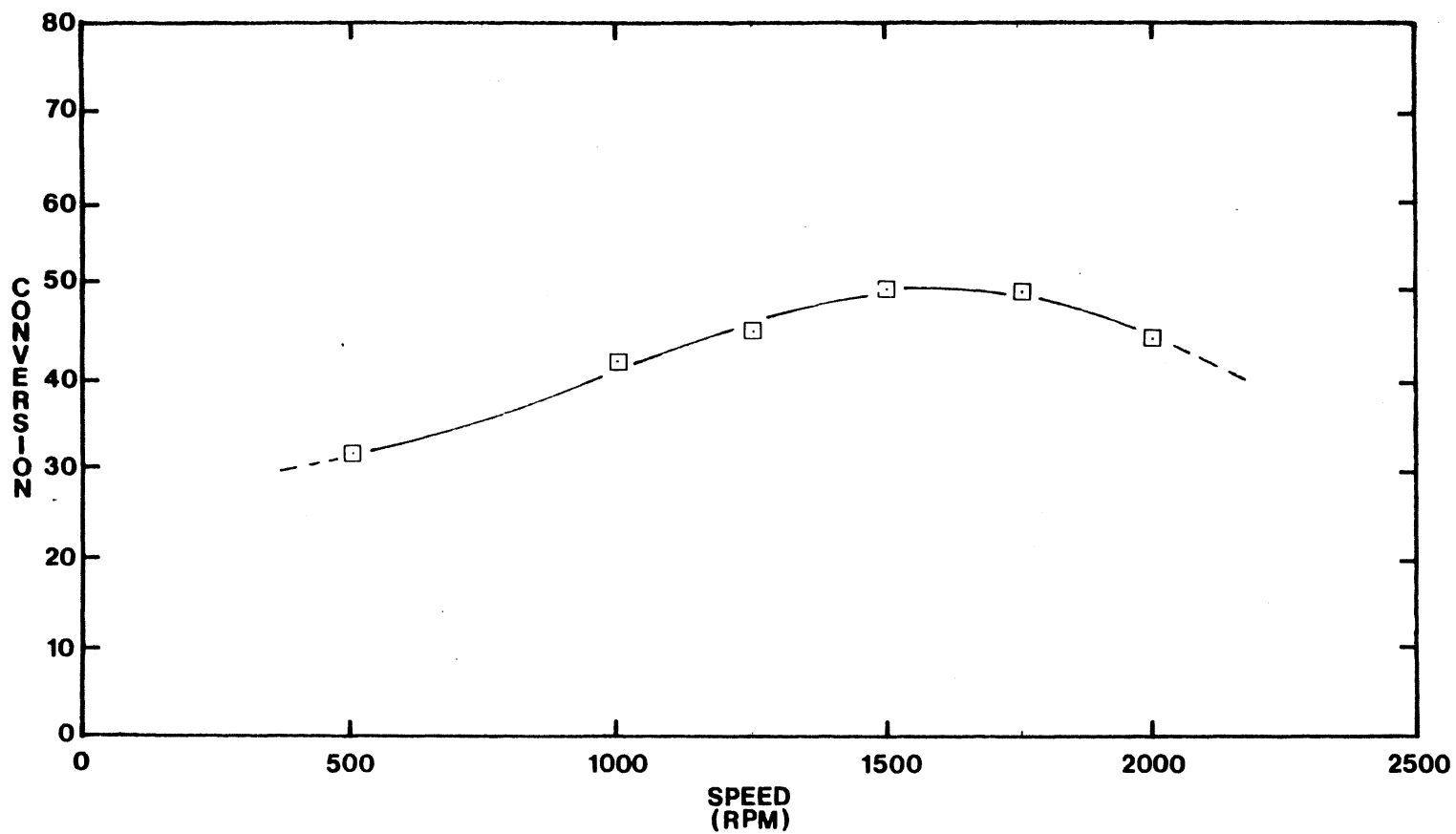


Figure 21. Comparison of Stirrer Speed on the Conversion of Tetralin to its Hydrogenerated Products

and titanocene dichloride. The conversion of Tetralin to the hydrogenated products of the other experimental runs will be compared to Run 7.

Run 9 is the duplicated run of Run 7. As indicated by Figure 22, there is a distinct difference in the conversion between these two runs. There is also a difference in the pore volume of the spent and regenerated catalyst samples as shown in Figure 15, but there is not any significant difference in the surface area, most frequent pore diameter or the amount of coke. Inspection of the operating data did indicate that the two runs were identical in the operating procedure and conditions, except for sulfiding the catalyst. The catalyst in all of the experimental runs was sulfided during a cool down cycle of the reactor except for Run 9 which was sulfided during a heat up cycle. During calcination and sulfiding, there was a swing in the temperature of the catalyst as recorded by a strip recorder. This was due to the temperature controller overshooting the setpoint. Therefore, the catalyst of Run 9 was at a lower temperature than the other runs when the sulfiding process began. Other than this difference in sulfiding, the operating procedure and conditions were the same.

Due to this difference in sulfiding, Run 7 will be used for comparison.

Experimental Run 7 and Run 8

Run 8 was operated at a temperature of 375°C (707°F) to investigate the effect of temperature on the hydrogenation of Tetralin. As seen in Figure 23, the conversion increased from about 42% overall to about 52% overall. This effect of temperature on hydrogenation of Tetralin was expected, but the degree of the increase was not known. Tscheikuna

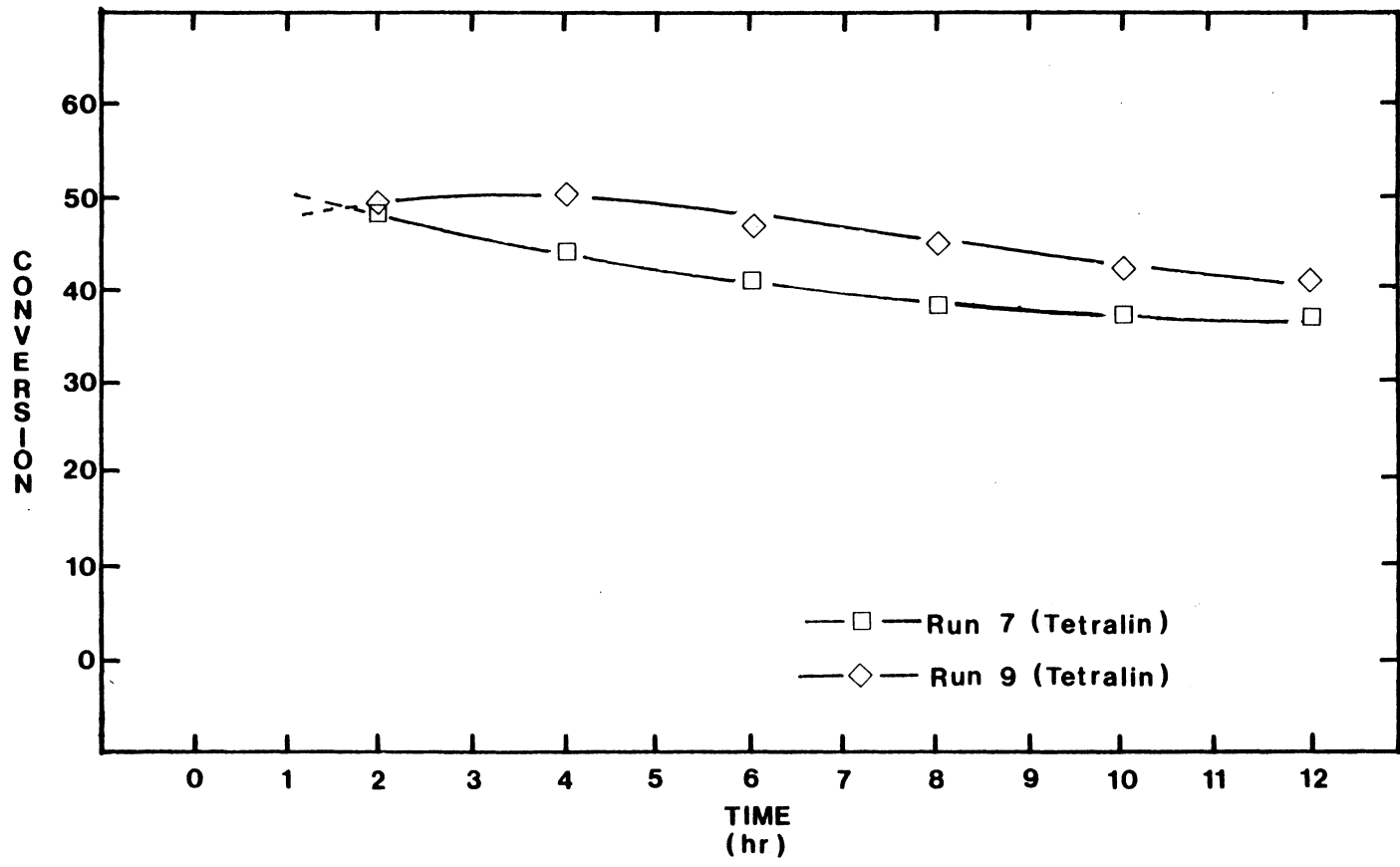


Figure 22. Comparison of Conversion of Tetralin as a Function of Time of Runs #7 and #9 (Duplicate Runs)

