EFFECTS OF TITANOCENE DICHLORIDE ON CATALYTIC HYDROGENATION OF HYDROCARBONS

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PREFACE

In an hydrotreatment processes of coal derived liquid, the problem of the catalyst deactivation by metal deposition has been received much attention. Titanium is one of the metals that survives the servere coal liquefaction process. It is present in coal derived liquid as an organometallic compound. Titanocene dichloride is a good representative of this compound. When titanocene dichloride is added to the coal derived liquid and hydrotreated, it shows an increase in hydrotreatment activities.

In order to study this phenomena in pure compound, titanocene dichloride is added to Tetralin and a mixture of 5 wt% phenanthrene in Tetralin and hydrotreated in a two-stage trickle bed reactor over a commerical Ni-Mo/alumina catalyst. The effect of titanocene dichloride on the hydrogenation activity and the coking of the catalyst are measured and studied. The hydrogen to carbon ratio of the products increases when titanocene dichloride is added to the feedstock.

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CHAPTER I

INTRODUCTION

One of the major problems in catalytic hydrotreatment processes is that the catalyst does not maintain its high activity and selectivity for a long period of time.

Process design and operating conditions have been studied in order to extend catalyst life and maintain its high activities. Deactivation mechanisms have also received considerable attention. The main factors for catalyst deactivation are: coking by carbonaceous material deposited on the catalyst surface, adsorption of basic nitrogen containing compounds, deposition of metal impurities in feedstock, and sintering of the catalyst.

The coke deposited on the catalyst can be burned off in a regeneration process. Metal deposition can cause a permanent loss of catalyst activity. Deposited metals can react with active metals during catalyst regeneration process and cause a permanent loss of catalyst activity due to structural changes of catalyst.

Chan (1) studied the changes in catalyst activities in hydrotreatment of coal derived liquids due to the pressure of titanocene dichloride. He doctored an SRC-II coal liquid with titanocene dichloride and hydrotreated with a Shell-324 catalyst. Instead of a loss in activities, he observed drastic improvements in catalyst activities and a decrease in coke formation on the catalyst surface.

Following those early observations, in this project, the role of titanocene dichloride on the hydrogenation of pure hydrocarbons is studied. A low coking and a high coking hydrocarbons are considered in this study.

Tetralin, which is a common hydrogen donor solvent in coal liquefaction processes (2-7), is selected as the low coking hydrocarbon; and phenanthrene, a compound commonly found in coal-derived liquids, is selected as the high coking hydrocarbon.

Tetralin and a mixture of 5 wt% of phenanthrene in Tetralin are doctored with titanocene dichloride and hydrotreated in a two-stage trickle-bed reactor system over a commercial Ni-Mo/alumina catalyst. The results are compared with the runs made without titanocene dichloride. The effect of titanocene dichloride on hydrogenation of the feedstocks, catalyst coking, titanium deposition on catalyst, and distillation characteristics of feedstocks and product oils are measured and studied.

The study shows that titanocen dichloride reacts with Titralin resulting in the formation of an insoluable titanium compound.

The effects of titanocene dichloride on the hydrogen activity and the coke formation of the catalyst depend on the type of the hydrocarbon feedstocks.

CHAPTER II

LITERATURE REVIEW

The literature will be reviewed on the following subjects.

1. Trickle bed reactor.
2. Catalyst Deactivation.
3. Reaction of Tetralin and Phenanthrene.
4. Titanocene Dichloride.

Trickle Bed Reactor

A trickle bed reactor is a fixed catalyst bed reactor in which usually a liquid and a gas flow concurrently downward. Trickle bed reactors are used in many chemical processes, such as hydrotreatment of heavy petroleum crudes. The commercial development of these reactors was mainly for the processing of petroleum fractions, particularly hydrodesulfurization and hydrocracking of heavy or residual oils and hydrotreating of lubricating oils.

In a trickle bed reactor, the flow pattern can usually be approximated by a plug flow model. The liquid trickles over the packing in essentially a laminar film and the gas continuously flows through the voids of the bed. The gas dissolves in the liquid and penetrates to the catalyst surface. After the reaction between adsorped species, the product gases and liquids desorb and transport to the bulk liquid where gas products evaporate into the gas phase.

In hydrodesulfurization, the liquid flow rates range from 1 to 10 kg/m^2. sec for heavy fractions to 10 to 25 kg/m^2. sec for naphtha, while hydrogen flow rates range from 0.470 m^3/kg for heavy gas oil to 0.840 m^3/kg for heavy residual oils. In hydrocracking, this ratio may be 1.7.

Liquid and Gas Distribution

The performance of a trickle bed reactor is a function of liquid and gas distributions. Satterfield (9) reported that in a narrow diameter trickle bed reactor, liquid migrates to the wall and the fraction flowing down the wall increases up to a steady state value typically reached in about 1/3 to 2/3 meters. When the ratio of the reactor diameter to the particle diameter is as high as 10, the steady state wall fraction is as much as 30-60%.

Liquid holdup (volume of liquid/volume of empty reactor) is a measure of the effectiveness of contacting between liquid and solid catalyst (9). It consists of the liquid held in the pores of the catalyst, which is called internal holdup, and outside the catalyst pellets called external holdup. The external holdup can be divided into free draining holdup and residual or static holdup. The fraction of the liquid remained on the packing after the bed has drained is called static holdup. The maximum internal holdup corresponds to the total pore volume of the catalyst and ranges from 0.15 to 0.40. The residual holdup varies from 0.02 to 0.05. The free draining holdup is a function of the gas and liquid flow rates, the fluid properties, and the catalyst characteristics. Ross (10) reported that the commercial reactor holdup was only about 2/3 that of the pilot reactor.

The external holdup is considered to be proportional to L^n or Re^n, where L is the liquid superficial flow rate and Re_L is the Renolds number for liquid flow. Davidson et al. (11) and Pelossof (12) reported n=1/3 for laminar film flow over a column of spheres and with no drag effect by flowing gas.

Henry and Gilbert (13) assumed that the reaction rate was proportional to liquid holdup and this holdup was proportional to the liquid superficial velocity to 1/3 power.

Mears (14) suggested that the reaction rate was proportional to the fraction of the outside catalyst surface which was effectively wetted by the flowing liquid. Puranik and Vogelpohl (59) reported that the wetted are was proportional to the 0.32 power of the liquid velocity.

Diffusion Resistance

Mass transfer from the bulk of the gas to the active sites of the catalyst involves several steps. Each step has its diffusion resistance which controls the amount of transferred reactants and products. The diffusion occurs both in the gas and the liquid phases and inside the pores of the catalyst.

In hydrotreating processes, hydrogen gas is used in an excess amount. It is assumed that vapor-liquid equilibrium is established between the gas and the gas-liquid interface, so that there is no significant mass transfer resistance in the gas phase. The dissolved gas must be transported from the gas-liquid interface to the bulk liquid and to the liquid-solid interface. Therefore, the liquid phase resistance is expected to be the rate controlling step (17).

Satterfield (18) showed that the liquid film surrounding the catalyst particles has an average thickness in the range of 0.01-0.1 millimeter under typical hydrotreating conditions. The average film thickness is so much less than the radius of the usual catalyst particle that it will not be a significant resistance unless the effectiveness factor of the catalyst pellets is quite low. Van Deemter (19) and Adlington and Thompson (20) concluded that the effectiveness factor in catalyst under industrial operating conditions was low. Satterfield (9) showed that the film resistance was negligible for these conditions.

Catalyst Deactivation

In the catalytic processes, catalysts usually lose their activities while in operation due to a) structural changes in the catalyst, b) irreversible chemisorption of some impurity in the feed stream which is called poisoning, c) deposition of carbonaceous residue from a reactant, product, or some intermediate which is called coking.

The effects of deactivation by metal poisoning and coking are received more attention than the structural changes. The following literature will be reviewed only on coking of catalyst in hydrotreatment processes and some metal poisoning.

In catalytic hydrotreatment processes, a portion of the feedstock is converted to a carbonaceous material or coke and deposited on the catalyst surface. The mechanism of the coke formation is difficult to establish even when working with pure compound feeds (8, 21). The composition, chemical structure, and molecular weight of the deposited material are not well understood. The main precursors of coke deposit are believed to be aromatic and S-, N-, and O- containing heterocyclic compounds (22). Catalytic coke is apparently a hydrocarbon of relatively low hydrogen content left over from the reactions. Thomas (25) reported a formula for the coke as $(C_3H_4)_n$.

Appleby et al. (23) concluded from their catalytic cracking of pure compounds that aromatic components from the catalytic cracking feedstocks were the source of the coke. They also suggested that the aromatics adsorbed on the catalyst surface and the adsorbed species reacted to from aromatic or unsaturated ions by condensation and hydrogen elimination. Thomas (24) reported that hydrogen elimination reactions could proceed by olefins interacting with adsorbed aromatics to form paraffins and hydrogen deficient coke.

Voorhies (26) correlated a relation for coking in the catalytic cracking of gas oil as

$$C_c = At^n \quad \text{with } 0.5 < n < 1.0$$

where A = a constant, depending on catalyst, feedstock, and temperature.

C_c = carbon, weight percent on catalyst.

t = catalyst residence time, minute.

n = constant, depending only slightly on catalyst, feedstock, and temeprature.

The origin of coke was not considered in Voorhies correlation.

Froment and Bischoff (27, 28) considered that the coke was formed either by a reaction path parallel to the main reaction

$$\begin{tikzcd}
\text{reactant} \arrow[r] \arrow[d] & \text{product} \\
\text{intermediates} \arrow[r] & \text{coke}
\end{tikzcd}$$

or by a reaction path consecutive to the main reaction.

reactant → product → intermediate → coke

They were the first to relate the composition of the reaction mixture, the temperature, and the catalyst activity, to the rate of coking.

Haldeman (29) studied the coke structure by X-ray diffraction. He showed that half of the carbon phase was in pseudo graphitic, or turbostratic structure. The remainder consisted of unorganized aromatic systems and of aliphatic and alicyclic appendager to polynuclear aromatic systems.

Eberly (8) used Infrared Spectroscopic techniques to study the structure of the coke deposit on silica-alumina cracking catalysts. He observed the presences of condensed ring aromatic structures and identified $-CH_3$, $-CH_2$, and aromatic -CH groups. He also concluded that the hydrogen elimination from adsorbed hydrocarbons could be because of either direct dehydrogeneration producing hydrogen gas or transfer of hydrogen to an unsaturated acceptor molecule. The direct dehydrogenation occurred when metal contaminants, such as nickel, were present on the catalyst surface.

Ternan et al. (30) suggested that two types of coke were present on the catalyst, a reactive coke which was converted to reaction products and an unreactive coke which blocked the active sites.

Hydrogen partial pressure and operating temperature have strong effects on coking rate (27, 31). Coking rate decreases with an increase in hydrogen partial pressure.

Coke deposition causes a decrease in catalyst activity due to a decrease in the active surface area (32, 33, 34). Coke catalysts can be regenerated by burning off the coke.

Metal deposition by the irreversible chemical reaction on the catalyst surface can cause a permanent loss in catalyst activity. The metal is usually present in the liquid feed in the form of organometallic or inorganic compounds. Chiou and Olson (35) showed that most organic metals deposit on the outer surface of the catalyst, whereas organometallics could penetrate into the catalyst pores and deposit inside the pores. Some investigators have indicated that the metal deposition could accelerate the coke formation. Habil (36) found that the metal deposition on the catalyst increased the coke content in a cracking process.

There are some arguments about the promoter on the catalyst. Ahmed (17) found that Ni was a better promoter that Co on Mo/alumina catalyst while Ternan et al. (30) found that the molybdenum content of the catalyst controlled the coke level rather that the promoter.

Reaction of Tetralin and Phenanthrene

In catalytic hydrotreatment of coal derived liquids, the processes are based on catalysts containing molybdenum promoted by cobalt or nickel and supported on alumina (2, 37, 38). Many investigators have studied hydrotreatment reactions using these catalysts under different operating conditions.

Badilla-Ohlbaum et al. (40) studies the hydrogenation of a model feedstock containing phenanthrene on nickel-molybdate-based catalysts at $400^{o}C$ and 6.89 MPa. The main products of phenanthrene were mixtures of di-, tetra-, octa-, and perhydrophenanthrenes.

Skowronski (41) found that a molten alkali metal hydroxide-carbonate mixture was an effective catalyst for the hydrgenation of phenanthrene. It was shown that both the hydrogenation and ring-opening reactions were occurring and the products were 6-butyl-, 1, 2, 3, 4-tetrahydronaphthalene, 9, 10-dihydrophenanthrene and 1, 2 , 3, 4-tetrahydrophenanthrene.

Sullivan et al. (42) reported that the prevailing products from the hydrocracking of phenanthrene on a NiS/Al_2O_3 catalyst at 293°C were Tetralin and methyl cyclohexane. They indicated that hydrocracking of phenanthrene could occur at low temperature, but it also depended on other operating conditions. Huang et al. (43), using $Co\text{-}Mo/Al_2O_3$ catalyst, reported that the main products of the hydrocracking reaction of phenanthrene were perhydrophenanthrene isomer.

Penninger and Slotboom (44) investigated the uncatalyzed thermal high-pressure hydrogenolysis of phenanthrene at a hydrogen pressure of 8.3 MPa and a temperature of 475°C. They concluded that the products of uncatalyzed hydrogenation of phenanthrene were 1, 2, 3, 4-tetrahydrophenanthrene and 9, 10-dihydrophenanthrene.

Friedman et al. (45) also observed the same products and octahydrophenanthrene when they used alkali metals, alkalie metal alloys, and alkali metal-alkali metal salt combinations as the catalyst.

Sullivan et al. (42), from their hydrocracking studies, suggested that three types of reactions occurred:

1. Cleavage of one of the terminal rings to form an alkane and a bicyclic compound such as Tetralin,

2. Ring saturation and cleavage of the central ring, which accounts for appreciable amounts of methylcyclohexane and ethylcyclohexane produced, and

3. An unusual cracking reaction that produced bicyclic hydrocarbons, principally Tetralin, without producing an equivalent amount of light alkanes.

Wiser (46) suggested that phenanthrene was an excellent model of one of the principal structures found in coal.

Tetralin is commonly employed as a hydrogen-donor solvent. In coal liquefaction process, Tetralin is considered a reasonably good hydrogen-donor for the hydrogenation of coal. Potgieter (39) studied the conversion of Tetralin during hydrogenation of coal and suggested that Tetralin coverted to naphthalene.

Dziewiecki et al. (47) studied the catalytic activities of a Ni-Mo/Alumina catalyst in dehydrogenation of Tetralin. They showed that the activities of a Ni-Mo/Alumina catalyst could be predicted in hydrogenation of coal-extract solution from its activities in dehydrogenation of Tetralin.

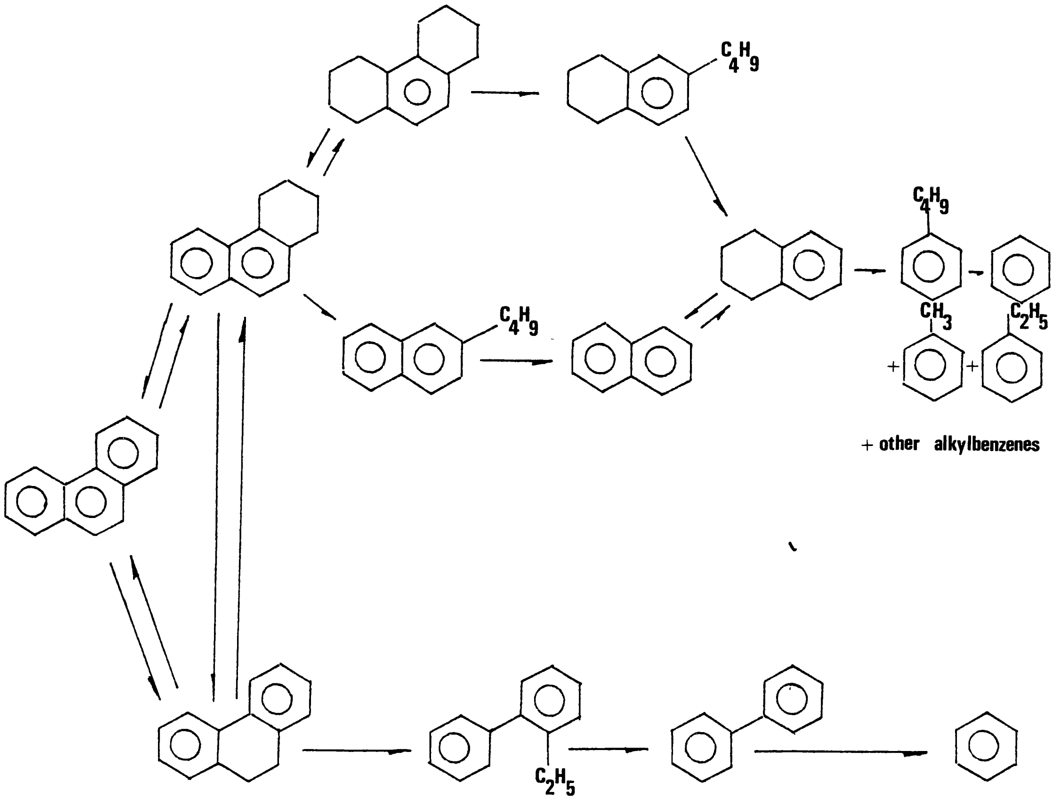
Curran et al. (6) observed that Tetralin decomposed to "C_4 benzenes and indane". Whitehurst et al. (48) pointed out that rearrangement of Tetralin occurred with the formation of 1-methyl indane.

Penninger and Slotboom (49, 50) heated Tetralin in hydrogen atmospheres o 1 to 10 MPa and temperatures of 460 to 560^oC. They identified butyl benzene, 1-methyl indane, styrene, ethylene, and o-propyltoluene as primary products. They also postulated the mechanism for the formation of 1-methyl indane and that hydrogen was required for initiation of the reaction.

Hooper et al. (7) studied the thermal cracking of Tetralin without hydrogen or coal. The main products formed were naphthalene and the Tetralin isomer 1-methyl indane. The reaction to produce 1-methyl indane was shown not to occur until some dehydrogenation of Tetralin to naphthalene had occurred.

Flinn et al. (51) studied the catalytic hydrocracking of some compounds over 3% nickel supported on a Houndry silica-alumina catalyst. Their results showed that Tetralin converted to isoparaffins, benzene, alkyl benzenes and naphthalene.

Wu et al. (56) summarized the available literature and suggested that the reaction paths of phenanthrene could be represented by:



Titanocene Dichloride

Titanium is one of the metals found in coal. It can survive the severe conditions of coal liquefaction processes and is present in coal liquid both in organic and inorganic forms. Many researchs have been conducted to identify the form and structure of titanium in coal liquid. Filby et al. (58) suggested that the formation of stable organometallic compounds, like titanocene dichloride, could occur under the highly reactive conditions and the complex chemical system in the coal liquefaction processes.