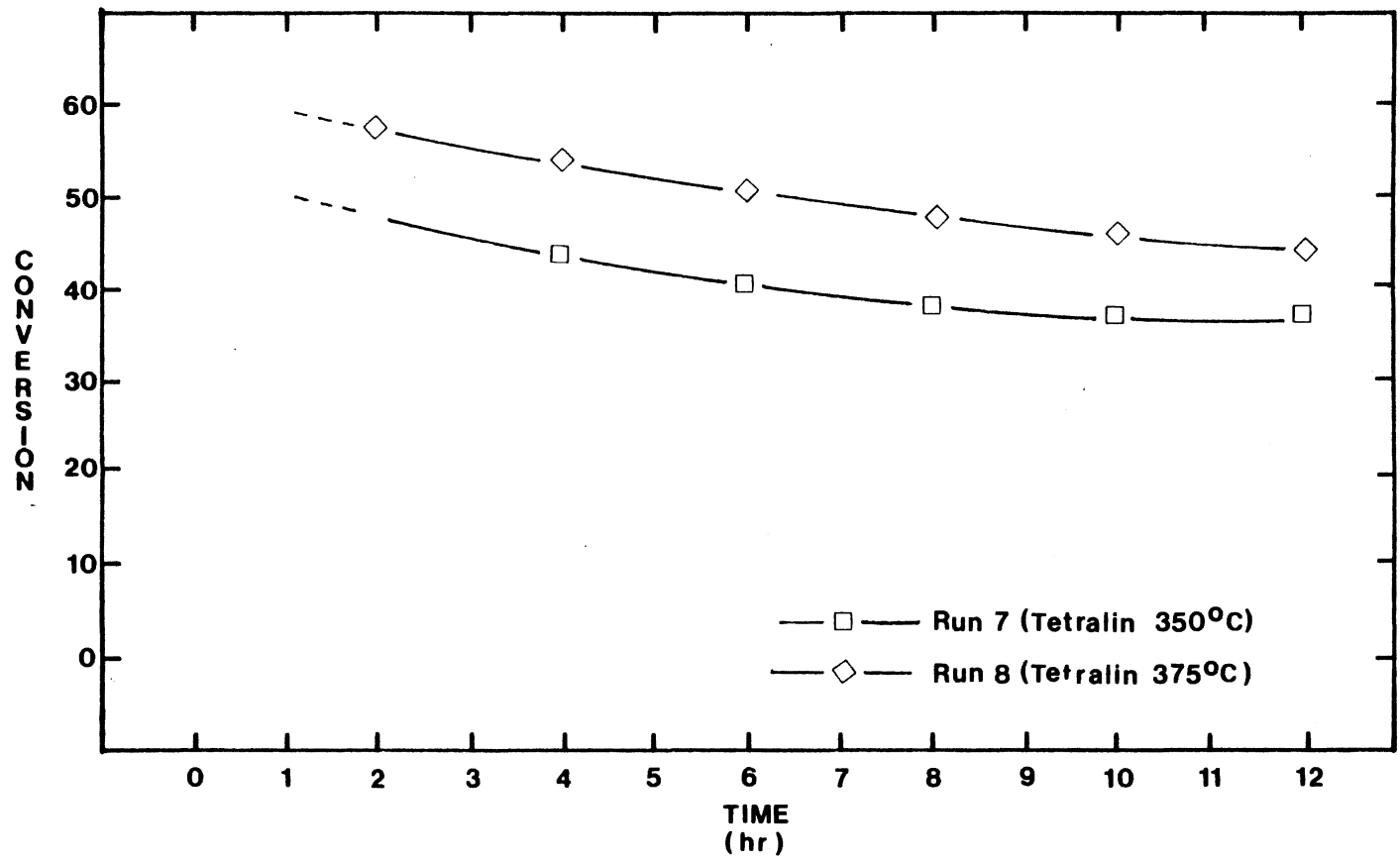


Figure 23. Comparison of Conversion of Tetralin as a Function of Time of Runs #7 and #8

(29) reported an increase in the conversion of Tetralin to the hydrogenated products with an increase in the temperature.

Experimental Run 7 and 10

Run 10 had the same operating conditions as Run 7 except for the feedstock. The feedstock for Run 10 was Tetralin and 5 wt% phenanthrene. Phenanthrene is considered to have a higher tendency to coke the catalyst, therefore, the conversion of Tetralin in the presence of phenanthrene should be lower. As seen in Figure 24, the conversion was lower. This agrees with the observations of Tscheikuna (29) in his trickle bed reactor experiments.

The conversion of phenanthrene to the hydrogenated products was complete. The GC did not detect any presence of phenanthrene, but several peaks that were not present in the previous runs were present. These peaks were assumed to be phenanthrene hydrogenated products. No further attempt was made to identify or quantify these peaks.

Experimental Run 10 and Run 11

Run 10 and Run 11 were identical experimental runs except for the feedstock. The feedstock for Run 10 was Tetralin and 5 wt% phenanthrene and for Run 11 the feedstock was Tetralin, 5 wt% phenanthrene and 100 ppm titanium as Titanocene dichloride. Chan (25) concluded that the addition of Titanocene dichloride would improve the hydrotreatment of coal liquids and reduce the formation of coke. However, as seen in Figure 25, there is no appreciable difference in the two runs. Tscheikuna (29) in a trickle bed experiment also did not see any conversion improvement by the addition of titanocene dichloride.

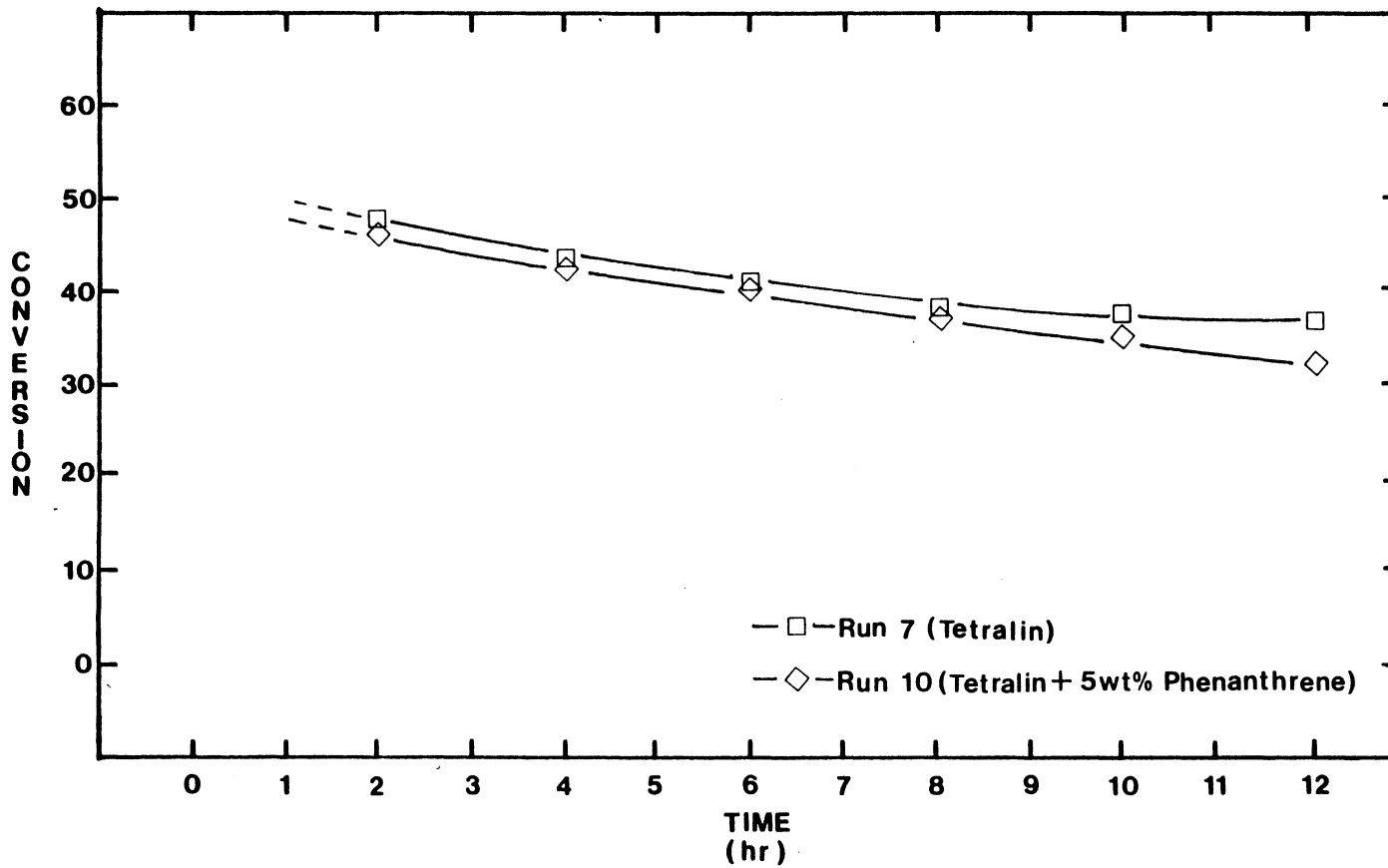


Figure 24. Comparison of Conversion of Tetralin as a Function of Time of Runs #7 and #10. Conversion of Phenanthrene was 100%

Experimental Run 7 and Run 12

Run 12 had a feedstock which was Tetralin and 100 ppm titanium as Titanocene dichloride and the operating conditions were the same as Run 7. As seen in Figure 26, the conversion of Tetralin was enhanced, yet the degree of the slope of the conversion was also increased. This may be due to the enhancement factor of Titanocene dichloride in the initial hydrogenation process and being later suppressed by deposition of titanium on the catalyst.

Catalyst Analysis

The coke formation on the catalyst of all the experimental runs excluding Runs 5 and 7 was statistically the same. The procedure for measuring the coke content is somewhat questionable. The procedure used later revealed that the changing of the metals from the sulfided state to the oxide state was not accounted for. Also, the weight of water initially present was not accounted for either. Therefore not too much emphasis will be placed on the coke content.

The pore volume and the most frequent pore diameter yielded some interesting points. The trend for the pore volume and the most frequent pore diameter was an increase in both the spent catalyst samples and the regenerated catalyst samples. This trend is due to the removal of the carbonaceous material which blocks the pores and reduces the pore volume and the pore diameter. However, the comparison of pore volumes from individual runs did not give any information. The range of each sample was near or included the overall average. The same thing held true for the most frequent pore diameter except for the last three runs which showed a downward shift. However, Run 10 did

not have any titanium present and the pore diameter still decreased. At the same time, the surface area for these three runs increased and the remaining did not. There is some interdependency between the surface area and the most frequent pore diameter, which is related to the surface area, pore volume and most frequent pore size being derived from the same data.

This surface area for the remaining runs is statistically the same and did not change from the spent catalyst samples and the regenerated samples. The regenerated samples are not shown because both spent and regenerated catalyst samples showed almost the same values of surface area.

Visual inspection of the catalyst samples from Run 11 and 12 which had Titanocene dichloride in the feedstock showed a blue deposit on the catalyst. This is due to the titanium compound depositing on the catalyst during the hydrogenation process. The internals of the reactor, the walls and the impeller, also had this same blue deposit present.