Titanocene dichloride is an organometallic compound with a chemical name of bis(cyclopentadienyl) titanium dichloride. It can be hydrolyzed in moist air to form $(C_5 H_5)_2$ Ti(OH)Cl. It is soluble in dilute acid and is decomposed by aqueous base with the formation of hydrated titanium dioxide (57).

Complexes formed by the reaction of titanocene dichloride with an alkylaluminum compound in nonaqueous solutions have been used as a soluable catalyst for polymerization of ethylene. The polyethylene prepared with these catalysts is highly linear and has a narrow molecular weight distribution (52, 53, 54, 55).

Chan (1) doctored an SRC-II coal drive liquid with titanocene dichloride and hydrotreated over a Ni-Mo/alumina catalyst. He concluded that the addition of titanocene dichloride improved the hydrotreatment activities of the catalyst and suppressed the coke formation on the catalyst. He also showed that the catalyst activity improvement depended on the concentration of titanocene dichloride. Titanium concentration of 100 to 200 ppm appeared to promote the catalyst.

Literature Summary

1. The factors that affect the performance of the trickle bed reactor are liquid and gas distributions and diffusion resistance.
2. The catalyst usually loses its activities due to the structural changes, metal poisoning and coking.
3. Coke is believed to be formed by the reaction between the hydrocarbon molecules adsorbed on the catalyst surface resulting in aromatic or unsaturated groups by condensation or hydrogen elimination.
4. The products of phenanthrene hydrogenation can be a mixture of di-, tetra-, octa, and perhydrophenanthrenes, 6-butyl-, 1, 2, 3, 4-tetrahydronaphthalene, 9, 10-dihydrophenanthrene and 1, 2, 3, 4-tetrahydrophenanthrene.
5. In hydrogenation processes, Tetralin can form cis- and trans-dicalin, 1-methly indane and styrene. Tetralin may also be dehydrogenated to naphthalene.

CHAPTER III

EXPERIMENTAL APPARATUS AND ANALYSiS TECHNIQUES

Figure 1 shows a schematic diagram of the trickle bed ractor system used in this study. The system was designed and used by an earlier investigator at Oklahoma State University (16). It has a capability to be used as a one- or two-stage reactor. No modification was made in this study.

Hydrogen gas flows into the top of reactor 1 from a hydrogen cylinder through valve 1. Hydrogen pressure is maintained unchanged by means of a "Mity-Mite" regulator valve. The upstream pressure of the "Mity-Mite" is controlled by a pressure regulator at the hydrogen cylinder. The flow rate of gas into the reactor is measured by a high pressure flow meter. A Heise pressure guage is used to monitor the inlet gas pressure. Oil is charged into the feed tank and then into the reactor by a Ruska feed pump. The feed oil pressure is monitored by pressure gauge 41. Oil and hydrogen gas flow concurrently through reactor 1, which is packed with catalyst and glass beads. A sampling system is installed at the bottom of reactor 1. This sampling system has the capability to take small liquid samples at any time without disturbing the operation. The fluids flow into reactor 2, which is packed with the same type of catalyst as in reactor 1. Product oil and gas flow through sample bomb 1 into sample bomb 2 where they are separated. The pressure of sample bomb 1, which is used as the reactor

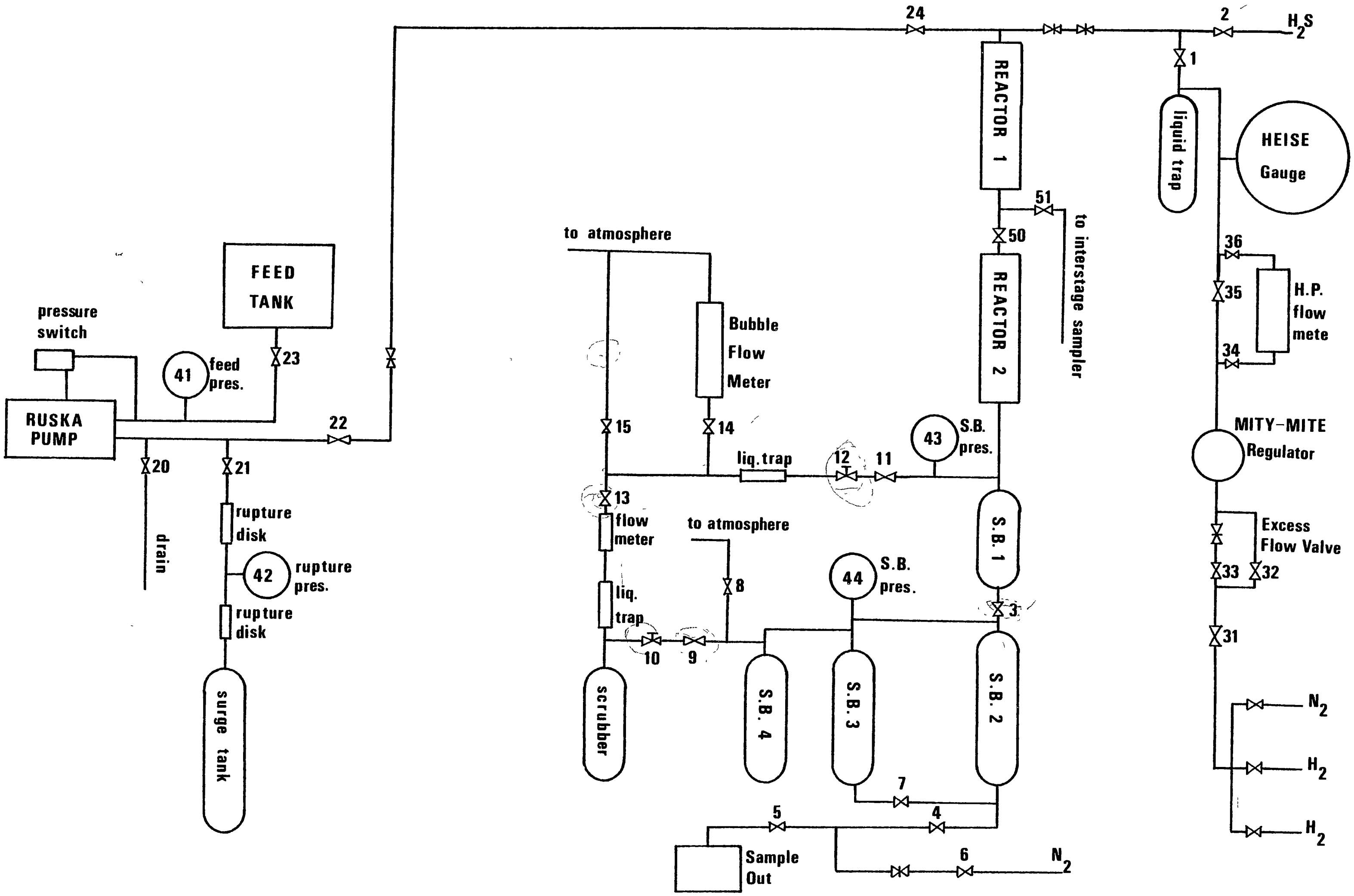


Figure 1. Schematic Diagram of the Reactor System

downstream pressure, and is measured by pressure gauge 43. The pressure of sample bomb 2 is measured by pressure gauge 44.

Sample bomb 3 is used to condense liquid. Sample bomb 4 is packed with alumina spheres and is used to trap liquid mist in the outlet gas stream. The outlet gas flow rate is controlled by valve 10. A scrubber filled with ethanolamine solution (60 vol% ethanolamine in water) is located after valve 10. The flow rate of outlet gases is measured by a bubble flow meter and is monitored by a low pressure flow meter. Temperatures of the reactors are separately controlled by two temperature programmer/controllers, and are also measured inside the catalyst beds and outside the reactor walls.

Detailed discriptions of the main components of the system and the experimental procedures are given in Appendix A and B.

The oil samples were taken every 12 hours during each experiment. The samples from the sampling system at the bottom of reactor 1 were called the interstage samples and the accumulated product oil in the sample bombs at the bottom of reactor 2 were called the product samples. After each run, the reactors were cut and the catalyst in each reactor were divided into three sections called top, middle, and bottom. Each oil sample and catalyst sample were labeled and kept for analyses.

Sample Analyses

Catalyst samples are analyzed for coke content, titanium content, and titanium distribution. Liquid samples are analyzed for carbon and hydrogen content, titanium concentration, chloride concentration, conversion of Tetralin and phenanthrene, and ASTM distillation curve.

Catalyst Characterization

The catalysts from each reactor are separated into top, middle, and bottom sections. Each sample is extracted with tetrahydrofuran in a Soxhlet extraction unit for 60 hours. The washed catalysts are dried and degassed at 82.2°C (180°F) for 6 hours.

Coke Content Determination: The coke content in this study is defined as the weight percent of loss of carbonaceous material by burning the catalyst at 550°C (1022°F) for 60 hours. The catalyst samples are weighed at room temperature and placed in a furnace at 550°C (1022°F) to burn off their carbonaceous material for 60 hours. The samples are allowed to cool down to room temperature then weighed. The amount of coke is calculated by:

$$\text{weight \% of coke content} = (W_1 - W_2) \times (100/W_1)$$

where

W_1 = Weight of spent catalyst

W_2 = Weight of burned catalyst

Titanium Content Determination: A Phillips X-ray Spectrometer PW 1410/70 equipped with an XRG-3000 generator is used to measure the weight percent of titanium deposited on the spent catalyst and glass beads. The principle of this method is that the analyte-line intensity $I_{A,M}$ from analyte A in a thick specimen having matrix M would be a simple function of weight fraction of A in M.

The standards of known titanium concentration are prepared by grinding fresh Shell-324 catalyst pellets and mixing the powder with titanium dioxide. The standards for glass beads are also prepared similarly using fresh glass beads and titanium dioxide. The catalyst and glass bead samples are grinded into powder and shaped into pellets. The titanium analyte-line intensity is measured and compared with the calibration curves. These intensities can be converted into weight percent of titanium in the samples.

Titanium Distribution Determination: A JEOL Model JFM-35 Electron Scanning Microscope equipped with an Energy Dispersive X-ray Analyzer is used to determine the titanium distribution in spent catalysts. The catalyst sample is cut and placed in a vacuum chamber. The metals in the catalyst are analyzed by the X-ray beam of different energies. The catalyst samples are analyzed at several points from the edge to the center of pellets.

Product Characterization

Nitrogen, Carbon, and Hydrogen Analysis: A Perkin Elmer elemental analyzer Model 240B is used to determine the amounts of carbon and hydrogen in the liquid samples. The analyzer consists of three major sections, which are combustion furnace, reduction furnace, and a detection system. In combustion furnace, the sample is combusted at high temperatures of approximately 960°C (1760°F) in a purified oxygen atmosphere catalyzed by silver tungstate and magnesium oxide. The gases are carried through the combustion tube by purified helium gas. Sulfur oxides and halogens in the gas are removed in the combustion tube by silver vanadate, silver oxide, and silver tungstate. The gases are passed through a reduction tube, operating at 600°C (1112°F), where nitrogen oxides are reduced to N_2. The remaining gases, which are CO_2, N_2, water vapor, and helium gas, are collected in a mixing volume at a constant temperature until equilibrium is reached. The gases are passed through a series of gas traps and thermal conductivity cells.

Water is trapped by magnesium perchlorate and the difference of thermal conductivity before and after the trap gives the water content which corresponds to the hydrogen content in the sample. Carbon dioxide is trapped in a special absorbent called Colorcarb and carbon signal is read by the same method. The remaining gases, N_2 and helium, are passed through a thermal conductivity cell where the nitrogen content is measured by comparing the signal with that of another cell measuring the thermal conductivity of the purified helium.

Titanium Concentration Determination: A Perkin Elmer 403 double beam Atomic Absorption Spectrometer is used to measure the titanium concentration in the feedstock and product oils.

Atomic absorption is a chemical analysis technique which uses light absorption by atoms in the gas phase to analyze the metal atoms. It is used to analyze metal samples in solutions in the range of parts-per-million (ppm). Although it is a very sensitive and quantitative technique, it can treat only one element at a time.

In atomic absorption spectroscopy, a solution of the sample is introduced into a chemical flame as a fine aerosol or mist. Here the solution droplets first undergo desolvation, and the resulting particles are dissociated into atoms. These atoms are in their normal electronic configuration, the "ground state" or zero energy state. An external light source is employed to emit the atomic line spectrum of the atom to be analyzed. The light from this source passes through the flame containing the sample and is absorbed by the ground state atoms in the flame cell. The photons emitted by the element in the external source have exactly the energy required to excite the same ground state element in the flame. The intensity of radiation emitted or absorbed by an element is proportional to the atomic concentration of that element.

The emission intensity is detected by a detector which generates the electric signal. A monochromator is usually employed in this process. The signal is then amplified and displayed or recorded by the read out system. The unknown signals are compared with the signal of standard solutions.

The titanium standard used in this study is a titanium-organic standard supplied by Continental Oil Company. It is mixed with Tetralin and diluted with methyl-isobutyl ketone to make standard solution with titanium concentrations of 100 ppm and below. A blank standard which is a solution of Tetralin and methyl-isobutyl ketone is also prepared and used to set the analyzer at zero titanium concentration.

The product oils are diluted with methyl-isobutyl ketone at the same ratio as the standard solution. Both the standard and the sample solutions have to be fresh in order to avoid any decomposition of titanium compounds.

Chloride Determination: Chloride in oil samples is extracted into water and analyzed by ASTM D-512 technique, the standard test method for analysis of chloride ion in water.

The oil samples are mixed with distilled water to extract chloride from oil phase to water phase. The water samples are then titrated with silver nitrate solution using potassium chromate as an indicator. Chloride concentration can be obtained from the amount of silver nitrate used in the titration. Details of the analysis and calculation techniques are described in ASTM D-512.

Gas Chromatographic Analysis of Tetralin, phenanthrene and products: A Varian Model 3700 Gas Chromatograph equipped with Analabs capillary column Model GB-5 is used to determine the amount of Tetralin, phenanthrene and their hydrogenation products in the liquid samples. The samples are mixed with tridecane which is used as a reference compound. Approximately 1 microliter of liquid sample is injected into the Gas Chromatograph. The sample is vaporized at a high temperature and mixed with a carrier gas. Part of the gas mixture is split and vented to the atmosphere, only a small portion of the gas mixture flows into the capillary column. Compounds in the gas mixture adsorb and desorb in the capillary column at different rates. Lighter compounds adsorb and desorb faster than heavier compounds. The desorbed gas is added to the make up gas to increase the gas flow rate. The gas mixture flows through a tip where the compounds are burned in a hydrogen flame. Flame Ionization Detector is used to detect the signal. The signals are plotted and integrated by a Hewlett-Packard reporting integrator Model 3390A.

ASTM D-1160 Distillation: Feed oil and selected product samples are fractionated following ASTM D-1160. The temperatures are recorded at every 10 cm^3 of distillate. The distillations are performed at a pressure of 1.34 kPa (10 mmHg), and the temperatures are converted to those of 102 kPa (760 mmHg). The detailed procedures can be found in ASTM D-1160.

CHAPTER IV

EXPERIMENTAL RESULTS

The results of analyses of the liquid and catalyst samples will be presented in this chapter. There were a total of five experimental runs, labeled 1 through 5, in this study.

Tetralin is a hydrogen-donor solvent commonly used in coal liquefaction processes. It is considered to be a low coking feedstock in the study of catalytic cracking over the silica-alumina cracking catalysts (8). Phenanthrene serves as an excellent model of the principal structure found in coal (46). It is a relatively high coking feedstock in catalytic cracking study over the synthetic silica-zirconia-alumina cracking catalyst (23).

Tetralin at high temperatures, approximately 500^{o}C (932^{o}F), decomposes by thermal cracking. At lower temperatures, 400^{o}C (752^{o}F), a very small fraction of Tetralin dicomposes (7, 15). In the operating temperatures of hydrotreatment, 350-450^{o} (662-842^{o}F), thermal cracking is expected to be minimal.

A set of preliminary experiments was conducted to study the coking ability of some hydrocarbons on Shell 324 hydrotreatment catalyst. The experiments were done at atmospheric pressure and the normal boiling point of each hydrocarbon.

Approximately 80 cm^3 of a pure hydrocarbon or hydrocarbon mixture and 2 gm of Shell 324 catalyst were placed in a flask and connected to a condenser. The mixture was boiled for 2 hours. The catalyst was washed with methyl-isobutyl ketone to remove the hydrocarbon liquid on the surface and dried in a furnace at 100°C (212°F) for 5 minutes. The catalyst was weighted at room temperature and then placed in a furnace to burn off the coke at 500°C (932°F) for 60 hours. The weight loss is considered as coke on the catalyst.

The preliminary coking results are shown in Table I. It indicates that the coke formation on the catalyst depends on the type of hydrocarbons. It also shows the effect of titanocene dichloride on the coke formation. Tetralin is an aromatic compound that gives less coke than other aromatic compounds such as anthracene and phenanthrene.

In this study, Tetralin and a mixture of 5 wt% phenanthrene in Tetralin were used as the low coking and high coking feedstocks, respectively.

Properties of Shell-324 catalyst, titanocene dichloride, Tetralin and phenanthrene are given in Table II, III, IV, and V.

The hydrotreatment experiments were conducted at a pressure of 10.4 MPa (1500 psig) and a temperature of 350°C (662°F). A liquid volume hourly space time of 0.20 hour and hydrogen to oil ratio of 1000 standard m^3H_2/m^3 oil (5620 SCF/bbl) were used. Each reactor was packed with 10 grams of Shell-324 catalyst to a height of 15.24 cm (6 inches). Table VI summaries the experimental conditions used in this study.

A pressure drop of 140 kPa (20 psig) across the reactors was observed in all runs. There was a hot spot at the entrance to the catalyst bed section. The temperature of the hot spot was approximately 40°C (113°F) higher than the normal operating temperature when oil and

TABLE I

PRELIMINARY COKING RESULTS

	Coke wt% Catalyst		Approx. Temp., °C
	without titanocene	with titanocene	
n-Hexadecane	4.45	9.40	287
Tetralin	12.24	11.75	207
Tetralin + 1% Anthracene	13.90	13.43	207
Tetralin + 8% Phenanthrene	17.83	10.76	207
Tetralin + 10.5% 1-methylnaphthalinene	19.29	---	207

Catalyst: Shell 324
(1/16 inch extrudate)

Contact Time: 2 hrs.

TABLE II

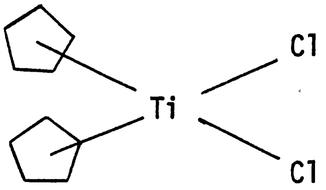
PROPERTIES OF SHELL-324 CATALYST*

Chemical Composition wt%	
NiO	3.4
MoO_3	19.3
Physical Properties	
Geometry	1.6 mm (1/16") extrudate
Surface area, m^2/kg	146 X 10^3
Pore Volume, m^3/kg	4.2 X 10^{-4}
Most frequent pore diameter, nm 11.8	
Pore size 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	6
Total	100

* From Supplier

TABLE III

PROPERTIES OF TITANOCENE DICHLORIDE*

Formula	$(C_5H_5)_2\ TiCl_2$
Sturcture	
Chemical Name	Bis(cyclopentadienyl) titanium dichloride
Physical Properties	
Molecular Weight	249.0
Form	Crystalline solid
Color	Red
Melting Point	287-289°C (with decomposition)
Titanium Content	19.24%
Chloride Content	28.48%
Oxidation Potential	$(C_5H_5)_2{}^{H_2O}\ {}^{+}\ (C_5H_5)_2Ti^{++}$
Solubility	Moderately soluble in toluene and chloroform and in alcohol and other hydroxylic solvents. Sparingly soluble in ether, benzen, carbon disulfide, carbon tetrachloride, pretroleum ether, and water
Supplier	Alpha Products

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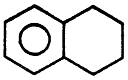
*From Supplier

TABLE IV

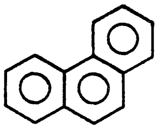
PROPERTIES OF TETRALIN*

Formula	$-C_6H_4CH_2(CH_2)_2CH_2-$
Structure	
Chemical Name	1, 2, 3, 4-tetrahydronaphthalene
Physical Properties	
Molecular Weight	132.2
Form	liquid
Color	yellow
Melting Point	-31°C
Boiling Point	206°C
Specific gravity	0.973
Solubility	insoluble in water soluble in alcohol and ether
Purity	99% (by supplier)
Supplier	Alfa Products

*From Chemical Engineering Handbook

TABLE V

PROPERTIES OF PHENANTHRENE*

Formula	$(C_6H_4CH)_2$
Structure	
Physical Properties	
Moleuclar Weight	178.22
Form	plate solid
Color	white
Melting Point	99-100°C
Boiling Point	340°C
Specific gravity	1.179
Solubility	insoluble in water
	soluble in ether
Purity	98% (by supplier)
Supplier	Aldrich Chemical Company, Inc.

*From Chemical Engineering Handbook

TABLE VI

EXPERIMENTAL CONDITIONS

Feedstock:	Run 1 - Tetralin (Reference run)
	Run 2 - Tetralin + 100 ppm of titanium (as titanocene dichloride)
	Run 3 - Tetralin + 5 wt% Phenanthrene
	Run 4 - Tetralin (Duplicate of reference run)
	Run 5 - Tetralin + 5 wt% Phenanthrene + 100 ppm of titanium (as titanocene dichloride)
Operating Conditions:	
	Reactor Temperature: 350°C (663°F)
	Pressure: 10.4 MPa (1500 psig)
	Feedstock flowrate: 30 cm^3/hour
	Hydrogen flowrate: 500 cm^3/minute
	Duration of run: 60 hours
	Sampling: every 12 hours

gas contacted the catalyst. The temperature of this hot spot gradually decreased to the normal operating temperature within 3-4 hours after start-up. The temperature in each reactor was almost constant ($\pm$ 4°C) along the catalyst bed, except at the hot spot. In run 4, there was a hot spot in the middle section of reactor 2 that brought the temperature up to 20°C (68°F) higher than the normal operating temperature. These hot spots were the results of exothermic hydrogenation reaction.

The plots of the temperature profile in the catalyst bed for each run and the temperature profile of the hot spot are presented in Appendix C.

Experimental Data

The data for liquid samples includes H/C atomic ratio, titanium concentration, chloride concentration, and ASTM distillation. The analysis for titanium concentration and titanium distribution on the catalyst show no titanium deposited on the catalyst. The data for catalyst samples will indicate only the coke content. The top section glass beads of run 2 and 5 are analyzed for titanium deposition. Coke content and titanium concentration of glass beads are shown in Table VII and VIII, respectively.

Table IX, X and XI show the hydrogen to carbon atomic ratio, titanium concentration, and chloride concentration in the products of each run. Table XII-XVI are the ASTM distillation data of the feedstock and the products at 48 hours.

A Perkin Elmer Elemental Analyzer Model 240B was used to analyze the coke on the catalyst. The summation of the weight percents of carbon and hydrogen is considered as the weight percent of coke. The

TABLE VII

COKE CONTENT ON THE CATALYST

RUN #	REACTOR #	Wt% COKE IN SECTION TOP	MIDDLE	BOTTOM
1	1	4.30	3.28	5.30
1	2	2.87	4.18	5.25
2	1	5.97	8.23	7.21
2	2	7.31	6.89	5.34
3	1	6.30	5.52	5.72
3	2	4.18	5.65	5.47
4	1	4.25	3.20	4.97
4	2	0.78	1.12	1.23
5	1	3.41	2.59	1.73
5	2	2.95	2.46	1.90

TABLE VIII

RESULTS OF THE GLASS BEADS ANALYSIS

RUN #	REACTOR #	SECTION	MASS OF GLASS BEADS (gram)	TITANIUM CONC. (wt. percent)
2	1	TOP	17.3	0.327
2	1	BOTTOM	20.5	0.05
2	2	TOP	20.8	0.0
5	1	TOP	14.2	0.430
5	1	BOTTOM	16.9	0.07
5	2	TOP	17.1	0.0

TABLE IX

RESULTS FROM RUNS 1 AND 2

SAMPLE #	HOURS IN OIL	H/C atomic ratio interstage	H/C atomic ratio product	Ti conc. (ppm)	Cl. conc. (gm/liter)
R1-0	0	-	1.26	0	0
R1-12	12	1.36	1.55	0	0
R1-24	24	1.34	1.52	0	0
R1-36	36	1.35	1.47	0	0
R1-48	48	1.35	1.45	0	0
R1-60	60	1.35	1.44	0	0
R2-0	0	-	1.26	100*	0.145
R2-12	12	1.46	1.57	0	0
R2-24	24	1.40	1.52	0	0
R2-36	36	1.37	1.50	0	0
R2-48	48	1.35	1.46	0	0
R2-60	60	1.35	1.46	0	0

* - initial concentration

TABLE X

RESULTS FROM RUNS 3 AND 5

SAMPLE #	HOURS IN OIL	H/C atomic ratio interstage	H/C atomic ratio product	Ti conc. (ppm)	Cl. conc. (gm/liter)
R-3-0	0	-	1.26	0	0
R-3-12	12	1.35	1.41	0	0
R3-24	24	1.35	1.42	0	0
R3-36	36	1.34	1.39	0	0
R3-48	48	1.34	1.38	0	0
R3-60	60	1.35	1.39	0	0
R5-0	0	-	1.26	100*	0.152
R5-12	12	1.36	1.53	0	0
R5-24	24	1.31	1.46	0	0
R5-36	36	1.30	1.40	0	0
R5-48	48	1.31	1.37	0	0
R5-60	60	1.31	1.37	0	0

* - initial concentration

TABLE XI

RESULTS OF RUN 4

SAMPLE #	HOURS IN OIL	H/C atomic ratio interstage	H/C atomic ratio product	Ti conc. (ppm)	Cl. conc. (gm/liter)
R4-0	0	-	1.26	0	0
R4-12	12	1.39	1.79	0	0
R4-24	24	1.37	1.91	0	0
R4-36	36	1.33	1.93	0	0
R4-48	48	1.34	1.90	0	0
R4-60	60	1.33	1.90	0	0

TABLE XII

DISTILLATION DATA FOR RUN 1

Vol%	Feedstock C	 F	Product @ 48 hr. C	 F
IBP	199	390	188	370
10	203	397	202	396
20	203	397	202	396
30	204	399	203	397
40	205	401	204	399
50	206	403	205	401
60	206	403	206	403
70	206	403	207	405
80	207	405	208	406
90	207	405	209	408
END POINT	208	406	214	417
Recovery	99		99	
Residue	1		1	
Lost	0		0	

TABLE XIII

DISTILLATION DATA FOR RUN 2

Vol%	Feedstock		Product @ 48 hr.	
	C	F	C	F
IBP	199	390	190	374
10	203	397	197	387
20	203	397	199	390
30	204	399	199	390
40	205	401	200	392
50	206	403	201	394
60	206	403	202	396
70	206	403	203	397
80	207	405	204	399
90	207	405	206	403
END POINT	208	406	211	412
Recovery	99		98	
Residue	1		2	
Lost	0		0	

TABLE XIV

DISTILLATION DATA FOR RUN 3

Vol%	Feedstock C	Feedstock F	Product @ 48 hr. C	Product @ 48 hr. F
IBP	200	392	202	396
10	202	396	203	397
20	202	396	204	399
30	202	396	205	401
40	203	397	206	403
50	203	397	207	405
60	204	399	207	405
70	205	401	208	406
80	206	403	209	408
90	211	412	223	433
END POINT	213	415	237	459
Recovery	95		96	
Residue	4		2	
Lost	1		2	

TABLE XV

DISTILLATION DATA FOR RUN 4

Vol%	Feedstock		Product @ 48 hr.	
	C	F	C	F
IBP	199	390	174	345
10	203	397	193	379
20	203	397	201	394
30	204	399	203	397
40	205	401	204	399
50	206	403	204	399
60	206	403	204	399
70	206	403	205	401
80	207	405	206	403
90	207	405	208	406
END POINT	208	406	210	410
Recovery	99		93	
Residue	1		1	
Lost	0		6	

TABLE XVI

DISTILLATION DATA FOR RUN 5

Vol%	Feedstock		Product @ 48 hr.	
	C	F	C	F
IBP	200	392	201	394
10	202	396	202	396
20	202	396	203	397
30	202	396	204	399
40	203	397	204	399
50	203	397	205	401
60	204	399	206	403
70	205	401	207	405
80	206	403	208	406
90	211	412	218	424
END POINT	213	415	224	435
Recovery	95		93	
Residue	4		5	
Lost	1		2	

results of the analysis show the interference of moisture adsorbed on the catalysts which increase the hydrogen content of the catalyst sample. In this technique the combusted catalysts still contain some coke inside their pores.

Direct combustion of catalyst in an oven and measurement of the weight loss give a more accurate coke percentage results. Table XVII shows the results of the analysis in carbon weight percent of the catalyst.

The liquid samples were analyzed for the concentrations of Tetralin, decalin, and phenanthrene by Gas Chromatography. The results are shown in Tables XVIII and XIX. The calculation techniques of the concentration of each component is not well developed yet in our laboratory. The results of the calculation showed that the summation of the mass fractions exceed unity.

A study of titanocene dichloride concentration in the feedstocks was conducted to determine the decomposition of titanocene dichloride in Tetralin. A homogeneous reaction between titanocene dichloride and Tetralin was observed. Four Tetralin samples were doctored with 100 ppm of titanium as titanocene dichloride at different times. The solid particles that were formed from the reaction were separated, washed with acetone, and dried at 82°C (180°F) for 2 hours.

The liquid samples were analyzed for titanium concentration using X-ray Spectrometer. The dried solid particles were analyzed for carbon and hydrogen using elemental analyzer and for titanium using X-ray Spectrometer. The results are shown in Table XX. The homogeneous reaction between titanocene dichloride and Tetralin will be dicussed in Chapter V.

TABLE XVII

CARBON CONTENT ON THE CATALYST

RUN #	REACTOR #	WT% CARBON IN SECTION TOP	 MIDDLE	 BOTTOM
1	1	1.40	1.20	1.80
1	2	1.40	1.67	1.72
2	1	1.47	1.07	0.68
2	2	0.85	0.75	0.70
3	1	1.70	1.52	1.13
3	2	1.45	1.21	1.04
4	1	1.35	1.07	1.38
4	2	-	-	-
5	1	1.43	1.30	1.47
5	2	1.20	1.08	1.11

* - indicates that there is no data available

TABLE XVIII

CONVERSION OF TETRALIN AND PHENANTHRENE OF INTERSTAGE PRODUCTS

RUN #	TIME (HOUR)	% TETRALIN		% PHENANTHRENE	
		WEIGHT	CONVERSION	WEIGHT	CONVERSION
1	0	100	0	-	-
1	12	80	20	-	-
1	24	84	16	-	-
1	36	89	11	-	-
1	48	92	8	-	-
1	60	94	6	-	-
2	0	100	0	-	-
2	12	84	16	-	-
2	24	91	9	-	-
2	36	96	4	-	-
2	48	99	1	-	-
2	60	99	1	-	-
3	0	95	0	5	0
3	12	88	7	0.6	88
3	24	89	6	1.3	74
3	36	90	5	1.0	80
3	48	90	5	1.8	64
3	60	92	3	2.1	58

TABLE XVIII (Continued)

RUN #	TIME (HOUR)	% TETRALIN WEIGHT	% TETRALIN CONVERSION	% PHENANTHRENE WEIGHT	% PHENANTHRENE CONVERSION
4	0	100	0	-	-
4	12	78	22	-	-
4	24	82	18	-	-
4	36	94	6	-	-
4	48	96	4	-	-
4	60	97	3	-	-
5	0	95	0	5	0
5	12	88	7	0.8	84
5	24	86	9	1.1	78
5	36	85	11	1.2	76
5	48	84	12	1.6	68
5	60	86	9	1.9	62

TABLE XIX

CONVERSION OF TETRALIN AND PHENANTHRENE OF PRODUCT OIL

RUN #	TIME (HOUR)	% TETRALIN WEIGHT	% TETRALIN CONVERSION	% PHENANTHRENE WEIGHT	% PHENANTHRENE CONVERSION
1	0	100	0	-	-
1	12	63	37	-	-
1	24	77	23	-	-
1	36	76	24	-	-
1	48	81	19	-	-
1	60	84	16	-	-
2	0	100	0	-	-
2	12	67	33	-	-
2	24	68	32	-	-
2	36	73	27	-	-
2	48	91	9	-	-
2	60	86	14	-	-
3	0	95	0	5	0
3	12	79	17	0.5	90
3	24	80	16	0	100
3	36	79	17	0	100
3	48	81	15	0	100
3	60	76	20	0	100

TABLE XIX (Continued)

RUN #	TIME (HOUR)	% TETRALIN		% PHENANTHRENE	
		WEIGHT	CONVERSION	WEIGHT	CONVERSION
4	0	100	0	-	-
4	12	21	79	-	-
4	24	10	90	-	-
4	36	18	82	-	-
4	48	11	89	-	-
4	60	11	89	-	-
5	0	95	0	5	0
5	12	67	30	0	100
5	24	82	14	0	100
5	36	81	15	0	100
5	48	90	5	0	100
5	60	90	5	0	100

TABLE XX

RESULTS OF THE HOMOGENEOUS STUDY

Titanium Concentration

TIME (hour)	Ti CONC (ppm)
18	60
45	40
69	30
114	20
2600	5

Composition of the Solid Particles

Element	% by weight
Hydrogen	4.65
Carbon	29.90
Titanium	65.45

The expected formula of the solid particles is $Ti(CH_2)_2$.

In Hydrogenation processes, the unsaturated hydrocarbon compounds can be hydrogenated resulting in an increase in hydrogen content of the oil. The phenomenon can be observed by an increase in hydrogen to carbon atomic ratio of the hydrogenated product.

Figures 2, 3, 4, 5, 6 and 7 show the plots of hydrogen to carbon atomic ratio as a function of both time and oil to catalyst mass ratio.

Figures 8, 9, 10, 11, 12 and 13 show the weight percent of coke on the catalyst as a function of reactor zone.

Feedstock and product oils at 48 hours of each run were fractionated following ASTM D-1160 procedure. The distillations were done at 1.34 kPa (10 mmHg) and the temperatures were converted to the temperatures required at 101.3 kPa (760 mmHg).

Figures 14, 15 and 16 show the distillation curves of runs 1 and 2, runs 3 and 5, and runs 1 and 4, respectively. Some of the hydrogenated products were observed to have lower boiling point ranges than the feedstocks, however, some high boiling point products raised the distillation curve up to higher temperature ranges.

Each point in the figures is the average of at least 3 analyses. The bar represents the ranges of the data points. The bar is not drawn when the data are in the point.

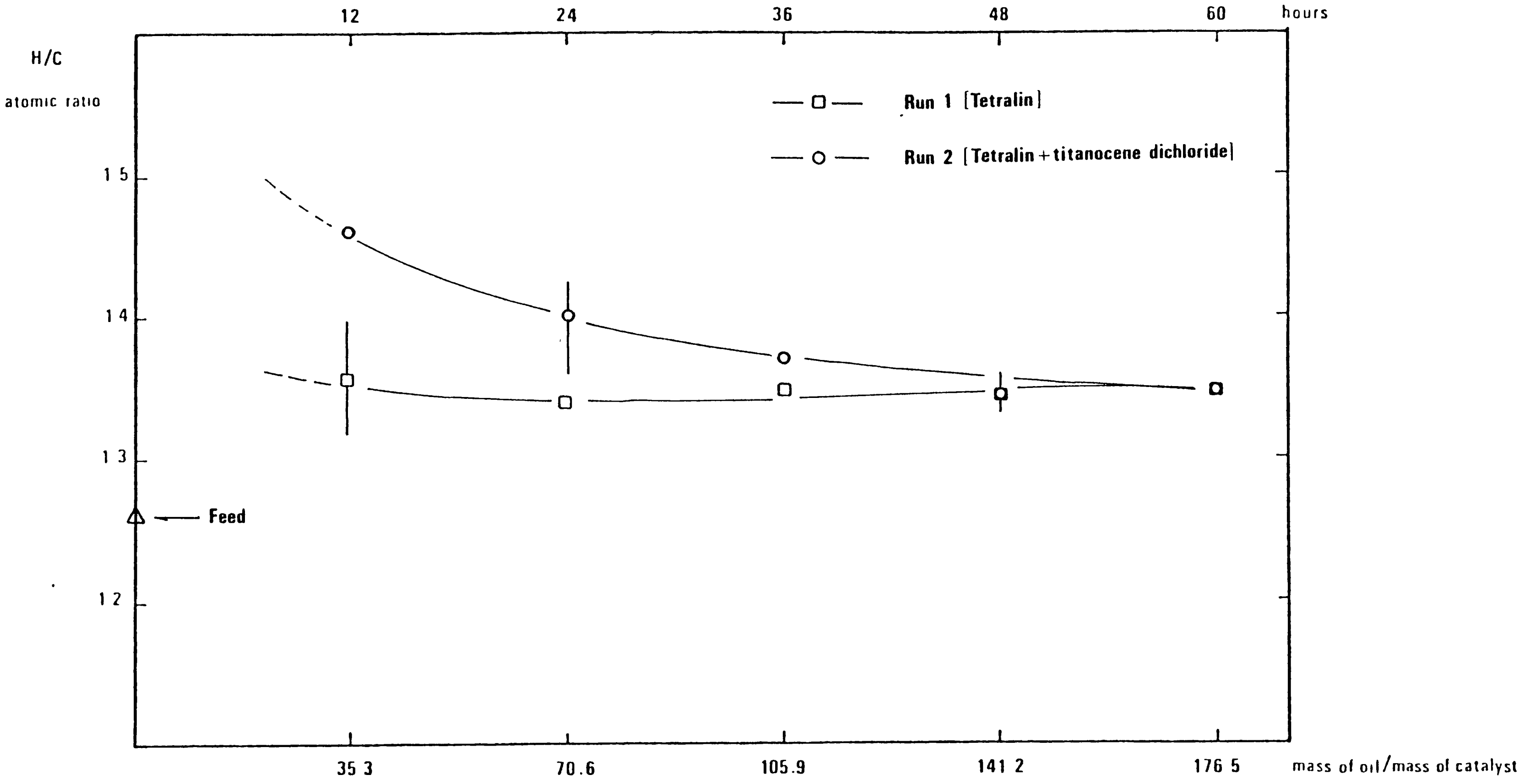


Figure 2. Hydrogenation Activity as a Function of Oil to Catalyst Mass Ratio for Reactor 1