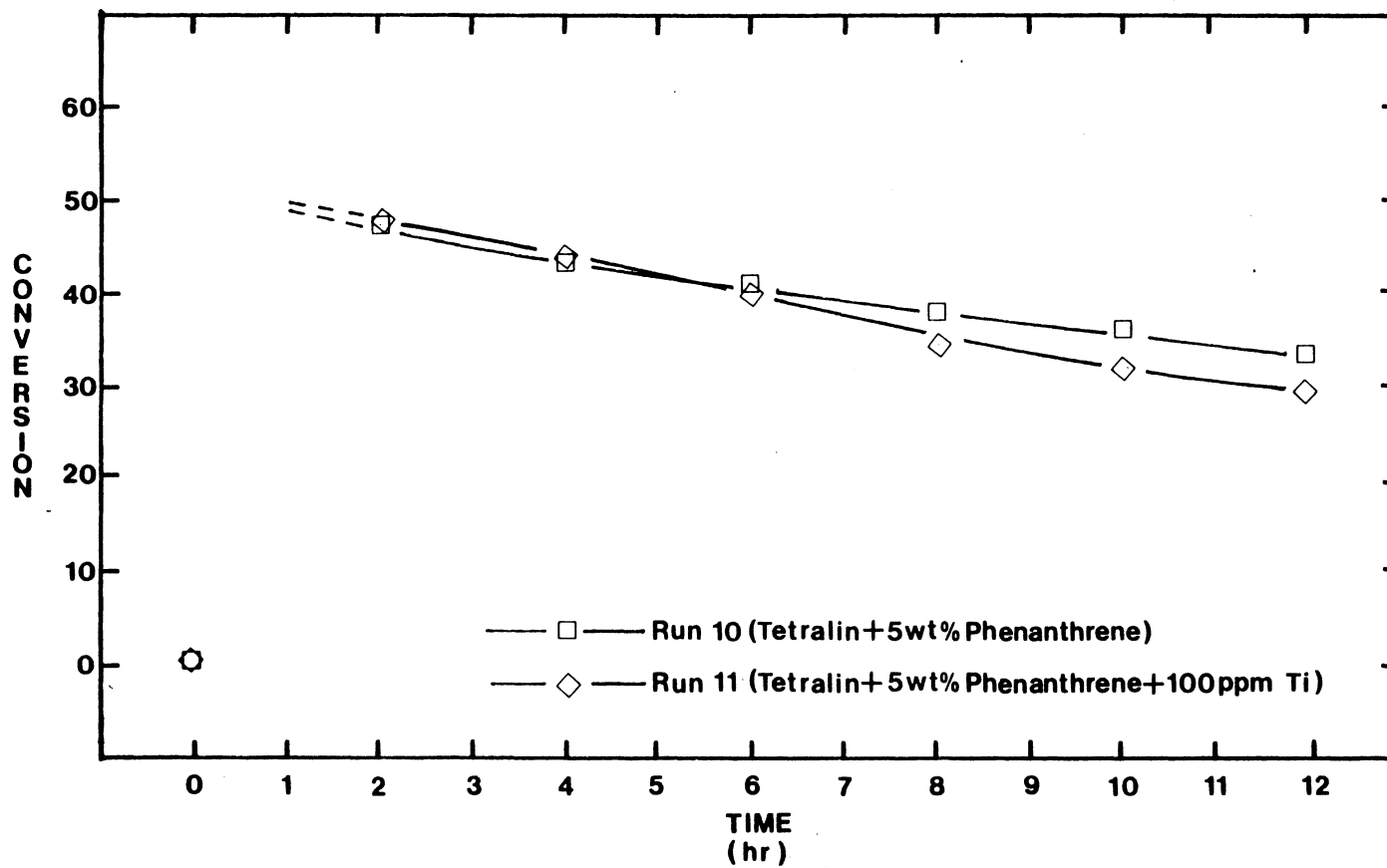


Figure 25. Comparison of Conversion of Tetralin as a Function of Time of Runs #10 and #11. Conversion of Phenanthrene was 100%

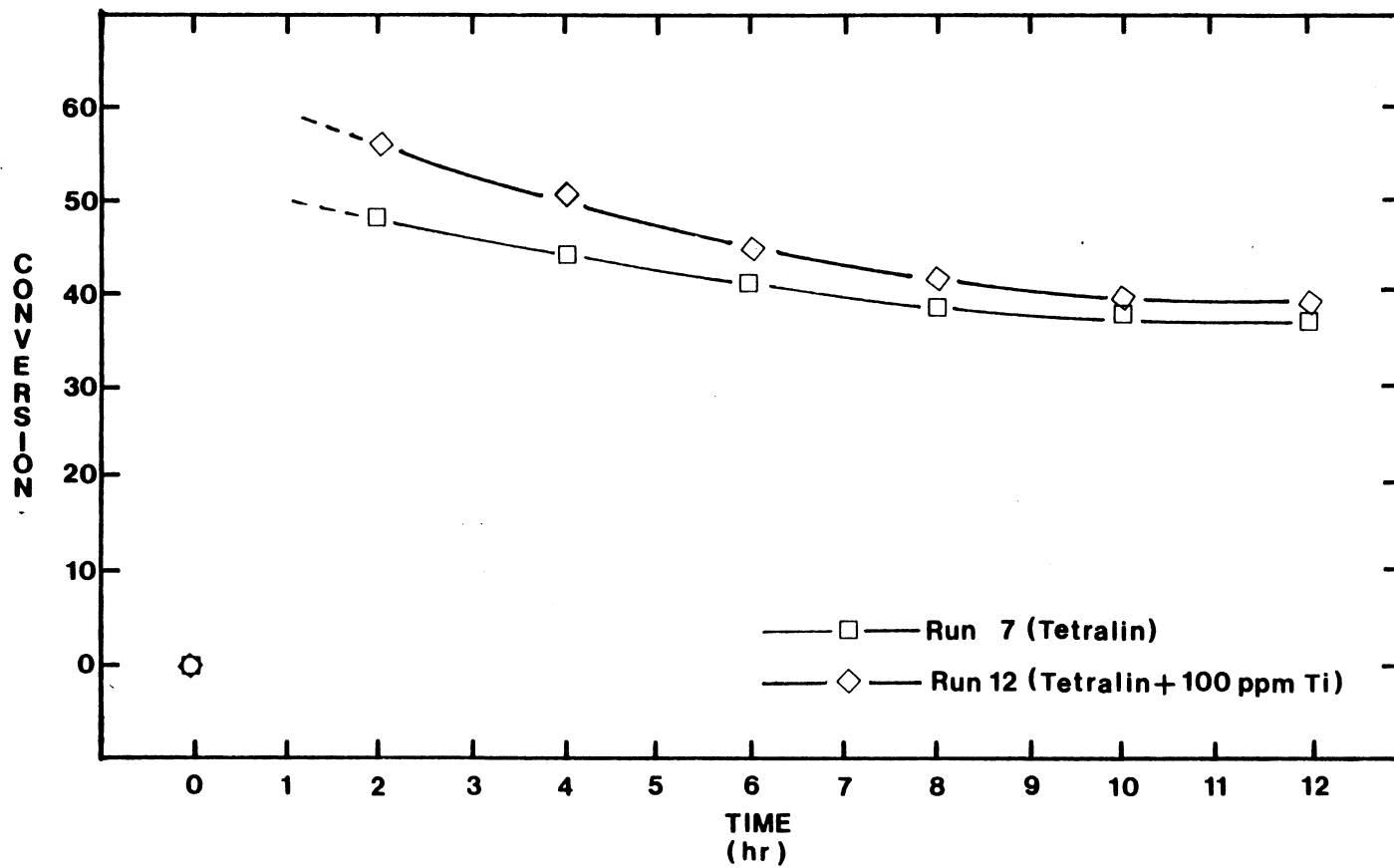


Figure 26. Comparison of Conversion of Tetralin as a Function of Time of Runs #7 and #12

Accomplishments, Preliminary Conclusions, Conclusions and Recommendations

Accomplishments

1. The design, construction and operation of the gradientless reactor system.

Preliminary Conclusions

1. The titanium compound, Titanocene dichloride, seemed to increase the hydrogenation of Tetralin using a Ni/Mo alumina catalyst.

2. An increase in the reactor temperature appeared to increase the hydrogenation of Tetralin.

3. The temperature of sulfidation seemed to have an effect on the hydrogenation and deactivation of the catalyst.

4. When Titanocene dichloride is in the presence of phenanthrene, titanium seemed to more readily penetrate the catalyst.

5. Titanocene dichloride does not appear to enhance the hydrogenation of Tetralin when in the presence of phenanthrene.

Conclusion

1. The optimum magne-drive stirrer speed for reducing to a minimum or eliminating the heat and mass transfer effects can be found by measuring the maximum conversion for a set speed. For this system, the magne-drive stirrer speed was 1500 rpm.

Recommendations

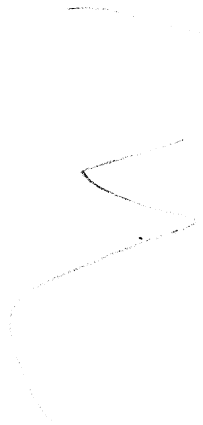
1. Conduct the same studies sulfiding at various temperatures, 225°C (437°F) and 275°C (527°F), to investigate the effects on the hydrogenation and catalyst deactivation.
2. Divide the catalyst basket into not only horizontal sections but also vertical sections to check the uniformity of coking in the catalyst basket.
3. Hydrogenate Tetralin and Tetralin/phenanthrene at different concentrations and at various temperatures to investigate fully the effects of temperature.

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APPENDICES



APPENDIX A

COMPONENTS OF HYDROGENATION UNIT

Reactor System

The Hydrogenation Reactor system consists of five sections: 1) the gas feed section, 2) the liquid feed section, 3) the reactor section, 4) the product separation section and 5) the control panel.

Gas Feed Section

The gas feed section allows either nitrogen, hydrogen or hydrogen sulfide to be supplied to the reactor section. Nitrogen can be supplied using a Victor 2-Stage regulator to the reactor and the product separation section for initial start-up, sampling and scrubbing of the sample. Hydrogen can be supplied to the reactor section using a Victor 2-Stage regulator for on-line operation only. Hydrogen sulfide is supplied using a Victor 2-Stage regulator to the reactor section for sulfiding of the catalyst. The gas delivery system pressure is more accurately regulated by a Mighty-Mite pressure reducing regulator. The maximum supply pressure for nitrogen and hydrogen is 13.9 MPa (2000 psig) and is 1.48 MPa (200 psig) for hydrogen sulfide.