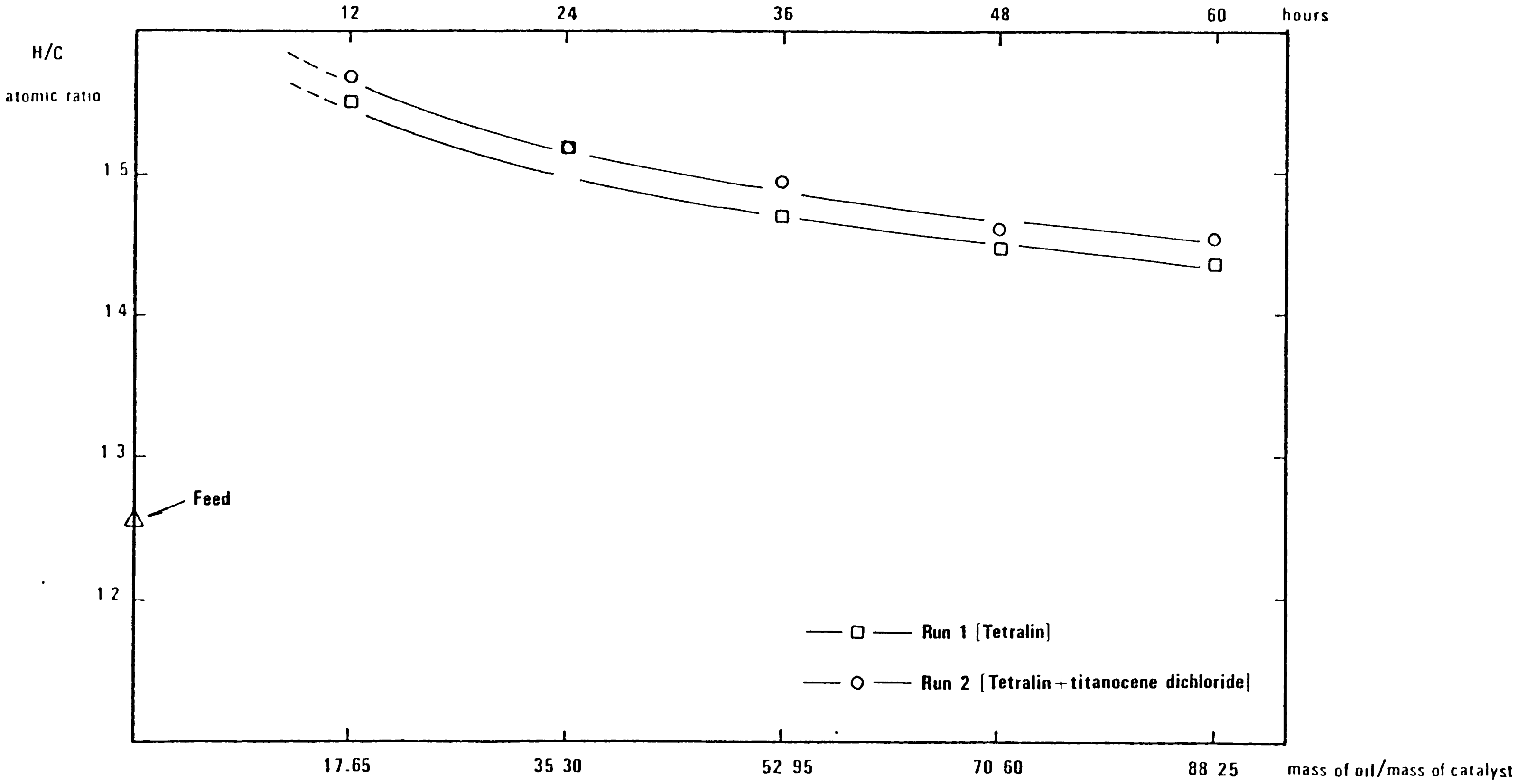


Figure 3. Hydrogenation Activity as a Function of Oil to Catalyst Mass Ratio for Reactor 2

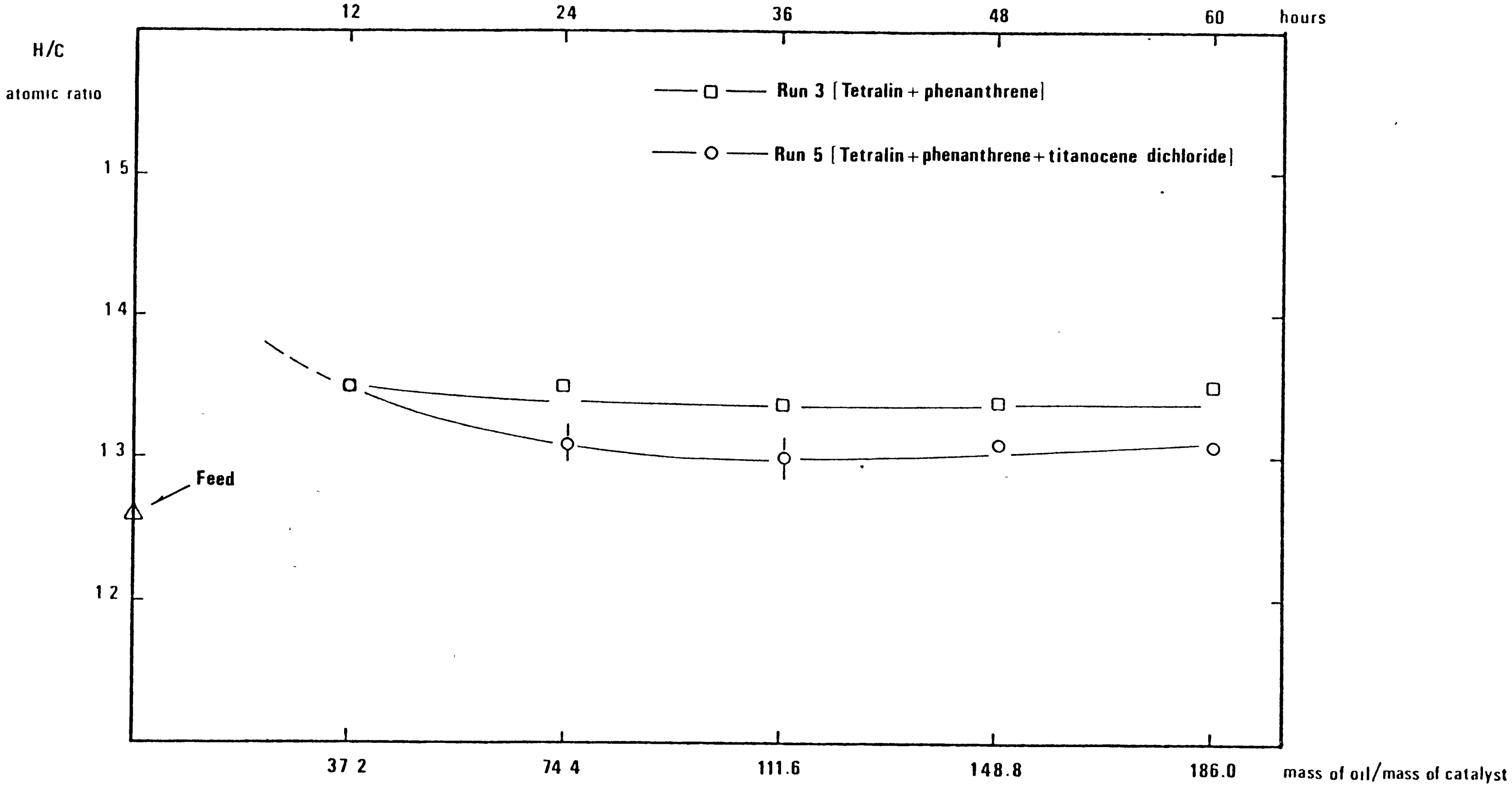


Figure 4. Hydrogenation Activity as a Function of Oil to Catalyst Mass Ratio for Reactor 1

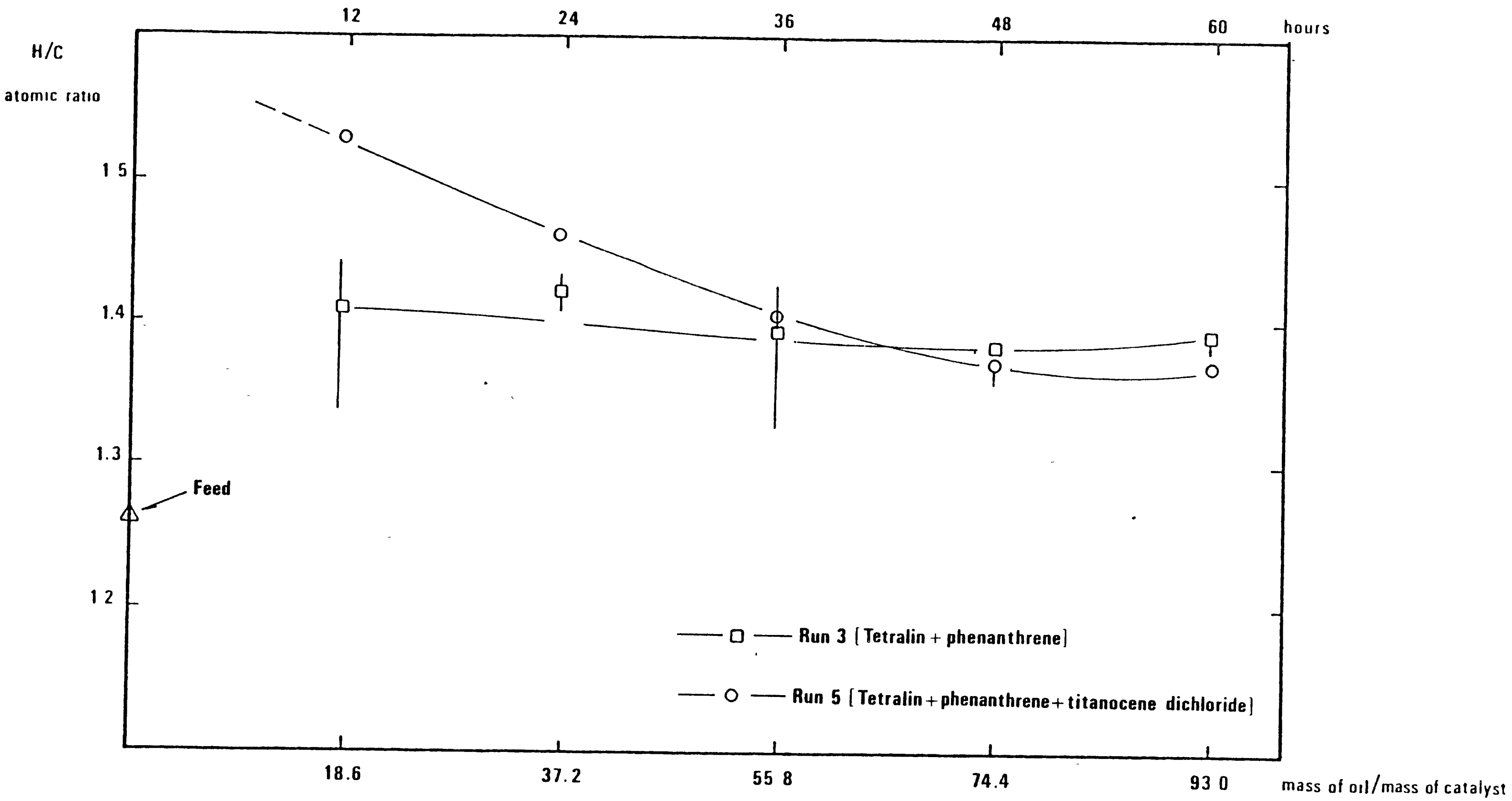


Figure 5. Hydrogenation Activity as a Function of Oil to Catalyst Mass Ratio for Reactor 2

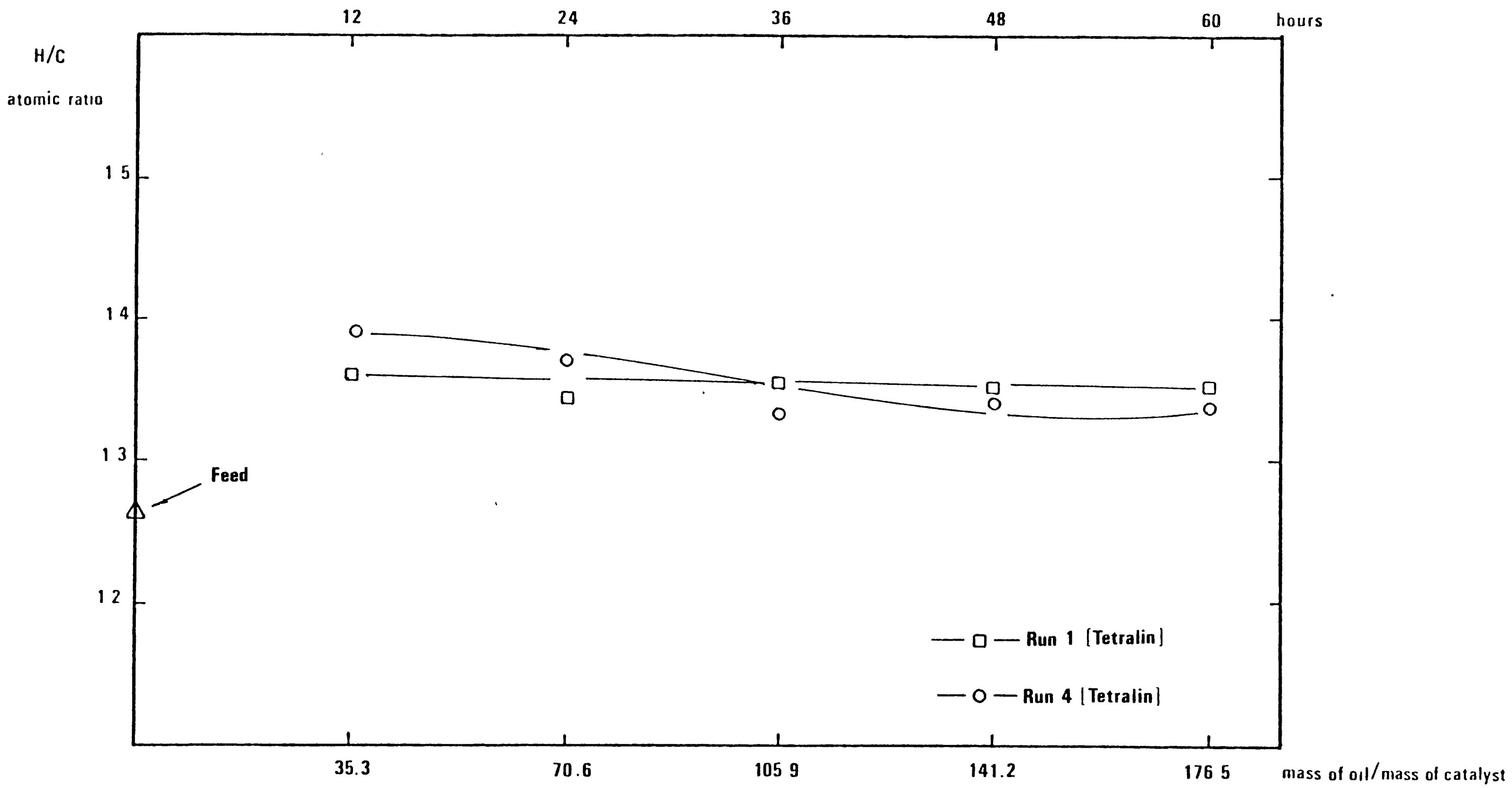


Figure 6. Hydrogenation Activity as a Function of Oil to Catalyst Mass Ratio for Reactor 1

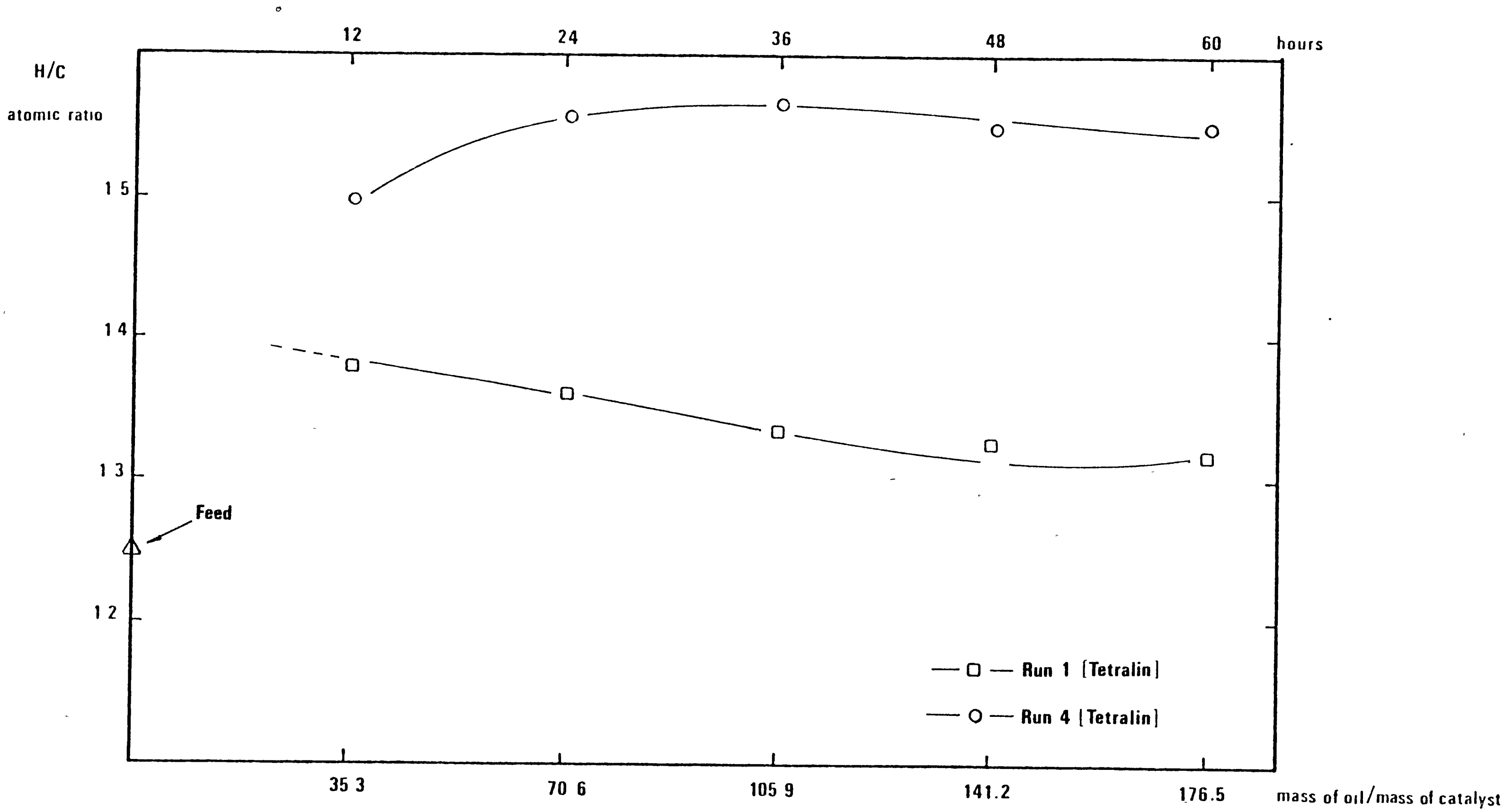


Figure 7. Hydrogenation Activity as a Function of Oil to Catalyst Mass Ratio for Reactor 2

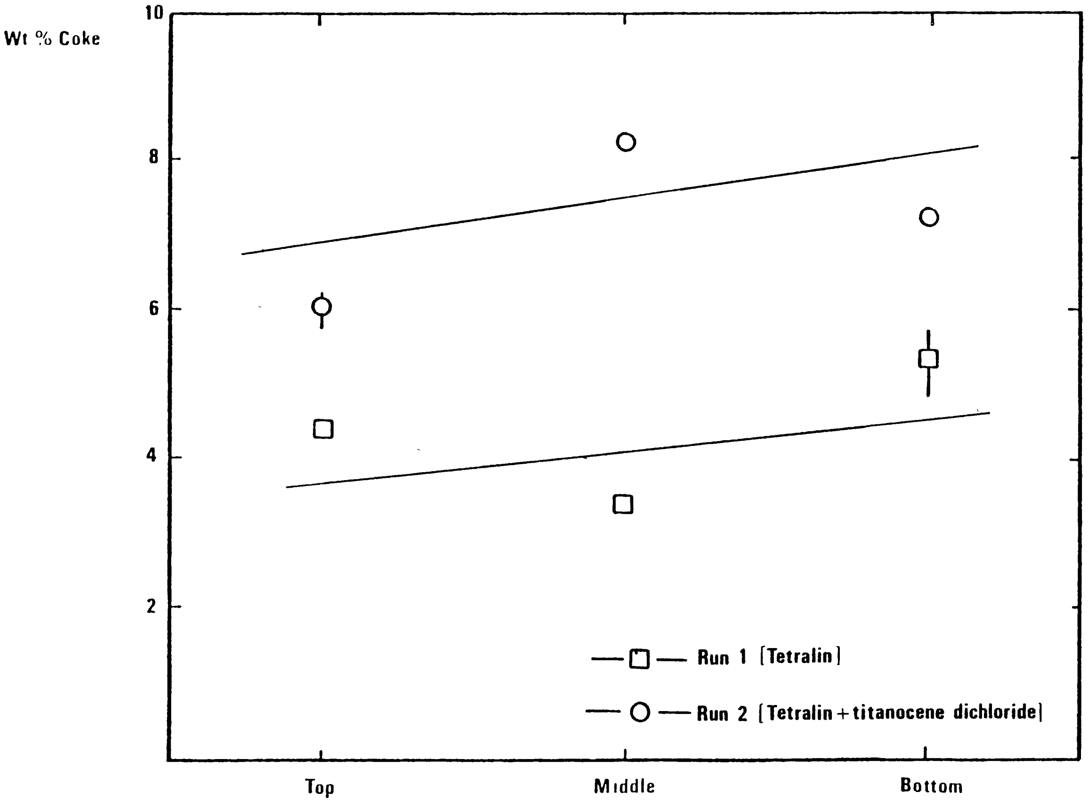


Figure 8. Coke Content as a Function of Reactor Zone for Reactor 1

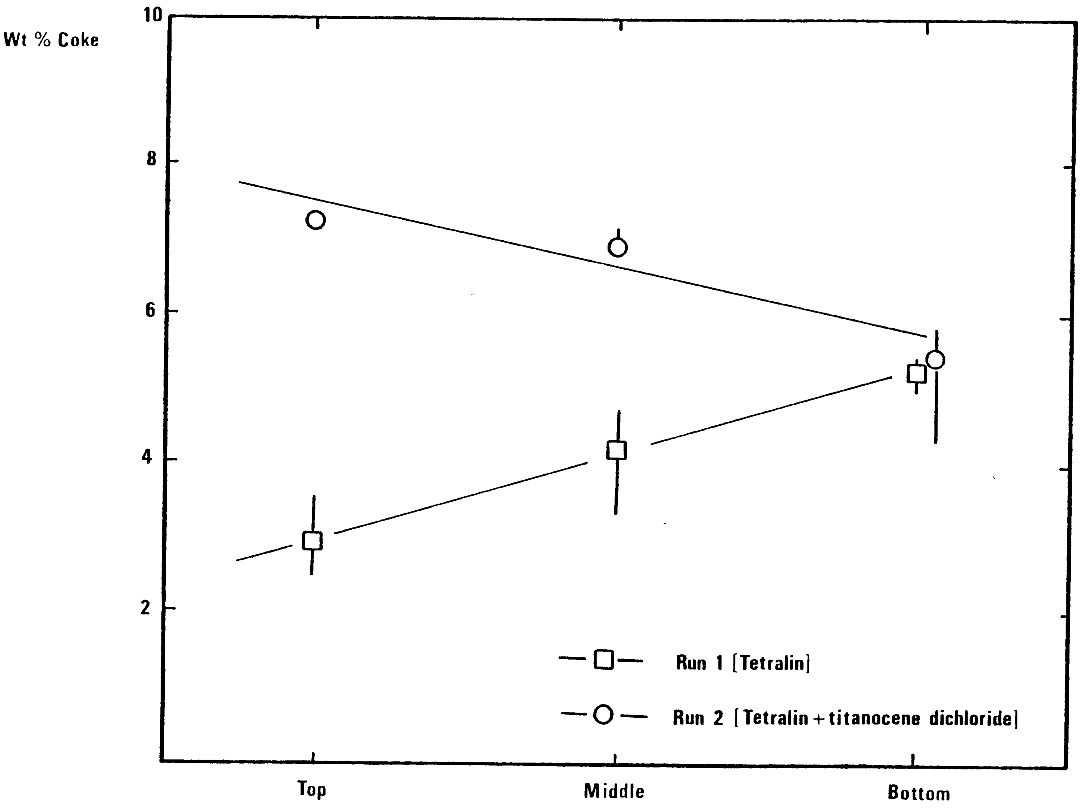


Figure 9. Coke Content as a Function of Reactor Zone for Reactor 2

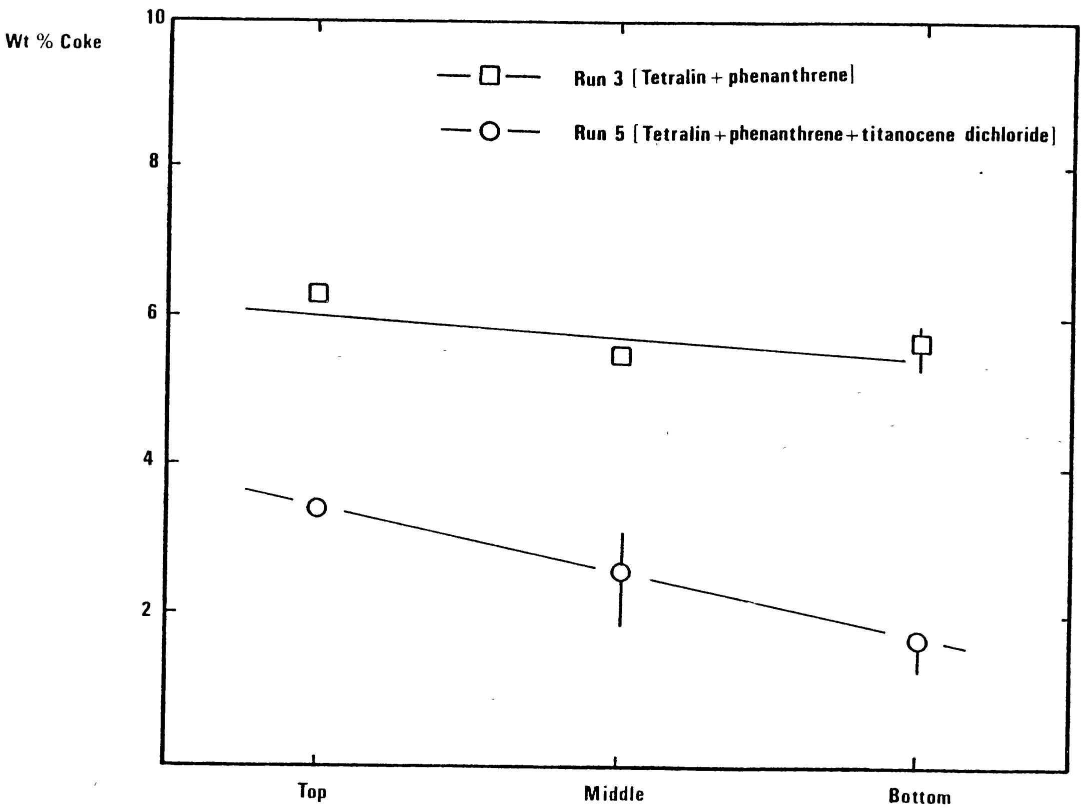


Figure 10. Coke Content as a Function of Reactor Zone for Reactor 1

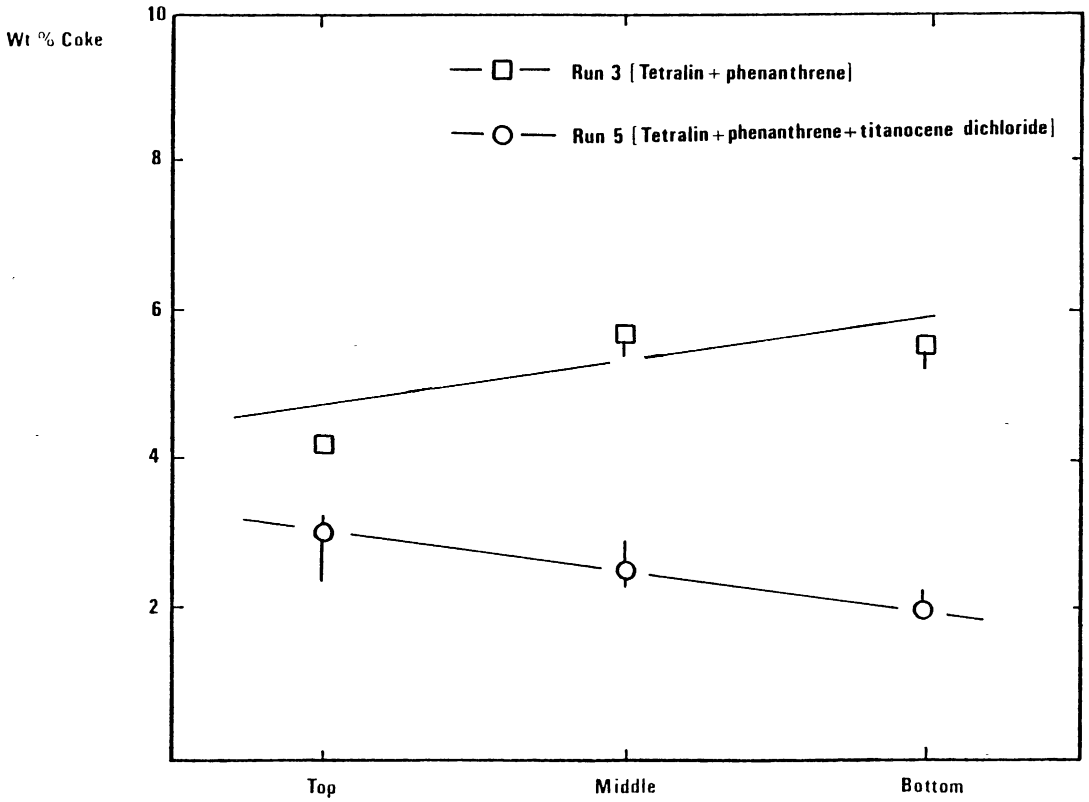


Figure 11. Coke Content as a Function of Reactor Zone for Reactor 2

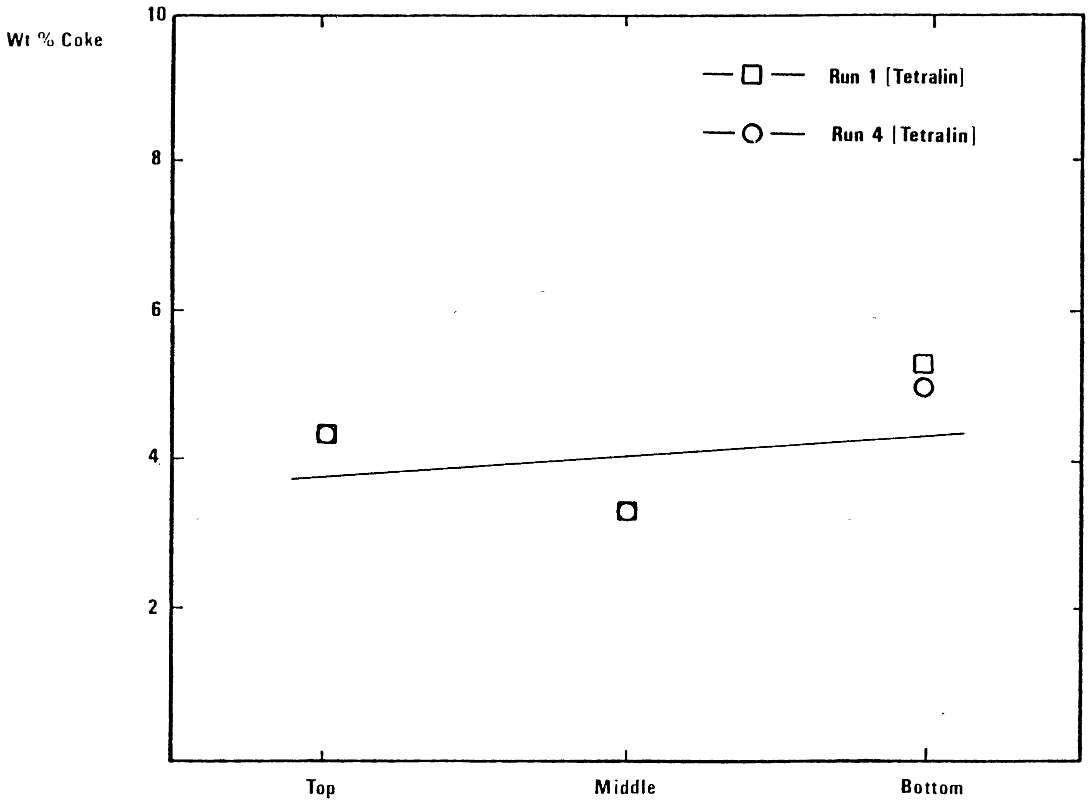


Figure 12. Coke Content as a Function of Reactor Zone for Reactor 1

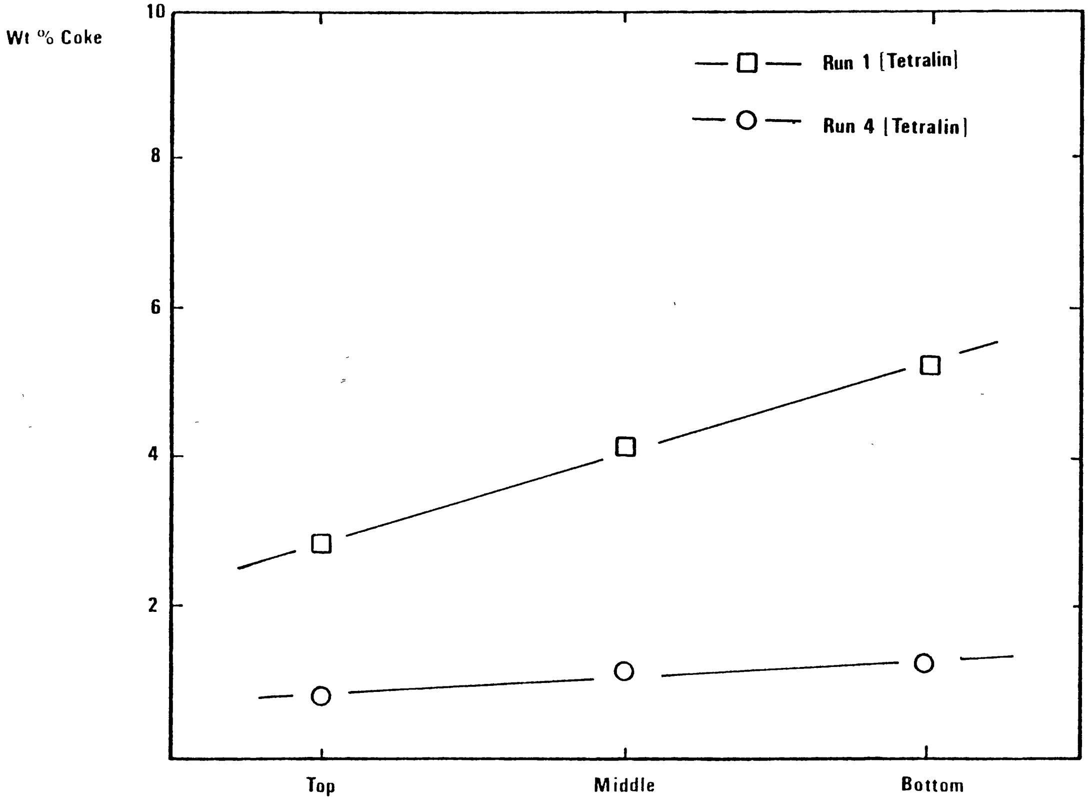


Figure 16. Coke Content as a Function of Reactor Zone for Reactor 2

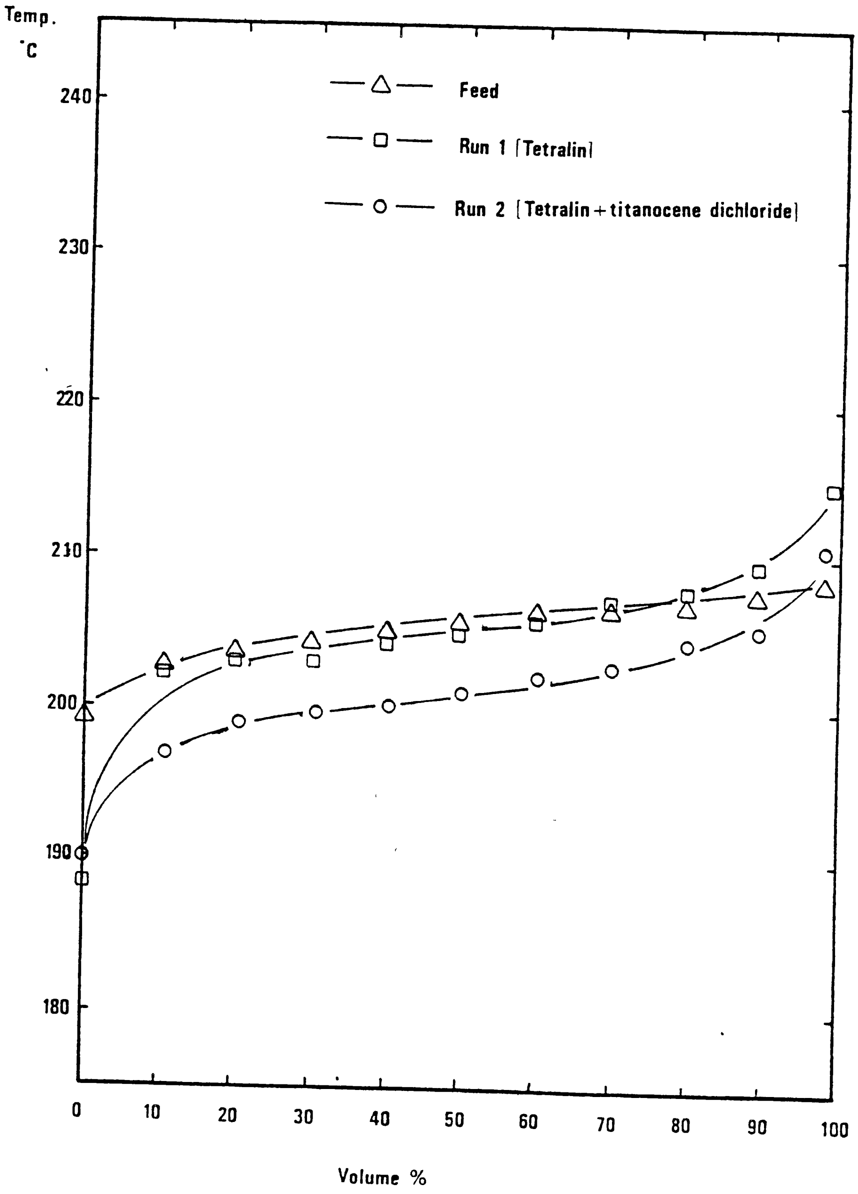


Figure 14. Distillation Curve for Feedstock and Product Oil at 48 hours

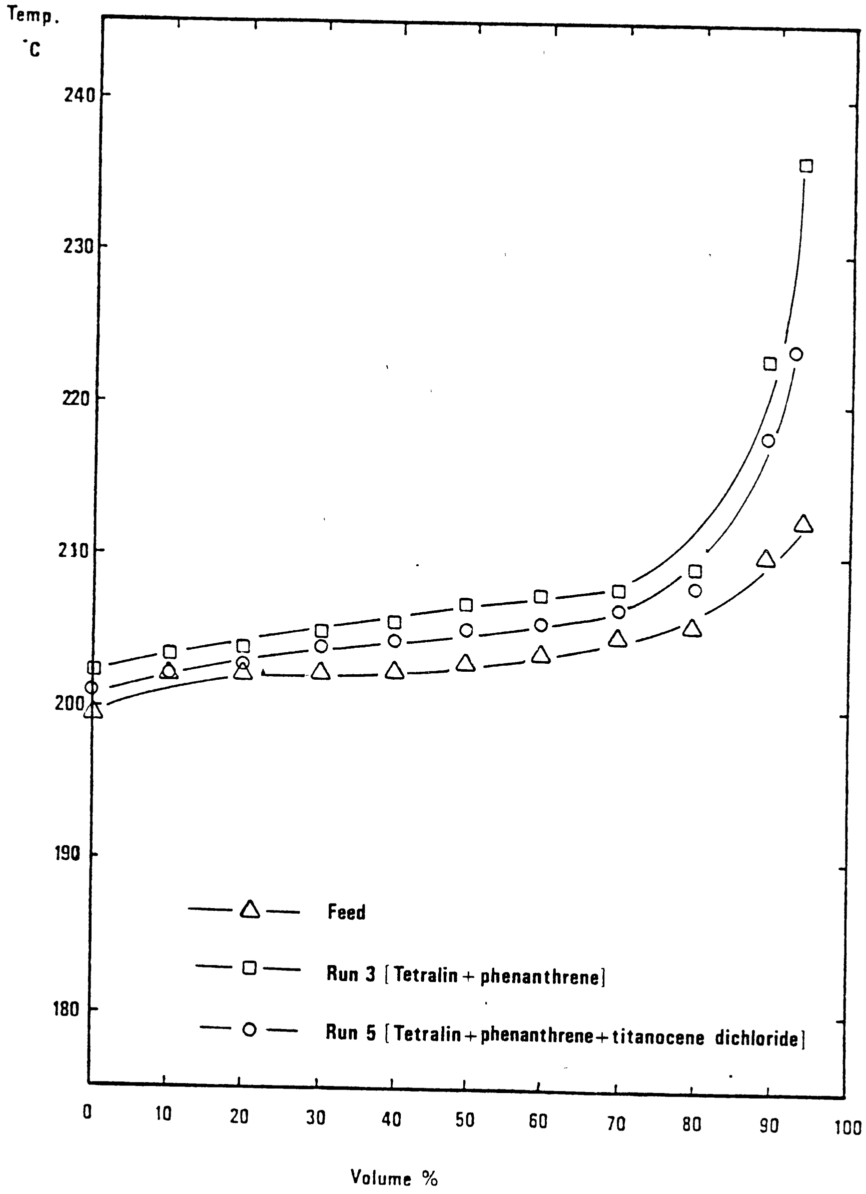


Figure 15. Distillation Curve for Feedstock and Product Oils at 48 hours

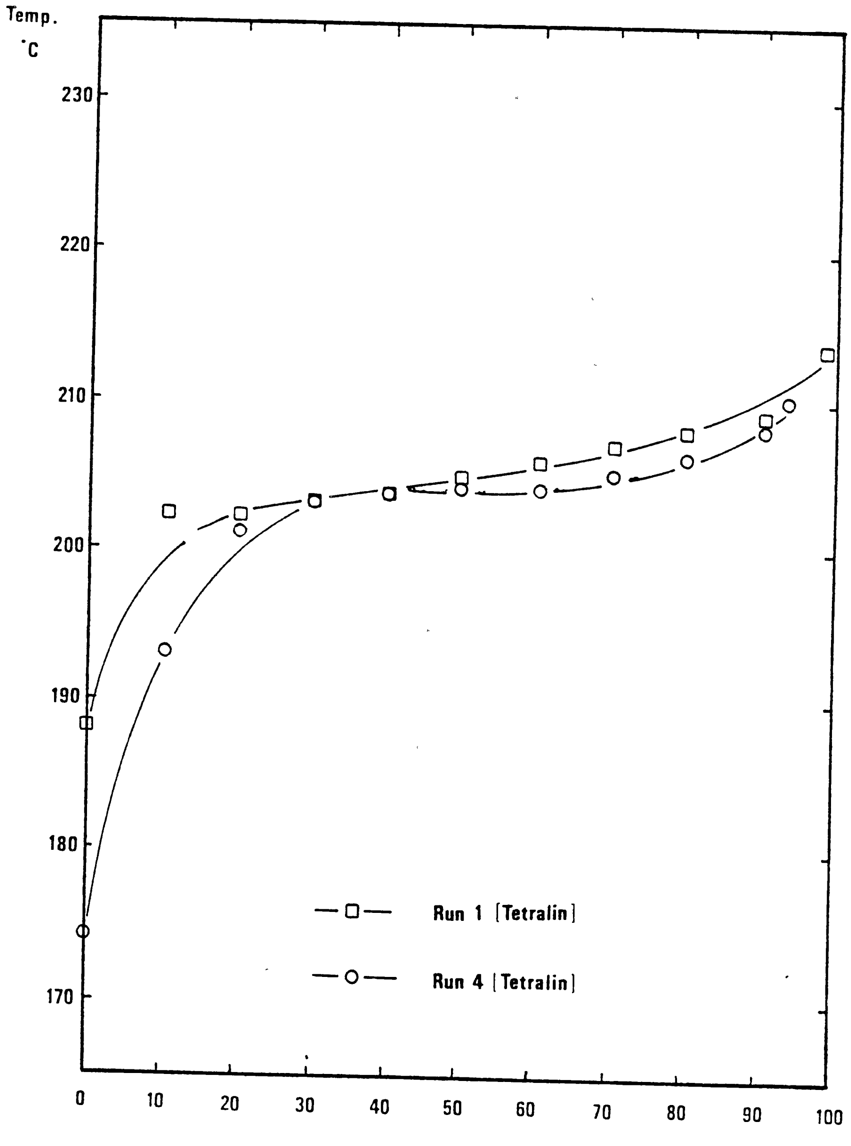


Figure 16. Distillation Curve for Product Oil at 48 hours

CHAPTER V

DISCUSSION

Homogeneous Reaction

Our studies showed that a homogeneous reaction occurred between Tetralin and titanocene dichloride. This reaction resulted in decomposition of titanocene dichloride and formation of an insoluble titanium compound which precipitates as small solid particles. The analysis of the particles showed that they mainly consisted of titanium, carbon and hydrogen. This homogeneous reaction also resulted in a decrease in the concentration of dissolved titanium in the feedstock. The analysis of the top section of glass beads showed that titanium was completely removed by the glass beads. There was no titanium found in the catalyst nor in the product oils. Therefore, the changes in hydrogen to carbon atom ratio in oils and the coke formation on catalyst, when titanocene dichloride was added to the feedstock, were not the results of interaction of titanium with catalyst.

Chloride ion was another product of this homogeneous reaction which remained in the feedstock. The chloride concentration in the feedstock was constant throughout the experimental period. A small amount of chloride was found at the top section of the glass beads. The analyses of catalysts showed that only a trace amount of chloride was deposited on the catalyst surface. No chloride was found in the oil products. Chloride in the feedstock is believed to have reacted with hydrogen gas and formed hydrogen chloride which has emitted to the atmosphere via the outlet gas stream.

Our data showed that the products collected during the first 36 hours of the experiments were different when titanocene dichloride was added to the feedstocks. However, these differences could not have resulted from the presence of chloride, because the chloride concentration remained constant throughout the runs.

This indicated that the differences occurred due to another factor besides chloride ions or titanium. Since titanocene dichloride undergoes a homogeneous reaction in the feed tank, the feedstock initially contained more titanocene dichloride than at the end of the run. The homogeneous reaction of titanocene dichloride and Tetralin was expected to generate some active organic molecules or free radicals in addition to the insoluble titanium compound and the chloride ion. The concentration of this free radical gradually decreased due to a decrease in the soluble titanium concentration in the feed. The initial difference in the hydrogen to carbon atom ratio and coke formation between runs with and without titanocene dichloride could be explained by the presence of this free radical.

Run 1 and Run 2