Liquid Feed Section

The liquid feed section supplies liquid hydrocarbon feed to the reactor. The pump, a Milton Roy Model 396-57 positive displacement pump, can supply liquids up to 34.5 MPa (5000 psig) with a variable flow rate of 8.06×10^{-9} - 8.08×10^{-8} m³/s (29-290 cm³/H). This section is protected by two rupture discs in series so accidental

over pressure can be handled. The rupture pressures are 17.5 MPa (2525 psig) and 24.9 MPa (3593 psig) respectively. The feed tank is a graduated buret with a capacity of 500 cm³ and in increments of 5 cm³.

Reactor Section

The reactor section consists of the reactor and the stirrer. The reactor is an Autoclave Engineers 76.4 mm (3 in.) 316 stainless steel gradientless catalytic reactor with Berty internals. The reactor has an approximate volume of 300 cm³ and can hold a maximum of 100 cm³ of catalyst. The reactor is rated for 24.2 MPa (3500 psig) at 538°C (1000°F) with seven ports: one gas inlet and one liquid inlet both located at the bottom of the reactor, two thermocouples (J-type), one rupture disc outlet, one product outlet and a drain. The stirrer is an Autoclave Engineers Magnedrive-II with a maximum allowable working pressure of 24.4 MPa (3520 psig), a maximum speed of 3000 rpm and a maximum power of 570 W (0.76 HP) which is cooled by a water jacket.

Product Separation Section

The product separation section is composed of a series of Hoke sampling cylinders rated at 31.1 MPa (4500 psig). There are two 500 cm³ and two 300 cm³ 316 stainless steel and one 1000 cm³ 304 stainless steel cylinders. The product from the reactor section is fed to the two 500 cm³ cylinders for separation of the liquids and the gases. The liquids collected in the first two cylinders are transferred to a 300 cm³ cylinder when a sample is desired. The gases are throttled to atmospheric pressure and any liquid knock out is collected in a

300 cm³ cylinder. The flow rate of gases is measured by a Brooks Sho Rate Model 1355 rotameter, then the exit gas is scrubbed in the 1000 cm³ cylinder with a sodium hydroxide solution. The sampling can be accomplished remotely by using Skinner solenoid valves Model 52V rated for 20.7 MPa (3000 psi) differential pressure, which are labeled 1A, 2A and 3A in Figure 1.

Control Panel Section

The control panel section is located inside the laboratory and is for remote control of the hydrogenation unit, samplings and pressure and temperature measurements. The control panel has five U.S. Gauge Solfrunt process gauges Model 1981 made of 316 stainless steel. There are four 24.1 MPa (3500 psig) and one 15.2 MPa (2200 psig) gauges. The 15.2 MPa (2200 psig) gauge is for more accurately measuring the reactor pressure. Also, included on the control panel is an Autoclave Engineers temperature controller, an Autoclave Engineers Magnedrive-II speed controller, the pump power switch and the solenoid valve switches.

APPENDIX B

EXPERIMENTAL PROCEDURE

The experimental procedure for the hydrogenation experiments conducted in this thesis consists of the following: catalyst preparation and assembly of the catalyst basket, pressure check procedures, calcination, sulfiding, start-up of liquid and gas flow, sampling, shut down and catalyst removal and clean-up.

Catalyst Preparation and Assembly of the Catalyst Basket

The catalyst is precalcined at 110°C (230°F) for two hours in an oven before each experimental run. The catalyst is loaded according to the following procedures.

1. Put the bottom screen and thermocouple well in the bottom of the Berty basket. The bottom screen must be flat on the bottom. On the outside of the catalyst basket under one of the support ears is inscribed an "N". The thermocouple well should be in line, looking down from the top, with the first vein to the left.
2. Pour in the desired catalyst.
3. Put in the top screen, Mesh 20, in the top of the basket approximately 0.32 cm (1/8 inch) down.
4. Put on top of the catalyst basket the large screen. Note: The large screen will not fit inside of the catalyst basket.
5. Place the catalyst basket into the reactor with the inscribed "N" support ear closest to the wall or back of the reactor stand.
6. Replace the cap gasket. The side of the gasket has inscribed an arrow and "up". Place the gasket with the arrow pointing up.

7. Install the catalyst thermocouple (longest thermocouple) into the cap port. There is one port with a larger hole than the other three. Thermocouple well should be in this port.
8. Place the thermocouple into the thermocouple well and slowly lower the cap. A slight turning of the cap may be necessary to align the thermocouple well and the port. Remove the thermocouple.
9. Align the cap screw holes.
10. Use a small amount of Silver Goop on the threads on the reactor, not on the threads of the bolts.
11. Tighten each bolt to 60 ft-lbs, if the gasket has been used. For a new Gasket, tighten to 90 ft-lbs for the first time only. Tighten the bolts diametrically opposite of each other.
12. Use a small amount of Silver Goop on the threads of the ports in the reactor cap, not on the gland threads.
13. Place the insulation cap on top of the reactor cap.
14. Install both thermocouples, product outlet line and the rupture disc line.
15. Tighten the glands.

Pressure Check Procedures

1. Close all valves.
2. Open valves #21, 4, 5, 3A, 3C, 14, 23, 24.
3. Set the pressure on the nitrogen regulator to 10.4 MPa (1500 psig).
4. Open slowly the nitrogen regulator outlet valve to allow the system to pressurize.
5. Close all valves, except #23, 24.
6. Allow the system to set for twelve hours. A pressure drop of

35kPa (5psi/hour) is an acceptable drop due to leaks. Note: An ambient temperature change of 10°C will translate to a pressure change of approximately 345kPa (50psi).

7. If the pressure drop due to leaks is greater than 35kPa/hour (5psi/hour), use Snoop to detect any leaks. Do not use a soapy solution. The most probable areas due to leaks are the reactor gasket, if not clean, the glands or the product line where it connects to the solenoid valve #3A.

Calcination

1. Close all valves.
2. Open valves #4, 6, 3A, 3C, 14, 17, 18, 21, 23, 24.
3. Start the water flow for the cooling jacket.
4. Turn the temperature controller on and set the following parameters:
 1. Furnance output to 90% of maximum output.
 2. Furnance setpoint to 150°C above the desired calcination temperature. Do not exceed 390°C because the alarm will trip and will shut off the temperature controller. The alarm can be set to a higher temperature, but is not recommended.
5. When the specimen temperature is at the desired setting, start the nitrogen flow at 400 cm³/min at 1.72 MPa (250 psig) for two hours. The flow can be controlled by valve #15 and measured by the wet test meter. Approximate rotameter setting is 12% of maximum flow.
6. After two hours, close valve #6 and depressurize the system to atmospheric pressure.
7. Calcination is complete and the catalyst is ready for sulfiding.

Sulfiding

1. Turn on the hydrogen sulfide detector and place on the reactor stand away from the reactor.
2. Open valves #7, 19 and close valves #18, 23, 24.
3. Start the hydrogen-hydrogen sulfide mixture flow at 552kPa (80 psig) and a flow rate of 400 cm³/min for one hour. Maintain a specimen temperature of 250°C. Note: There can be a specimen temperature rise due to sulfiding.
4. After one hour, close the hydrogen-hydrogen sulfide cylinder and allow the system to depressurize to atmospheric pressure.
5. After the pressure drops to atmospheric pressure, close valve #7 and the hydrogen-hydrogen sulfide regulator outlet valve.
6. Open valve #6 and purge the system with nitrogen at 1.72MPa (250 psig) and a flow rate of 400 cm³/min.
7. Sulfiding is complete and ready for heating up to the desired operating temperature.

Start of Liquid and Gas Flow

1. Set the specimen temperature to the desired operating temperature which must be below 390°C.
2. Set the furnace setpoint to 150°C above the specimen temperature.
3. Allow the system to reach thermal equilibrium.
4. When at thermal equilibrium, close valves #3A, 2A, 15, 21.
5. Open valve #4.
6. Set the hydrogen regulator pressure to 10.4 MPa (1500 psig) and slowly open the hydrogen regulator outlet valve to pressurize the gas feed and reactor section. The hydrogen regulator may

need to be adjusted slightly to achieve the operating pressure of 10.4 MPa (1500 psig). Note: The reactor section must be pressurized before the separation section.

7. Set the nitrogen regulator to 10.4 MPa (1500 psig) and slowly open the nitrogen regulator outlet valve.
8. Open valve #10 to pressurize the product separation section to 10.4 MPa (1500 psig).
9. Open valve #3A, 2A and adjust valve #15 to the desired flow rate.
10. Fill the feed tank.
11. Open the feed tank valve and valve #8 and 9.
12. Turn on the pump power switch. The pump pressure will slowly rise until it reaches 172kPa (25 psi) above the operating pressure.
13. The liquid flow rate can be adjusted by the mic on the pump.
14. Set the magne drive speed to the desired speed.
15. The system is on line.

Sampling

1. Put the sampling jar under the liquid sample product outlet line.
2. Make sure valve #12 is closed.
3. Close valve #3, 2A.
4. Open valve #1A; the pressure P2 and P3 will drop.
5. Close valve #1A.
6. Open valve #10 to pressurize the product separation section. The pressure P2 and P3 needs to be exactly the same as P1. The nitrogen regulator can be adjusted so P2 and P3 will be the same as P1.
7. After P2 and P3 reach 10.4 MPa (1500 psig), close valve #10 and open valve #3A, 2A.

8. The system is back on line.
9. Open valve #12 slowly to allow the liquid product into the sample jar. A pressure gauge is located on the sample bomb to allow the operator to know when all the sample is out.
10. Close valve #12.
11. Measure the volume and pour into the sample jar and label.