Run 1 is a reference run. The data on the amount of coke formed on the catalyst, the hydrogenation activity, and the distillation curve are used as a basis of comparison with the other runs.

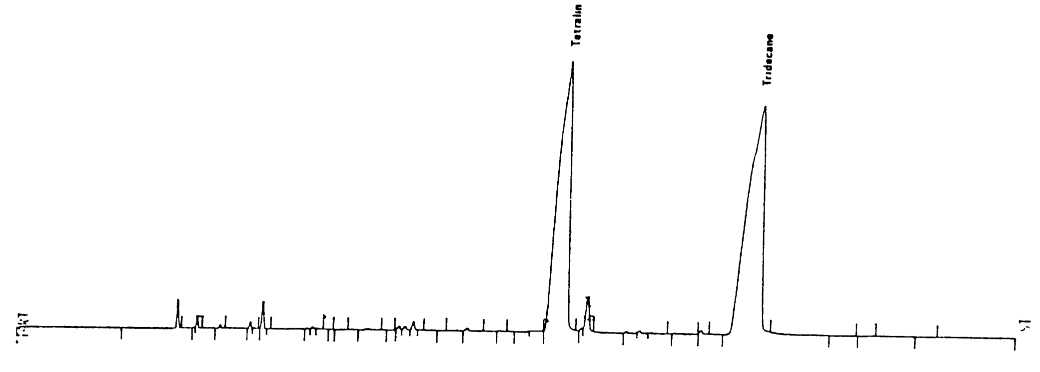
In run 2, 100 ppm of titanium as titanocene dichloride was added to Tetralin. The feedstock was hydrotreated at the same operating conditions as in run 1. The analyses show that the hydrogen to carbon atom ratio of the products increase when titanocene dichloride is added to Tetralin. This is confirmed by the shift of distillation curve to the lower boiling point range when the products of the two runs are compared.

When the distillation curves of the products and the feedstock are compared, it is shown that the products of both runs consist both of lighter components and heavier components. The Gas Chromatograph analyses show that the lighter components are cis- and trans- decalin (b.p. 193^{o}C, and 185^{o}C respectively), the products of Tetralin hydrogenation reaction, and the heavier component is naphthalene (b.p. 218^{o}C), the product of Tetralin dehydrogenation reaction. As shown by the Gas Chromatograph analysis, the conversion of Tetralin is low. This conversion is expected to be about 20 percent. Figure 17 shows the results from Gas Chromatograph analysis.

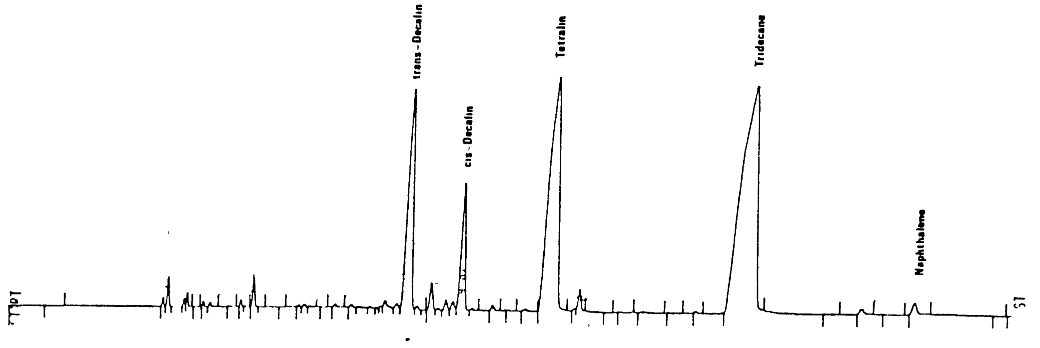
More coke is formed on the catalyst when titanocene dichloride is present in the feedstock. Coke is believed to form by polymerization and dehydrogenation or hydrogen elimination reactions of the absorbed hydrocarbon molecules on the catalyst. The eliminated hydrogen atoms from coke formation reactions are probably more active and react with Tetralin easier than the hydrogen gas. It is possible that the increase in hydrogen to carbon atom ratio of the products of run 2 is not the result of hydrogenation reaction only, but it is also the product of coke formation reactions.

Run 1 and Run 4

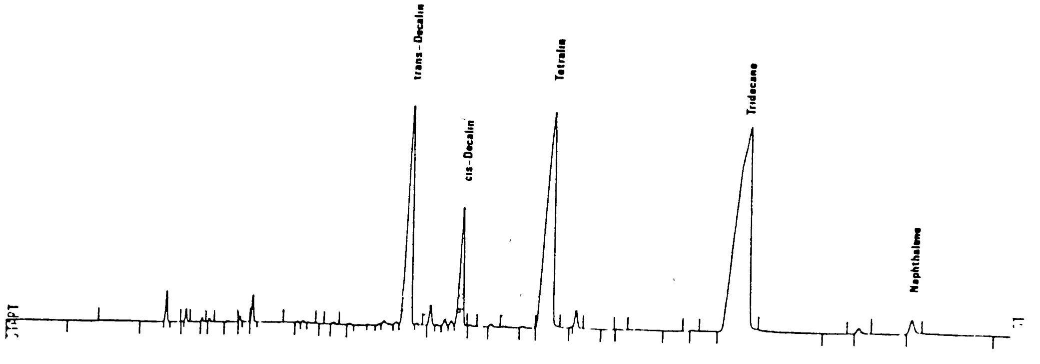
The effect of temperature on hydrogenation of Tetralin is clearly shown by run 4. The hydrogen to carbon atom ratio of the products of



Feed



Run 1 at 12 hrs



Run 2 at 12 hrs

Figure 17. Gas Chromatograph Analyses for Feedstock and Product Oils at 12 hours

run 4 are much higher than the products of run 1 and that the amount of coke formed on the catalyst is much less. The increase in hydrogen to carbon atom ratio is expected to be the result of higher hydrogenation reaction rather than the hydrogen elimination reaction. The adsorbed hydrocarbon molecules on the catalyst react with hydrogen and form the hydrogenated products. Gas Chromatograph analysis show that the main products are again cis- and trans-dicalin (Figure 18). The change in hydrogen to carbon atom ratio is the result of higher conversion which is about 80 percent.

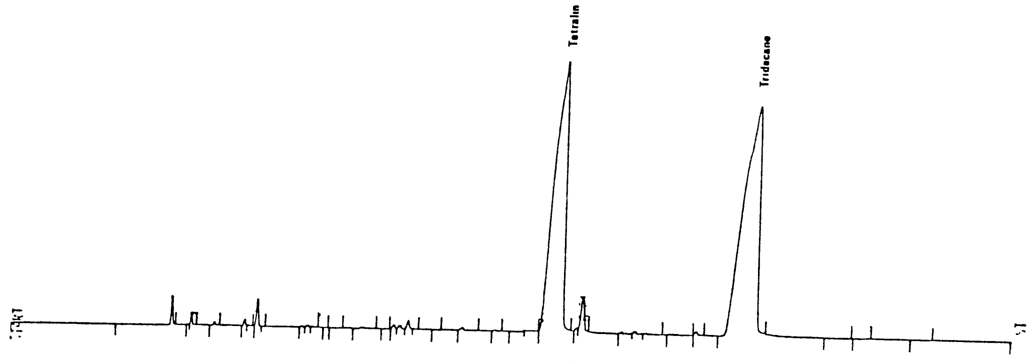
The high temperature zone in reactor 2 of run 4 is expected to be the result of higher hydrogenation reaction caused by localized liquid holdup. A nonuniform packing of the catalyst creates a spacial restriction in the reactor which causes a localized increase in the liquid holdup.

The reaction rate is proportional to the liquid holdup (13). An increase in the localized liquid holdup causes an increase in the reaction rate in reactor 2, which results in the temperature zone due to an exothermic hydrogenation reaction.

The coke formation in reactor 2 of run 4 is less than the one in run 1. Turan et al. (30) suggested that two types of coke were present on the catalyst, a reactive coke and an unreactive coke. In run 4, the coke that is formed on the catalyst surface may be the reactive coke which is converted to reaction products rather than the unreactive coke.