Shutdown

1. After the last sample has been taken, turn off the pump, the magne-drive and the furnace output.
2. Allow the system to cool down to 250°C (482°F) while under a hydrogen atmosphere at 10.4 MPa (1500 psig).
3. When the specimen temperature reaches 250°C (482°F), the system can be depressurized to 1.38 MPa (200 psig) by closing the hydrogen cylinder.
4. Keep the flow rate of the exit gas constant by adjusting valve #15.
5. When the system pressure reaches 1.38 MPa (200 psig), close the hydrogen regulator outlet valve and set the nitrogen regulator to 1.72 MPa (250 psig).
6. Open valve #21 slowly to pressurize the system with nitrogen.
7. Set the flow rate to 400 cm³/min or 12% of maximum flow on the rotameter.
8. Keep the system under nitrogen until the system is completely cooled down. Approximately twelve hours.
9. After the system has completely cooled down, completely depressurize the system by closing the nitrogen cylinder valve.

10. The system is ready to be opened up for removal of catalyst and clean up.

Catalyst Removal and Clean Up

1. After the system has been depressurized, remove the two thermocouples, the rupture disc line and the product outlet line.
Note: Slowly loosen the glands to make sure the reactor is not accidentally under pressure.
2. Remove the insulation cap.
3. Remove the eight cap screws. A hammer may be used to break loose the cap screws.
4. Remove the cap of the reactor.
5. Remove the catalyst basket and the top screens.
6. Pour the catalyst into a sample jar and label.
Note: The following three steps should be done under the hood and goggles, rubber gloves and an apron should be worn.
7. In a stainless steel can mix up a strong sodium hydroxide solution (NaOH).
8. Place in the strong sodium hydroxide solution, the cap, the cap screws, the gasket, the product line and the rupture disc line. This is to remove any char and residual Silver Goop. Allow to soak for a couple of hours.
9. Rinse the items with hot water well and dry off. The items will feel soapy if all the sodium hydroxide solution is not rinsed off.
10. Drain the magne drive by removing the plug in the bottom of the magne drive.

11. Close valve #3A, 3B, 3C, 6.
12. Set the nitrogen regulator to 1.72 MPa (250 psig) and open the nitrogen regulator outlet valve.
13. Open valve #10 to pressurize the product separation section. Close valve #10 after pressurized.
14. Open valve #1B, 1C to drain the separation section of any residual liquid.
15. Open valve #12 to drain out the residual liquid into the sample jar and depressurize the product separation section.

APPENDIX C
ELEMENTAL ANALYZER AND GAS CHROMATOGRAPHIC
COMPARISON

In the analysis of the liquid samples, both the Varian Chromatograph and the Perkin Elmer Elemental Analyzer were used. By knowing all or the major peaks in the chromatogram, an atomic ratio (H/C) could be calculated by the following equation and compared to the data from the Perkins Elmer Analyzer

$$(H/C) \text{ Calculated} = \frac{\sum \frac{C_i * H}{M_{wi}}}{\sum \frac{C_i * C}{M_{wi}}}$$

where C_i = Component i area percent

H = The number of hydrogen atoms

C = The number of carbon atoms

M_{wi} = The molecular weight of component i

This technique was used to provide a check between the two instruments. At first, there was good agreement between the two instruments until Run #4 Sample #6 at which time an 11% difference appeared. The difference between Run #4 Sample #5 and Sample #6 is the operator of the elemental analyzer stopped analyzing the first batch of samples, Run #1 Sample #1 thru Run #4 Sample #5, and allowed a period of a few days to pass before analyzing another set of samples, Run #4 Sample #6 thru Run #5 Sample #5. All the samples included in this batch had a difference of about 9%. The third batch of samples analyzed Run #5 Sample #6 thru Run #8 Sample #6 all showed a difference of approximately 18%. See Tables VII and XIII and Figures 27 thru 34.

Two conclusions can be drawn, one, there should be a method for checking the results of an instrument. Second, the Perkins Elmer Analyzer proves to be an unreliable instrument, especially when actual coal liquids are used and a gas chromatograph is impractical since all the compounds can not be identified. Therefore, when using the elemental analyzer only, either all the samples should be done at one time or when done at separate time, a previously ran sample be analyzed again to check the machine.

The results throughout this thesis are based on the gas chromatographic and analysis the elemental analyzer is used as a check for the gas chromatograph.

TABLE X
ATOMIC RATIO COMPARISON

<u>Run #</u>	<u>Sample #</u>	<u>H/C Atomic Ratio</u>		<u>Percentage Difference</u>
		<u>Measured</u>	<u>Calculated</u>	
1	0	1.194	1.197	0.31
1	1	-	-	-
1	2	-	-	-
1	3	1.360	1.365	0.33
1	4	1.359	1.370	0.75
1	5	1.373	1.367	0.47
1	6	1.382	1.364	1.30
2	1	1.436	1.422	1.00
2	2	1.462	1.444	1.18
2	3	1.447	1.440	0.51
2	4	1.420	1.432	0.87
2	5	1.431	1.425	0.46
2	6	1.429	1.424	0.37
3	1	1.456	1.470	0.97
3	2	1.516	1.479	2.43
3	3	1.507	1.475	2.10
3	4	1.512	1.482	2.01
3	5	1.454	1.460	0.44
3	6	1.429	1.430	0.10
3	7	1.425	1.420	0.35
4	1	1.461	1.443	1.28
4	2	1.483	1.441	2.82
4	3	1.462	1.438	1.63
4	4	1.433	1.428	0.33
4	5	1.419	1.419	0.00
4	6	1.262	1.412	11.95

TABLE X (continued)

<u>Run #</u>	<u>Sample #</u>	<u>H/C Atomic Ratio</u>		<u>Percentage Difference</u>
		<u>Measured</u>	<u>Calculated</u>	
5	1	1.404	1.476	5.11
5	2	1.338	1.472	10.02
5	3	1.327	1.455	9.65
5	4	1.327	1.450	9.23
5	5	1.334	1.441	8.05
5	6	1.172	1.432	22.11
6	1	1.223	1.446	18.21
6	2	1.194	1.436	20.29
6	3	1.216	1.432	17.79
6	4	1.235	1.424	15.29
6	5	1.215	1.417	16.67
6	6	1.201	1.408	17.21
7	1	1.272	1.467	15.29
7	2	1.216	1.450	19.27
7	3	1.249	1.438	15.14
7	4	1.179	1.424	20.83
7	5	1.208	1.418	17.36
7	6	1.185	1.414	19.33
8	1	1.284	1.501	16.88
8	2	1.260	1.484	17.79
8	3	1.244	1.465	17.77
8	4	1.231	1.454	18.11
8	5	1.217	1.437	18.08
8	6	1.218	1.432	17.57