Run 3 and Run 5

In runs 3 and 5, the feedstock is a 5 wt% mixture phenanthrene in Tetralin. The amount of coke formed on the catalyst in run 3 is higher



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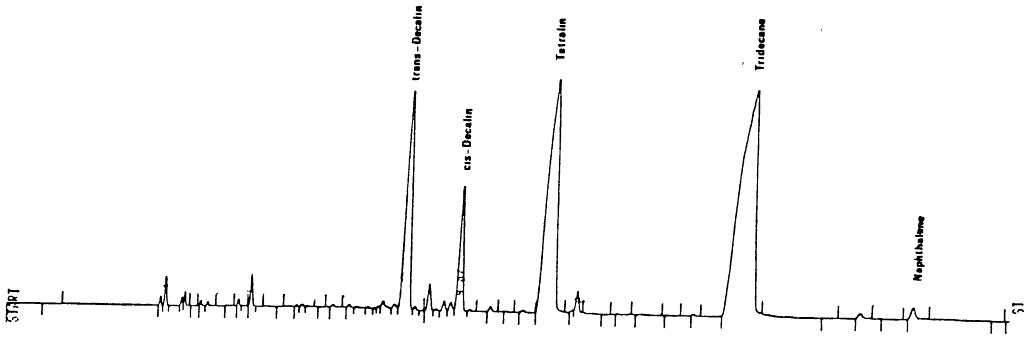
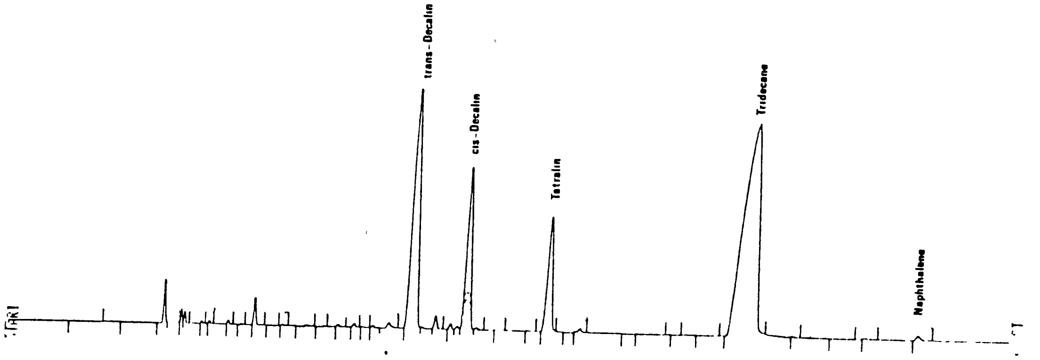


Run 1 at 12 hrs



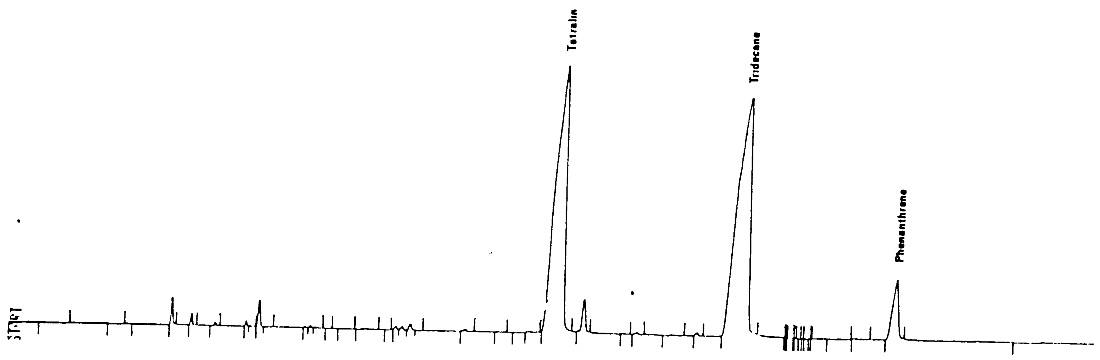
Run 4 at 12 hrs

Figure 18. Gas Chromatograph Analyses for Feedstock and Product Oils at 12 hours

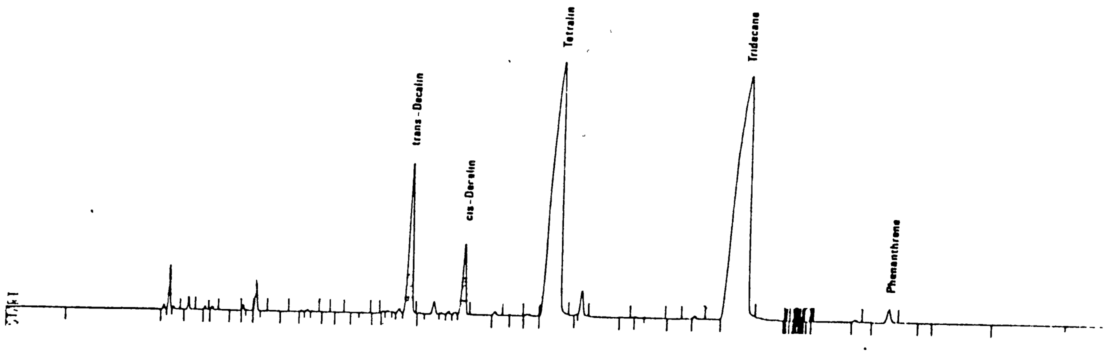
than that of run 1. Phenanthrene has a higher tendency to form coke than Tetralin because of its larger molecular size and higher aromaticity.

In run 5, when titanocene dichloride is added to the feedstock, the amount of coke decreases. The interference of titanocene dichloride with coke formation mechanism is not yet known. The effect of titanocene dichloride on hydrogenation activity is shown by the change in the hydrogen to carbon atom ratio. The hydrogen to carbon atom ratio of the products increases when titanocene dichloride is added to the feedstock. Titanocene dichloride also affects the distillation curves. The distillation curve shifts down to the lower boiling point ranges when titanocene dichloride is present.

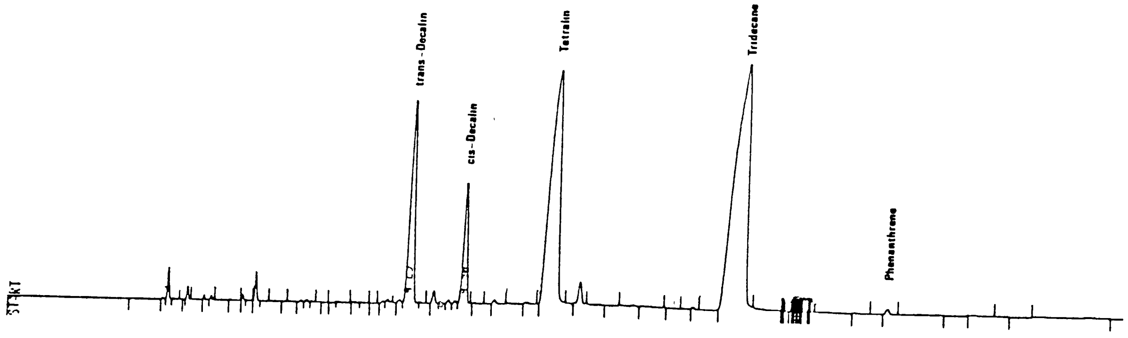
Gas Chromatographic analyses showed that most of phenanthrene was hydrogenated. The hydrogenated products of phenanthrene were not clearly detected by the analyzer. Figure 19 shows the Gas Chromstographic analyses of runs 3 and 5.



Feed



Run 3 at 12 hrs



Run 5 at 12 hrs

Figure 19. Gas Chromatograph Analyses for Feedstock and Product Oils at 12 hours

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the experimental results:

1. In the hydrogenation of Tetralin over Ni-Mo/alumina catalyst the addition of titanocene dichloride to Tetralin results in an increase in hydrogen to carbon atom ratio.

2. The increase in hydrogen to carbon atom ratio at the low temperature of 350°C (662°F) is believed to be the results of coke formation reaction rather than hydrogenation reaction.

3. Titanocene dichloride affects the coke formation on the catalyst. The effects depend on the type of hydrocarbon feedstocks.

4. A homogeneous reaction between titanocene dichloride and Tetralin results in the decomposition of titanocene dichloride and formation of an insoluble titanium compound.

5. The differences in the hydrogenation activity and the coke formation are expected to be the results of the organic part or the free radicals, generated form homogeneous reaction of titanocene dichloride.

Recommendations

1. The same set of studies should be done using other types of

organometallic compounds such as ferrocene or nickelocene to study the effect of the other metal compounds.

2. Hydrochloric acid should be used instead of organometallic compounds to study the effects of chloride ions.

3. The same set of study should be conducted at a higher operating temperature to study the effect of temperature on the hydrogenation reaction.

4. A homogenous reaction between titanocene dichloride and Tetralin should be studied. The product oil and solid particles from the homogeneous reaction should be analyzed to identify the compounds and structures.

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APPENDIXES

APPENDIX A

MAIN COMPONENTS OF THE SYSTEM

Reactor System

The reactor system consists of two trickle bed reactors connected in series and equipped with temperature programmer/controllers and heating system.

Reactor 1

Reactor 1 consists of a 43.2 cm (17 inch) long, 1.27 cm (0.5 inch) O.D., and 0.089 cm (0.035 inch) thick, 316 stainless steel tube, fitted with a 1/2 inch Swagelok cross at the top and union at the bottom. The effective reactor length is 40.6 cm (16 inch) as shown in Figure 20. A 1/2-inch Swagelok cross is connected to the top of the reactor. Two 1/2-inch to 1/4-inch reducers are connected to both sides of the cross. A 1/8-inch O.D., 316 stainless steel tube, with one end welded shut is used as a thermowell. The thermowell is secured in the middle of the reactor by means of a 1/4-inch to 1/8-inch reducing union which is drilled for inserting the thermowell. The 1/4-inch to 1/8-inch reducing union is connected to 1/2-inch cross by means of a 1/2-inch to 1/4-inch reducing union. Two stainless steel screens of 50 mesh are used to support the catalyst bed. The bottom of the reactor is fitted with a 1/2-inch to 1/4-inch reducer to enable it to be connected to the sampling system.

Reactor 2

Reactor 2 is the same as reactor 1 except it is a 45.7 cm (18 inch) long. The effective reactor length is 43.2 cm (17 inch) as shown in Figure 21. A 1/2-inch Swagelok tee is connected to the top of this

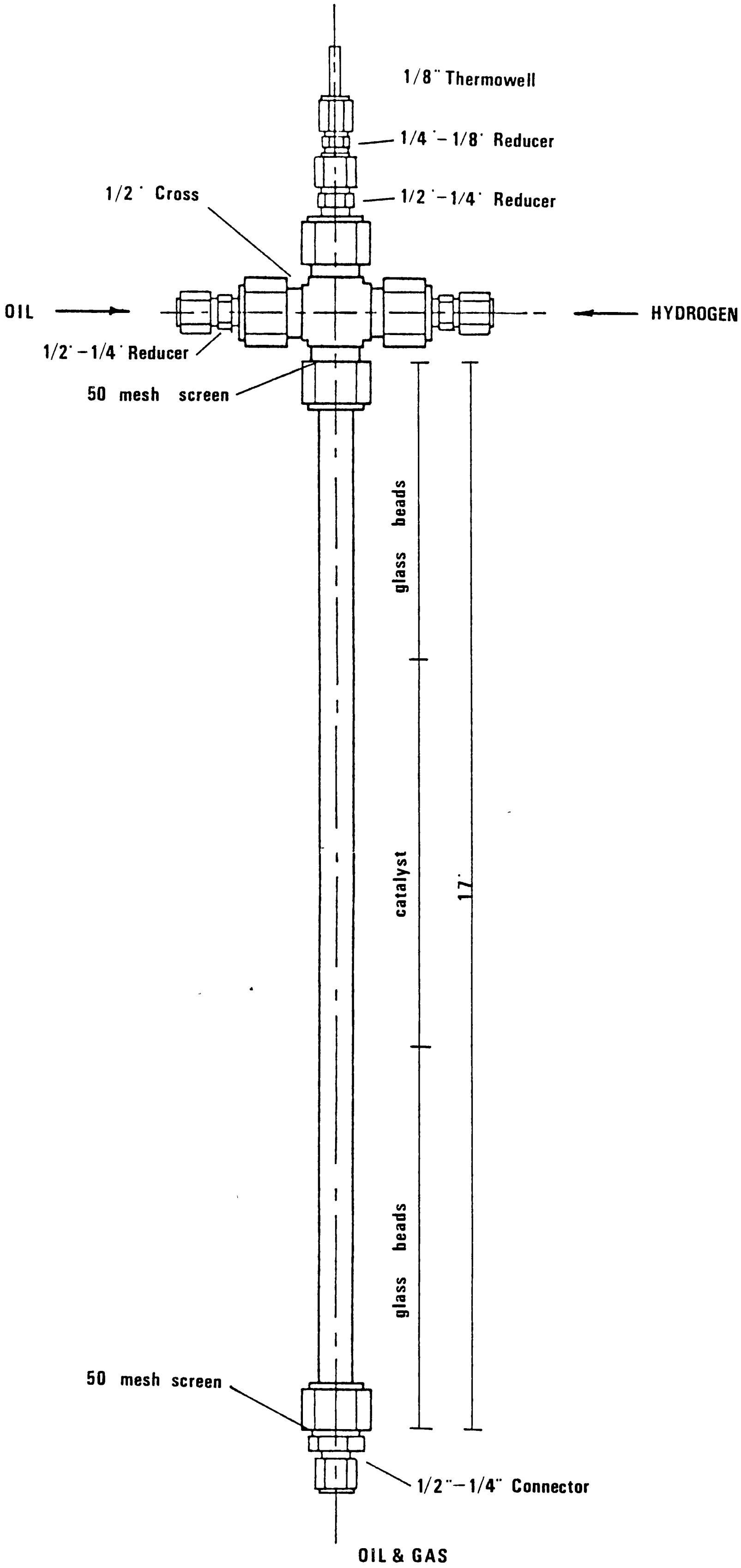


Figure 20. Reactor 1

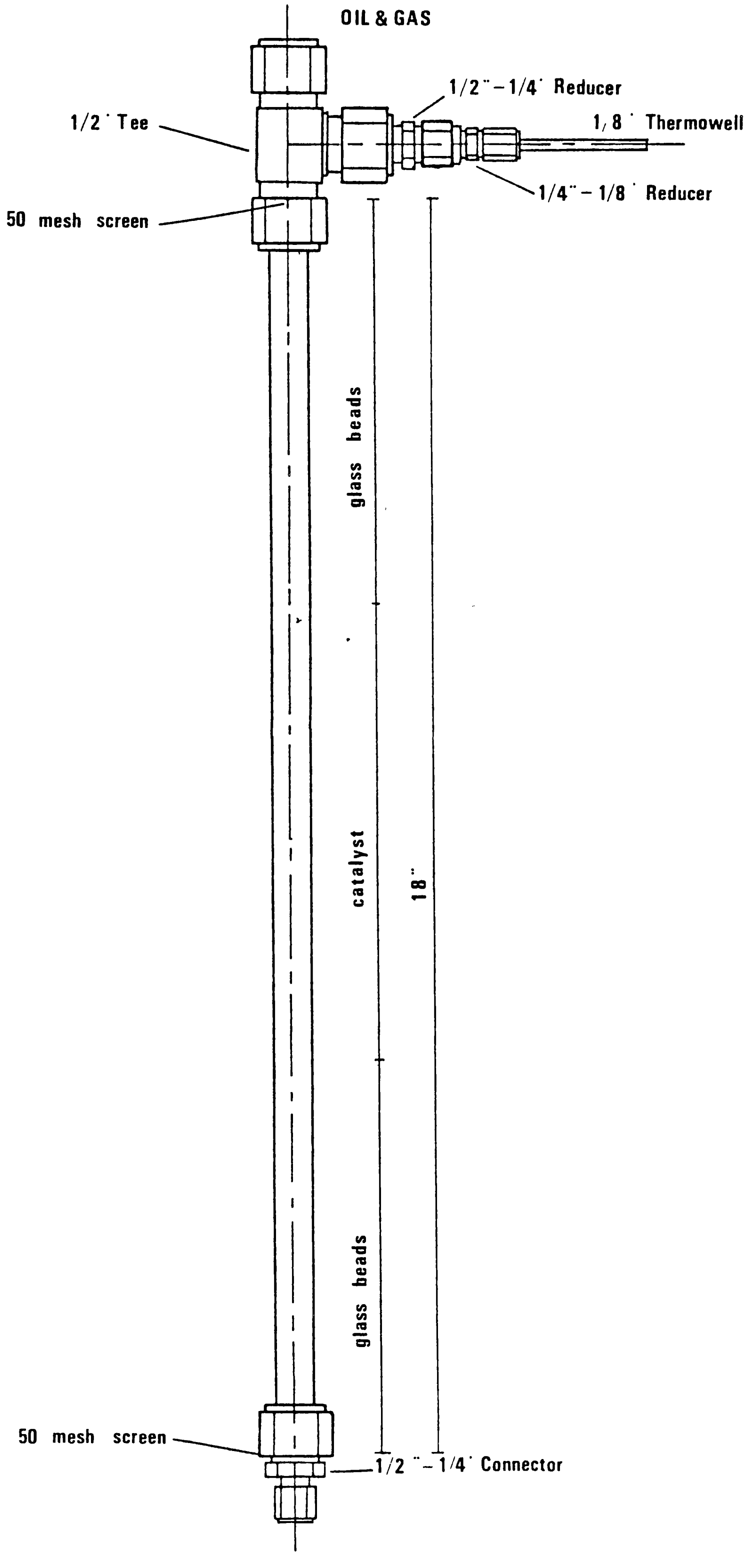


Figure 21. Reactor 2

reactor. The thermowell is secured in the middle of reactor 2 by the same system used in reactor 1 except the open end of the thermowell is put through the side of the tee. The top of reactor 2 is connected to an interstage sampling system through which oil and gas from reactor 1 flow. The bottom of the reactor is fitted with a 1/2-inch to 1/4-inch reducer and is connected to the sample bomb 1.

Reactor Heating System

Two monolithic aluminum blocks, with grooves of reactor diameter running across their entire length are used as the heating blocks. The blocks are secured and bolted together around the reactor tubes. The heating blocks for reactor 1 are 35.6 cm (14 inch) long and the heating blocks for reactor 2 are 40.6 cm (16 inch) long. The heating blocks are made to be fitted with 10.2 cm (4-inch) heating bands which are placed around the assembled block. Three heating bands, 15.24 cm (5 inch) long, rated at 300 watts are secured around each reactor. The power is supplied to the heating band from two temperature programmer/controllers which allow separate temperature control for each reactor. Two platinum resistance thermocouples are placed in the holes drilled in the aluminum blocks. The output signal of these thermocouples are fed into the temperature programmer/controllers for precise temperature control.

Felt material in the form of cylinders, split in the middle, are used for insulating the reactors. In addition to the felt insulation, fiberglass is also wrapped around the reactors.

Oil Feed System

The oil feed system consists of a tank, Ruska positive displacement pump, and safety line. The feed tank is a stainless steel tank, 20.32 cm (8 inch) in diameter and 35.56 cm (14 inch) high. The tank is designed to handle highly viscous liquids. The liquid can be stirred and mixed inside the tank before transferred to the Ruska pump. A set of baffles is fitted inside the tank to provide better mixing. Two heating bands wrapped around the tank are used to warm the feed oil to any desired temperature. The feed tank can be sealed and pressurized up to 208 kPa (30 psig). A thermocouple fitted in a thermowell can be used to monitor the temperature in the tank.