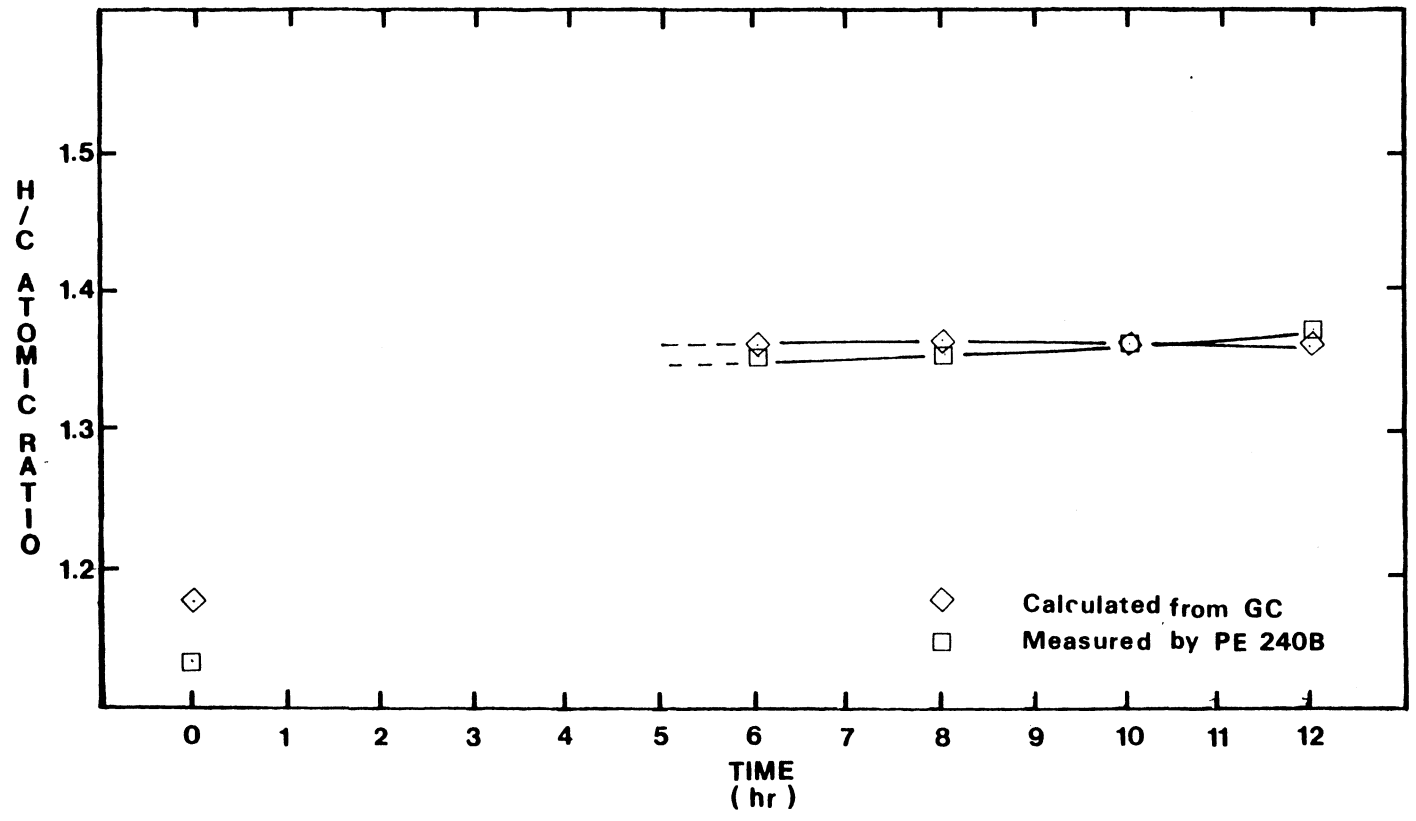


Figure 27. Comparison of the Calculated and Measured H/C Atomic Ratio for Run #1

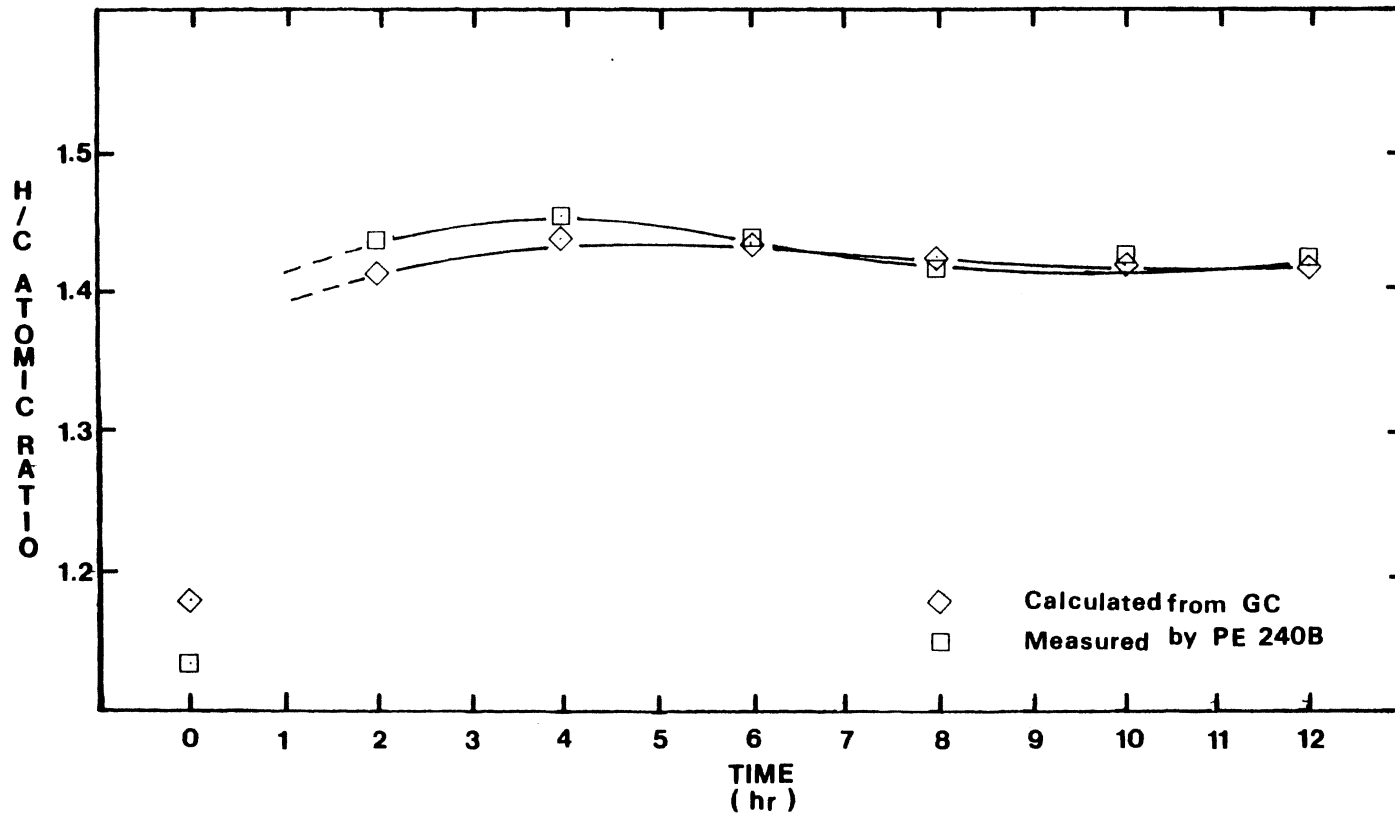


Figure 28. Comparison of the Calculated and Measured H/C Atomic Ratio for Run #2

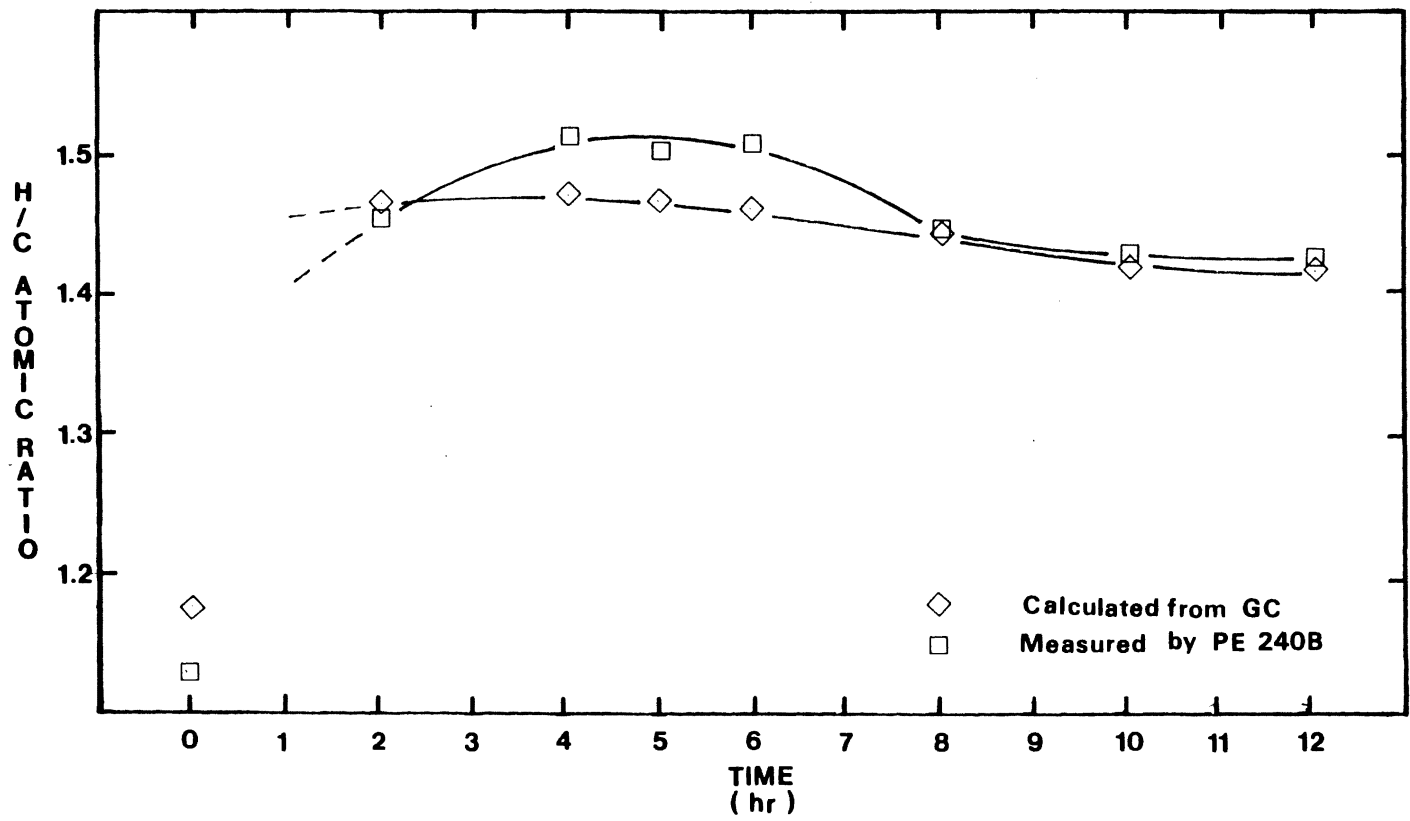


Figure 29. Comparison of Calculated and Measured H/C Atomic Ratio for Run #3

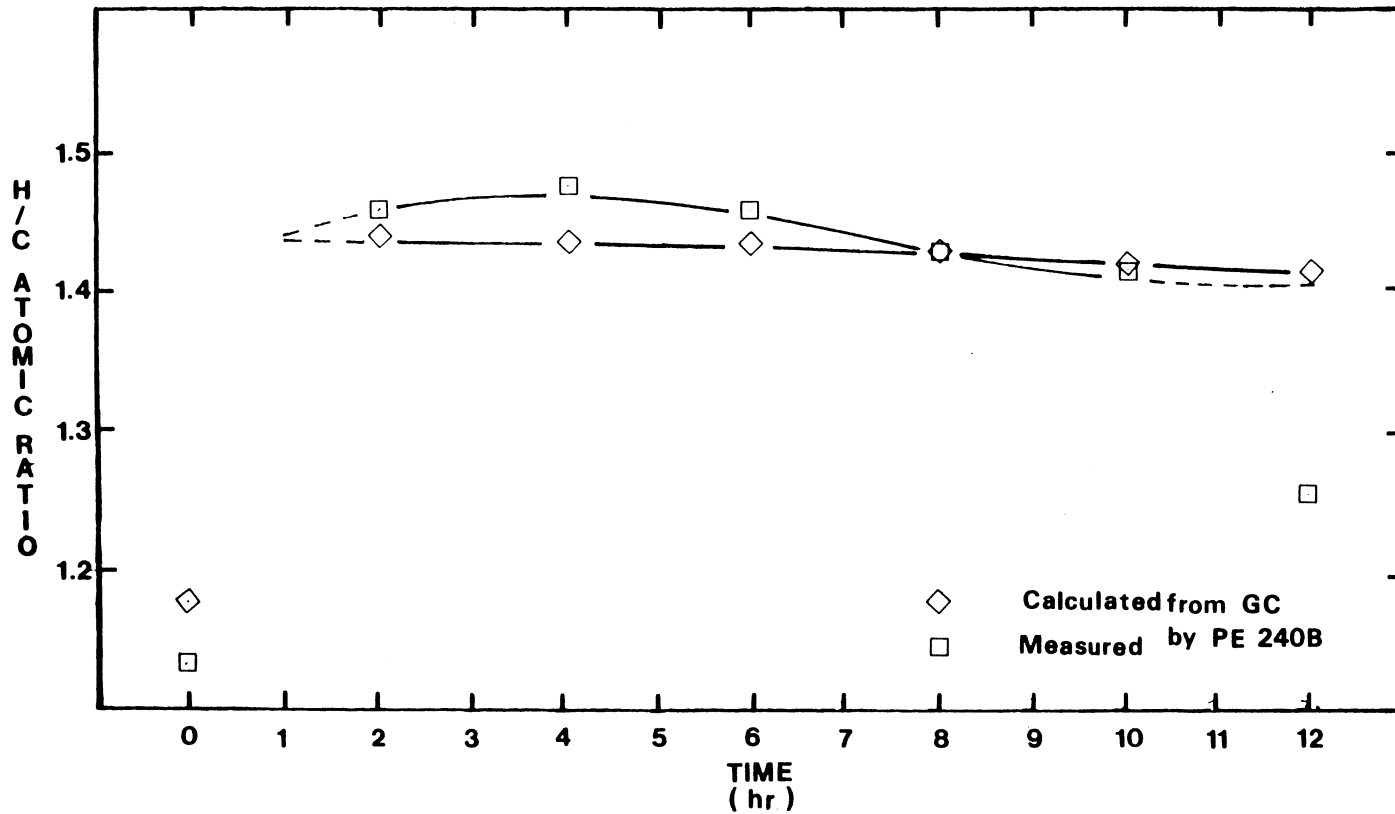


Figure 30. Comparison of Calculated and Measured H/C Atomic Ratio for Run #4

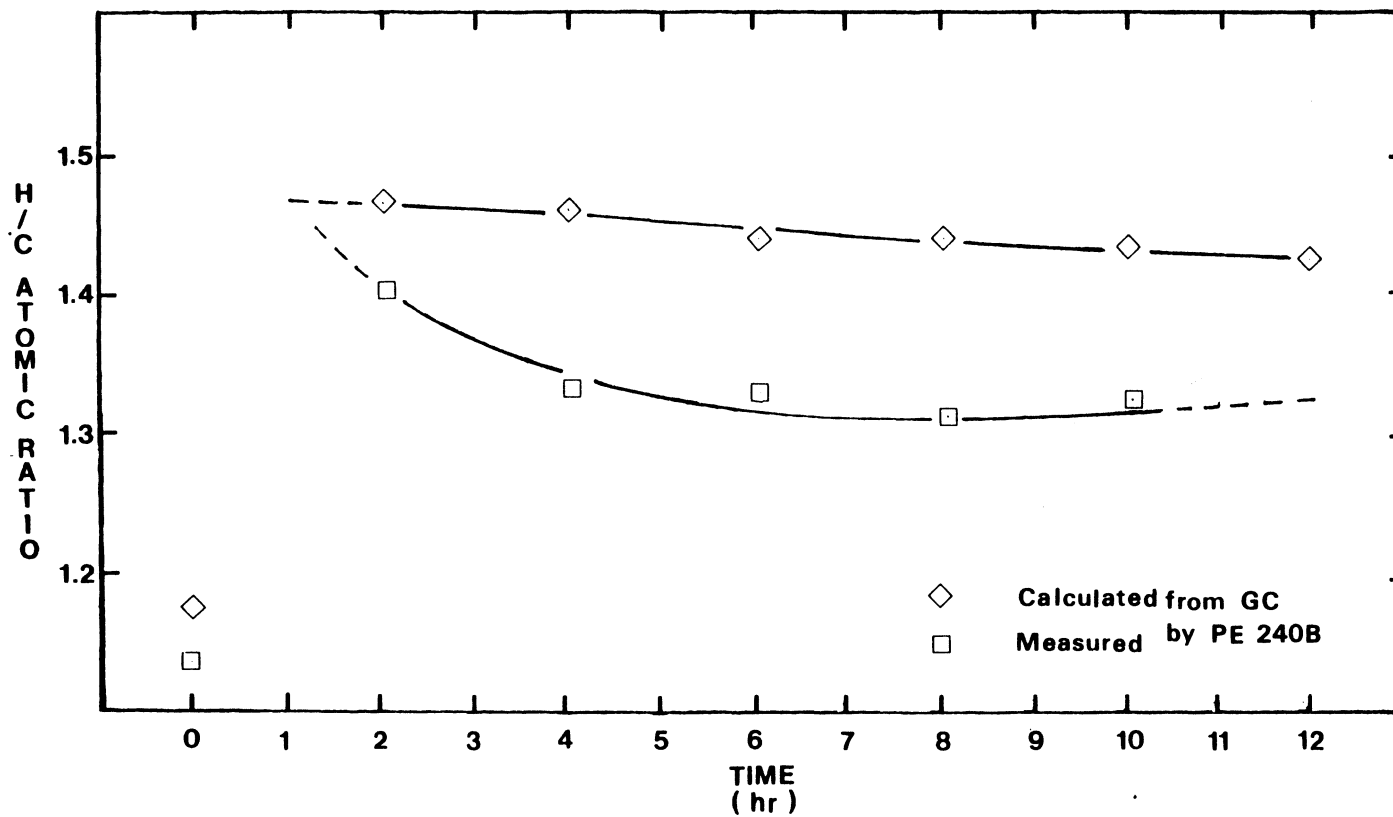


Figure 31. Comparison of Calculated and Measured H/C Atomic Ratio for Run #5

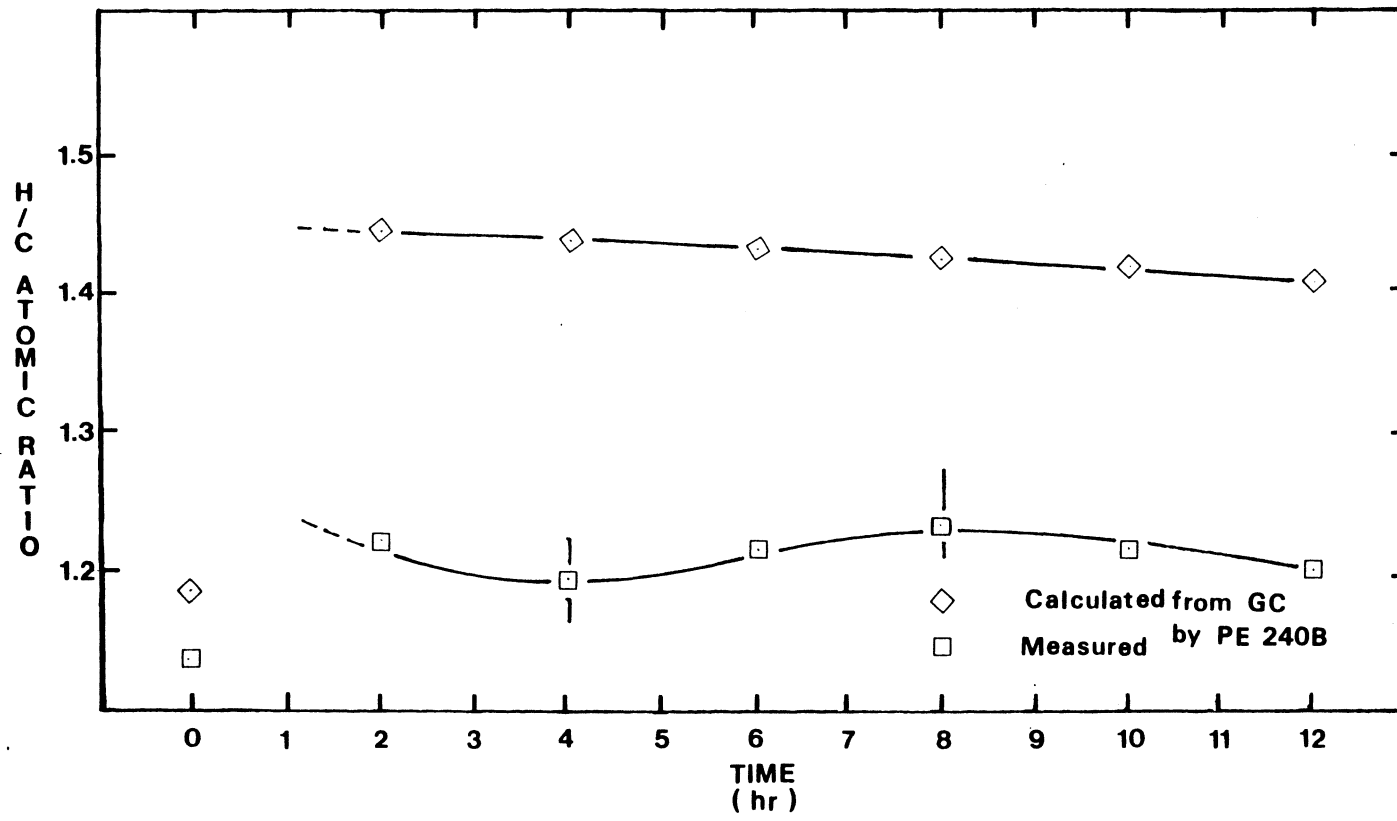


Figure 32. Comparison of Calculated and Measured H/C Atomic Ratio for Run #6

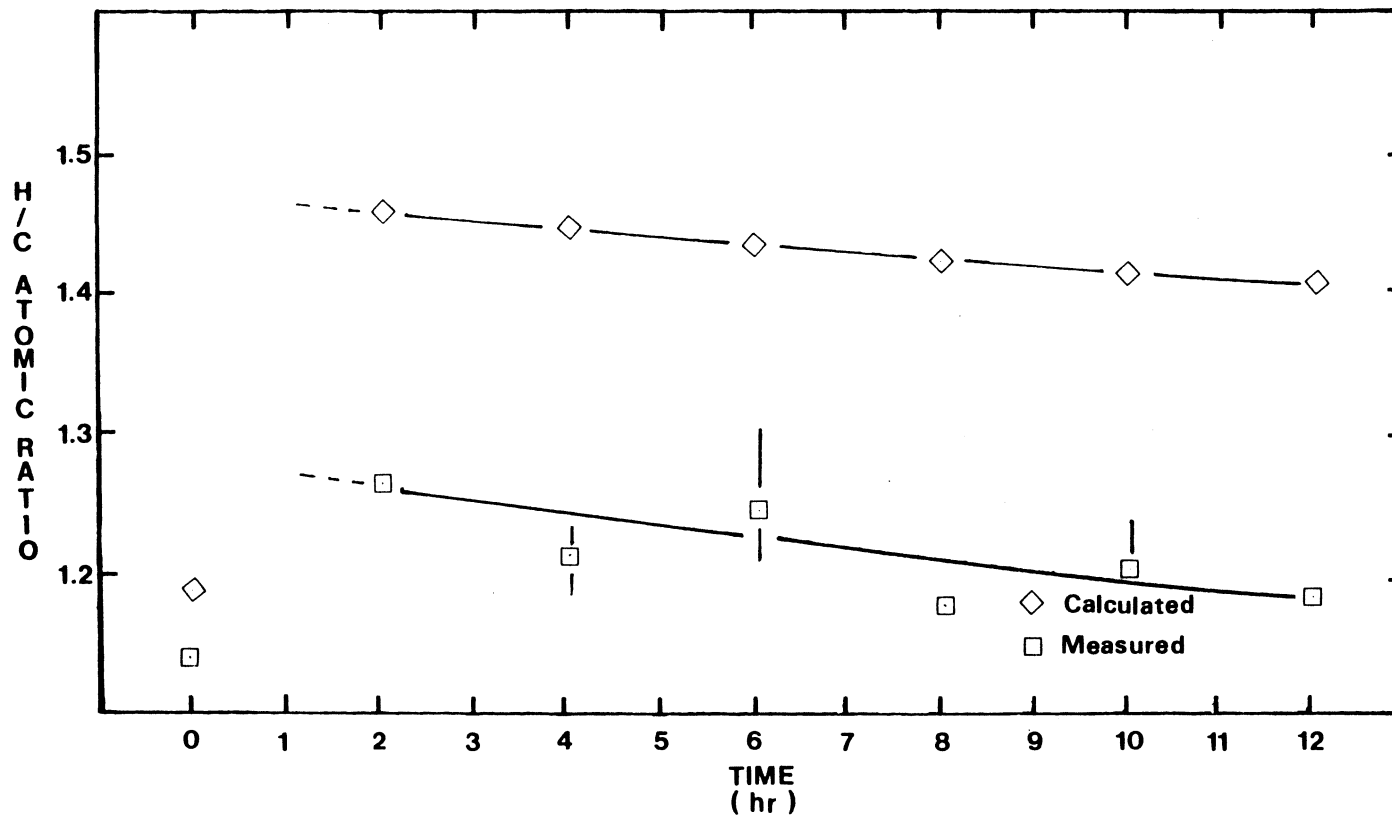


Figure 33. Comparison of Calculated and Measured H/C Atomic Ratio for Run #7

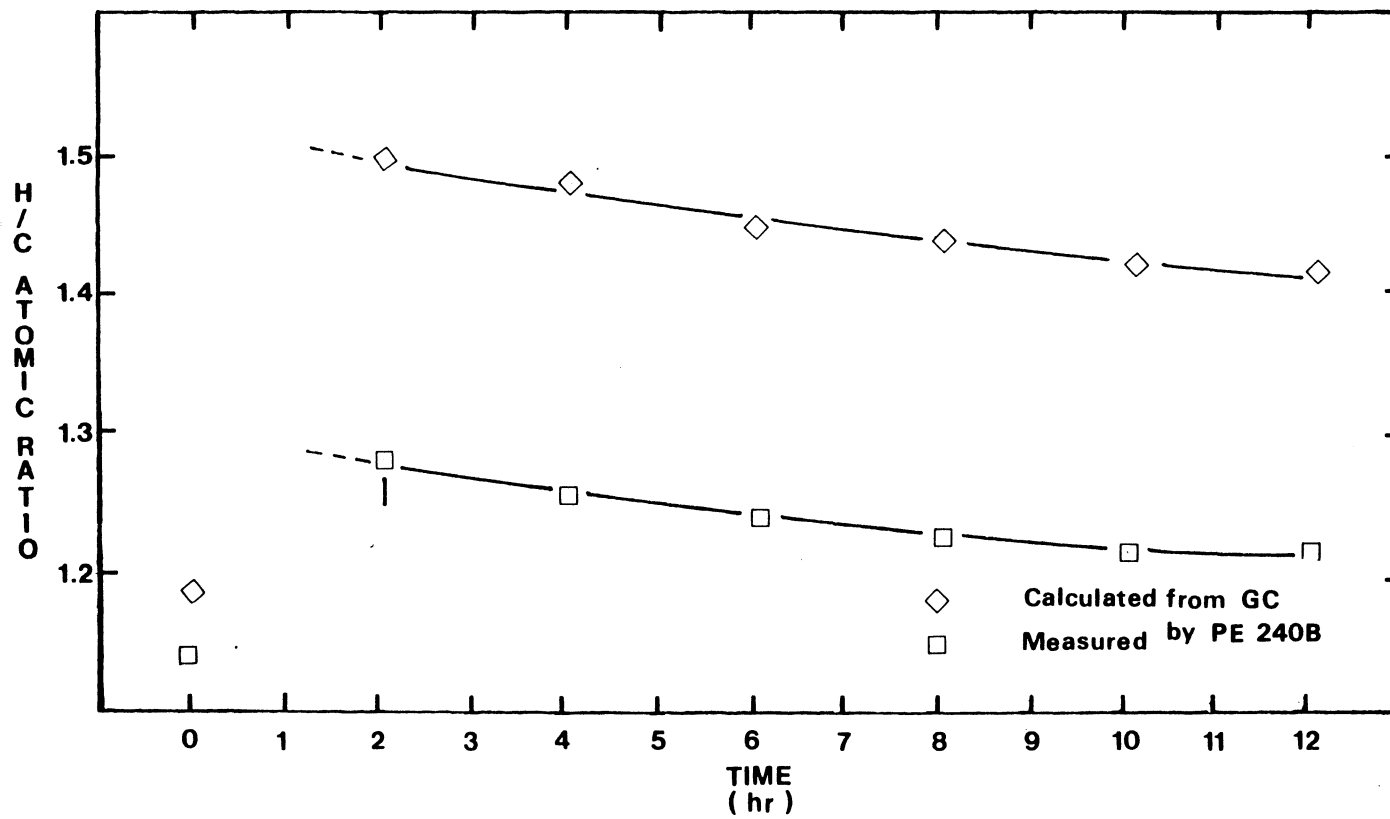
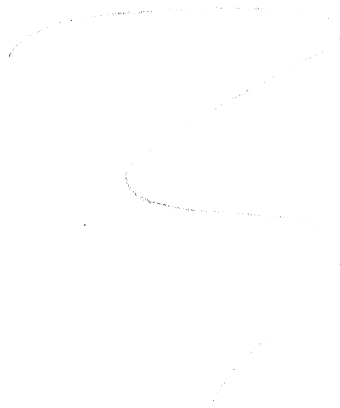


Figure 34. Comparison of Calculated and Measured H/C Atomic Ratio for Run #8

APPENDIX D



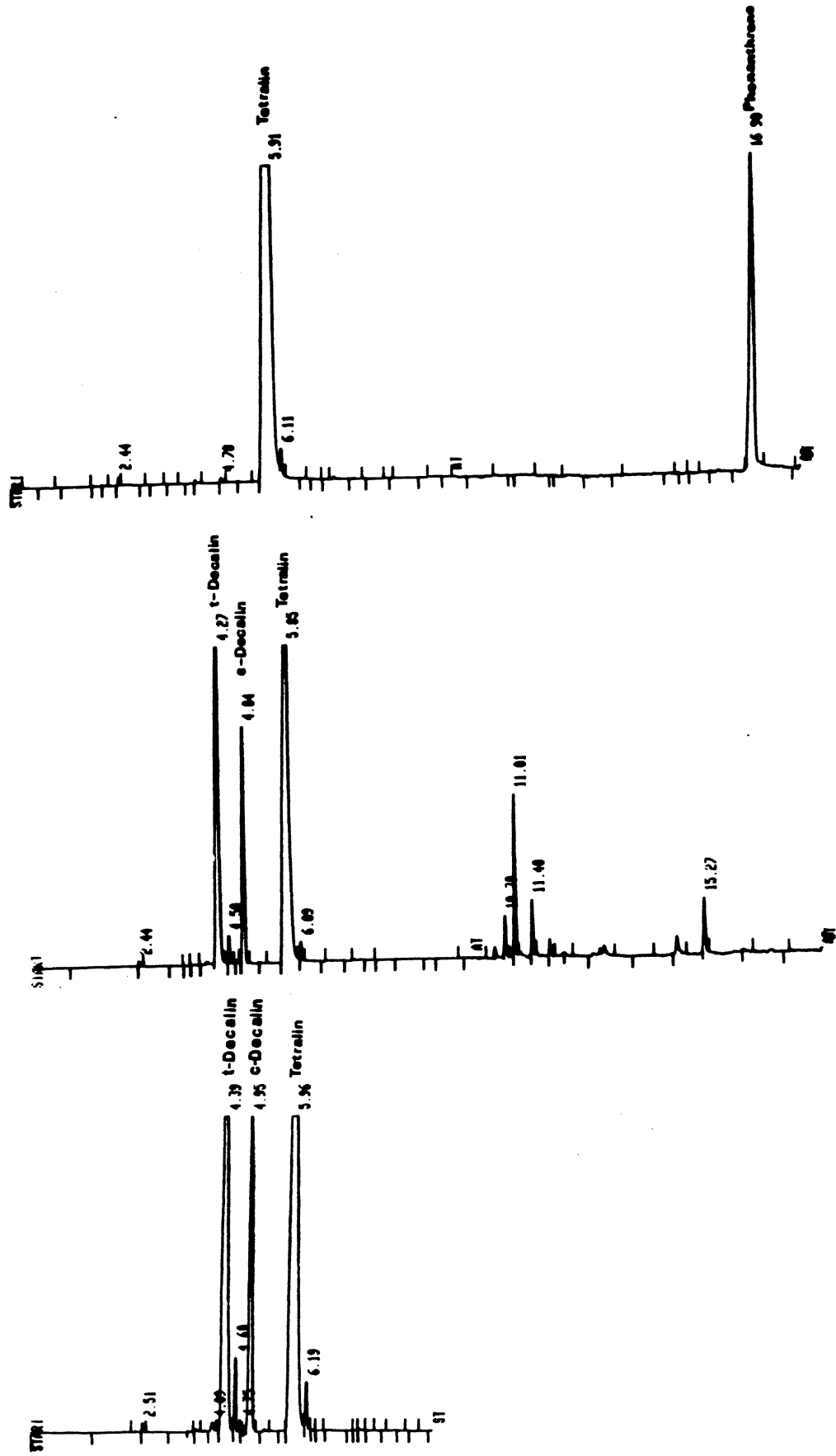


Figure 35. Sample Gas Chromatograph Analysis

VITA

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