Liquid is fed to the reactor with the Ruska positive displacement pump which can be operated at pressures as high as 68 MPa (10000 psig). The pump can be heated in case of highly viscous liquids for easier flow. Feed lines are wrapped with flexible heating tapes. In this study, most of the heaters in the oil feed are not used. Output pressure is measured by pressure gauge 41. The liquid flow rate is preset at the desired value before the pump is started.

In order to protect the oil feed system from excessive pressure, a switch set at 17 MPa (2500 psig) is used to shut off the Ruska pump power supply when the pressure exceeds the set limit. In case the pressure switch fails to operate, the system is still protected by the safety line, which is equipped with two rupture disks, rated at 18.4 MPa (2700 psig) and 21.8 MPa (3200 psig), respectively, and a surge tank.

Gas Feed System

Hydrogen gas from bottles flows directly through a manifold, which allows the changing of hydrogen cylinders without interrupting the run. The hydrogen gas is metered through a high pressure flow meter which can be operated up to 34 MPa (5000 psig). A "Mity-Mite" pressure regulator is used to regulate upstream hydrogen pressure. The regulator is preset at the desired operating pressure, and a Heise pressure gauge is used to measure the pressure.

An excessive gas flow-check valve is installed close to the manifold to shut off the hydrogen gas supply in case of a line ruptures. A guarter-turn valve is also installed for rapid manual cut off of the hydrogen supply to the system.

Two check valves are installed at the entrance to the reactor to prevent oil to flow in reverse direction.

Pressure and Flow Control

The upstream pressure of the system is monitored by a 0-20.8 MPa (0-3000 psig) Heise pressure gauge. The downstream pressures are indicated by pressure gauges 43 and 44, which are connected to sample bomb 1 and sample bomb 2, respectively. The upstream pressure is considered as the reactor or system pressure. The system pressure is controlled by means of a "Mity-Mite" pressure regulator. Upstream pressure of the regulator is maintained by the manifold pressure regulator.

The gas flow rate is maintained by means of micrometer valve 10. The gas flow is monitored downstream from the micrometer valve by means of a 0-500 cm^3 bubble flow meter. A bypass line is connected between the bubble flow meter and the low pressure rotameter to avoid continuous gas flow through the bubble flow meter.

The exit gas is scrubbed in a 60 vol% ethanolamine solution. Liquid traps, containing alumina spheres, are used to prevent liquid particles from flowing into the gas measuring devices.

Temperature Measurement

Temperatures are measured inside the catalyst beds and outside the reactors walls. Three iron-constantan thermocouples (J-type), of 1/8-inch diameter, are used for each reactor. The thermocouples are placed over a 7.62 cm (3 inch) intervals to measure the outside temperature at the reactor wall. The temperatures inside the catalyst bed for each reactor are measured with three thermocouples, 0.0254 mm (0.001 inch) diameter, which are placed at 7.62 cm (3 inch) intervals along the catalyst bed inside the thermowell. The output from the thermocouples is fed to an Omega digital indicator through a multipoint temperature selector switch.

Sampling System

There are two sampling systems used in the experiment. These are the product sampling system and the interstage sampling system.

Product Sampling System

The system consists of four sample bombs. Two sample bombs are used for the liquid sampling, whereas the other two are used to avoid liquid entrainment into the gas outlet line.

First sample bomb, a 180 cm^3 and 34 MPa (5000 psig) maximum pressure bomb, is connected to the bottom end of the reactor with a 1/4-inch stainless steel tube. The top of the sample bomb is connected to the gas outlet line. The bottom of the first sample bomb is connected to the second sample bomb with a high pressure valve. This valve is kept closed during the sampling process so that the system is not interrupted.

Liquid and gasous products flow into the second sample bomb of 600 cm^3 capacity where they are separated. The gasous from the second sample bomb flow into the third sample bomb where the condensed vapors are collected and separated. The third sample bomb is connected to the second sample bomb through a bottom line and valve 7 to return the collected liquids into the second sample bomb.

The gas from the third sample bomb passes into a fourth sample bomb, where any entrained liquid is removed. This sample bomb can be kept at low temperatures by placing it in an ice bath.

The gas from the fourth sample bomb flows through a metering valve, a gas scrubber, and a low pressure rotameter before exhausting to the atmosphere.

Interstage Sampling System

The interstage sampling system is installed between reactor 1 and reactor 2. It is designed to collect 3-5 cm^3 of liquid sample without disturbing the normal operation of the system. The system consists of a three way valve, a pressure gauge, and a high pressure liquid-sample holder (Figure 22).

Gas and liquid products from reactor 1 normally flow through the three way valve into the top of reactor 2. During sampling, the valve is closed and the liquid product is allowed to accumulate in the bottom part of reactor 1 for approximately 5-10 minutes, depending on the

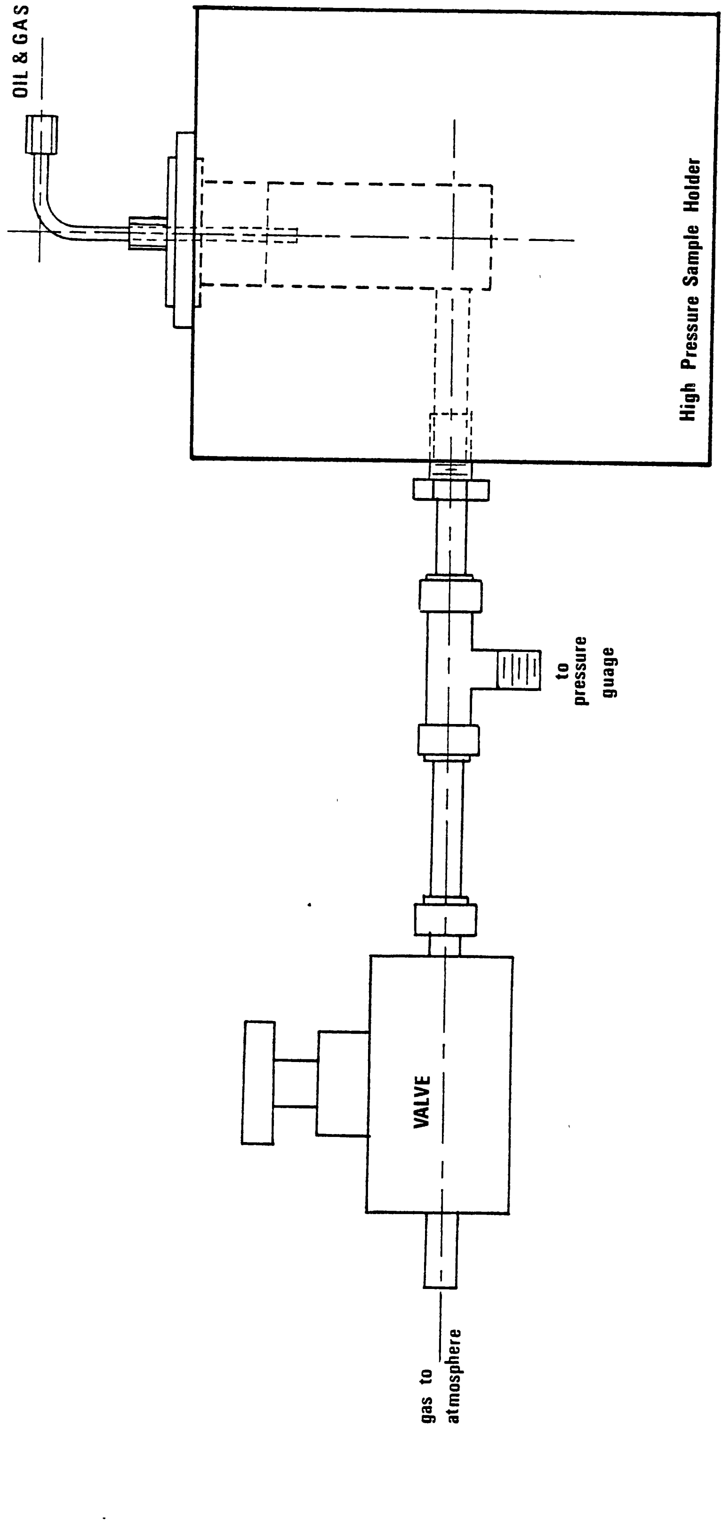


Figure 22. Interstage Sampling System

liquid flow rate. The flow is then diverted into the liquid-sample holder where liquid sample is collected in a small sample vial. The liquid-sample holder is depressurized after the flow is diverted back to normal path.

The three way valve is maintained at the high temperature of the system by a heating tape and is insulated with fiberglass insulations.

Gas Detector

A combustible gas detector, MSA Model 501, is installed in the laboratory, with two detector heads located over the hydrogen cylinders and the reactor system. A red light and audible alarm will come on once the hydrogen concentration in the room reaches 40% of the lower explosive limit.

A portable hydrogen sulfide detector is also used during catalyst presulfiding. The warning alarm will sound when the hydrogen sulfide concentration exceeds 17-20 ppm. It also provides a digital output of the instantaneous, average, and maximum hydrogen sulfide concentrations during a specified time interval.

Inert Gas Purging Facility

The liquid product samples are pruged with nitrogen gas in sample bombs 2 and 3 to remove gases that may be dissolved in the liquid samples. Nitrogen gas is also used to pressurize the sample bomb in order to remove liquid sample. Nitrogen is directly supplied to the bottom of sample bomb 2 from the supply cylinder and its pressure is set by the pressure regulator on the cylinder. The nitrogen gas flows into the sample bomb through a flow-check valve and is vented to the atmosphere through valve 8.

APPENDIX B

EXPERIMENTAL PROCEDURES

The experimental procedure consists of the following steps: catalyst preparation and loading, catalyst calcination, catalyst presulfiding, start-up, normal operation, sampling and shut down. Detailed description of each step follows.

Catalyst Preparation and Loading

The catalyst used in this study is a commercial 1/16-inch extrudate Shell-324 Ni-Mo/alumina. The catalyst is precalcined at 110°C (230°F) vacuum for 2 days hours in an oven and kept in a desiccator before loading into the reactor. The catalyst is packed only in the middle section of the reactor to avoid the end effects. Both ends of the reactor are packed with glass beads. The upper layer of the glass beads acts as a preheater and provides uniform liquid distribution. The bottom layer of the glass beads is used as a catalyst support. The reactor is packed according to the following steps:

Reactor 1

1. A 50 mesh size screen is wedged at the bottom of the reactor.
2. The thermowell is held centrally inside the reactor.
3. The glass beads are poured into the reactor while gently tapping the reactor for uniform packing around the thermowell. The glass beads are packed to a height of 15.24 cm (6 inch) in the bottom section.
4. While gently tapping the reactor, the catalysts are poured into the reactor. In all runs, 10 grams of catalyst is packed to a height of 15.24 cm (6 inch).

5. The glass beads are poured into the reactor while gently tapping the reactor for uniform packing. The height of glass beads is 12.7 cm (5 inch).
6. A 50 mesh size screen with a 1/8-inch diameter hole in the center is slid down the thermowell, until it touches the top of the glass beads section.
7. The packed reactor is then fitted with a 1/2-inch Swagelok cross fitting, as shown in Figure 20. The thermowell is secured by a 1/8-inch Swagelok fitting. The bottom of the reactor is fitted with a 1/2-inch to 1/4-inch reducer so that it can be connected to the three way interstage sampling valve.
8. The reactor is placed in the middle of the heating blocks. The heating blocks are tightened to the reactor and three 12.7 cm (5-inch) heating bands are wrapped around it. The heating blocks are then insulated.
9. Two side legs of the Swagelok cross on the top of the reactor are connected to the hydrogen gas and the oil feed lines. The bottom of the reactor is connected to the three way valve used for interstage sampling system.

Reactor 2

1. A 50 mesh size screen is wedged at the bottom of the reactor.
2. A thermowell is placed and held centrally inside the reactor.
3. Glass beads are poured into the reactor while gently tapping the reactor for uniform packing around the thermowell. The glass beads are packed to a height of 15.24 cm (6 inch) in the bottom section.

4. While gently tapping the reactor, the catalysts are poured into the reactor. In all runs, 10 grams of catalyst is packed to a height of 15.24 cm (6 inch).
5. The glass beads are poured into the reactor while gently tapping the reactor for uniform packing. The height of glass beads in the top section is also 15.24 cm (6 inch).
6. A 50 mesh size screen with a 1/8-inch diameter hole in the center is slid down the thermowell until it touches the top of the glass beads.
7. The thermowell is bent 90 degrees and the top of the packed reactor is fitted with a 1/2-inch union tee, as shown in Figure 21. The thermowell is secured by a 1/8-inch Swagelok fitting. The bottom of the reactor is fitted with a 1/2-inch to 1/4-inch reducer so that it can be connected to the first sample bomb.
8. The reactor is placed in the middle of the heating blocks. The heating blocks are tightened to the reactor. Three 12.7 cm (5-inch) heating bands are wrapped around the heating blocks. The heating blocks are then insulated.
9. The top of the Swagelok tee is connected to the three way valve. The bottom of the reactor is connected to a 1/4-inch stainless steel tube which is connected to the first sample bomb.

Each fitting in the reactor system is checked for leaks by gradually pressurizing the system with nitrogen gas. The pressure test is done at 11.09 MPa (1600 psig) which is 693.33 kPa (100 psig) higher than the reactor operating pressure. A pressure drop of 138.67 kPa (20 psig) in one hour is the maximum acceptable leak.

Finally, the electrical wires of the heating bands are connected to the corresponding temperature programmer/controllers.

Catalyst Calcination

The catalyst has to be calcined to remove the remaining moisture and adsorbed gases on the surface. Calcination procedure is described as below:

1. Close valves 2, 3, 13, 14, 24, 32, 35, 51.
   Open valves 1, 11, 12, 15, 31, 33, 34, 36, 50.
2. Turn the temperature programmer/controllers on and control the heating rate at 120-150°C (248-302°F) per hour.
3. When the temperatures inside the reactors reach 200°C (392°F), start nitrogen flow through the reactors to carry moisture and gases out of the system. Nitrogen flow rate is set at 400 cm^3 per minute at a pressure of 1723 2068 1730-2080 kPa (250-300 psig).
4. When the reactor temperatures reach 400°C (~~482°F~~ 752°F), set the temperature programmer/controllers to control the temperature isothermally for 1 hour.
5. Then set the temperature programmer/controllers at 250°C (482°F) and wait until the temperatures reach the set points.
6. Nitrogen may be cut off now, since the calcination is completed and the catalyst can be sulfided.

Catalyst Sulfiding

In this study, a mixture of 5 vol% H_2S in H_2 was used for sulfiding. Catalyst sulfiding steps are described below:

1. Turn on the H_2S detector.

2. To avoid and protect the Heise gauge from H_2S corrosion, close valve 1.
3. Open valve 2, and start the H_2S-H_2 flow through the reactor at a pressure of 555 kPa (80 psig) and a flow rate of 400 cm^3 per minute.
4. Maintain the reactor temperatures around 250°C (482°F) during sulfiding. After 60 minutes of sulfiding, cut off H_2S-H_2 gas by closing the main valve on the H_2S-H_2 bottle and wait until the gas flows out of the system. This is indicated by the pressure gauge on the H_2S-H_2 bottle and the pressure gauge 43 which will read zero.
5. Close valve 2.
6. Flush the system with nitrogen gas for 20 minutes by opening valve 1 and the main valve of nitrogen bottle. The nitrogen flow rate is set at 400 cm^3 per minute at a pressure of 1730-2080 kPa (250-300 psig).

Start up Procedure

When the catalyst calcination and sulfiding are completed, the temperature programmer/controllers are set at about 10°C (18°F) lower than the desired operating temperature. At the same time, the feedstock is charged into the feed tank. Ruska pump feed rate is set at the desired liquid flow rate of 30 cm^3 per hour. Then the listed steps are followed:

1. Charge the feedstock into Ruska pump by opening valve 23, and traverse the pump to suck the feedstock into the pump.

2. Close valve 23 and open valve 22. Make sure that valve 24 is closed.
3. Traverse the pump manually until the pressure of the pump is 10.4 MPa (1500 psig).
4. Close valve 11. Make sure valve 3 is closed.
5. Pressurize the reactor with H_2 to 10.4 MPa (1500 psig).
6. Open valves 4 and 9. Make sure valves 5, 7, 8, and 13 are closed.
7. Pressurize the sample bombs with nitrogen to 10.06 MPa (1450 psig) by opening valve 6. After the pressure reaches 10.06 MPa (1450 psig), close valves 4 and 6.
8. Open valves 1, 3, 9, and 13. Adjust the hydrogen flow rate at 500 cm^3 per minute by means of the needle valve 10 and bubble flow meter.
9. Start Ruska pump and open valve 24.
10. Adjust the temperature programmer/controllers at the desired operating temperature.

Normal Operation

The system is considered to be at normal operation when temperature and pressure are stable. A maximum variation of 138.67 kPa (20 psig) in the pressure is tolerable. A temperature variation of $3^{o}C$ ($5.4^{o}F$) along the catalyst bed is the maximum for normal operation before oil hits the catalyst.

After the start-up, the temperature profile inside the reactor and the temperature of the heating blocks, pressure gauge reading, pump scale reading, inlet gas flow rate, off gas flow rate, and hydrogen gas bottle pressure are recorded at every hour. The temperature profile inside the catalyst beds is are measured at 7.62 cm (3 inch) intervals.

Under normal operation, the reactor upstream pressure indicated by the Heise pressure gauge should be equal to the downstream pressure indicated by pressure gauge 43. If the reactor is clogged, the downstream pressure will gradually drop down. Depressurization of sample bombs should generate a large pressure difference between upstream and downstream of the reactor which could open the clogging.

The system is operated manually so the position of the valves are is very important and must be checked right after start-up and after every sampling and refilling of the feedstock.

A summary of the valve throttle position during normal operation is given in Table XXI.

Sampling Procedure

Samples are taken every 12 hours from the interstage sampling system at the bottom of reactor 1 and accumulated sample in the sample bomb. To minimize the possible operational disturbances due to sampling, the steps below are followed:

1. Close valves 3, 13 and 50.
2. Very slowly open valve 8, allowing the pressure on sample bomb 2 gauge (gauge 44) to drop to the atmospheric pressure.
3. Connect the interstage sampling system to valve 51.
4. After 5 minutes, there will be an approximately 2-3 cm^3 of liquid sample accumulated at the bottom of reactor 1. Very slowly open valve 51. The interstage sampling system can be pressurized with nitrogen gas to any desired pressure. Open

TABLE XXI

VALVE THROTTLE POSITION SUMMARY DURING NORMAL OPERATION

Position	Valve Number
Open	1, 3, 9, 10, 13, 15, 21, 22, 24, 31, 33, 34, 36, 50.
Closed	2, 4, 5, 6, 7, 8, 11, 14*, 20, 23, 32, 35, 51.

* Opened when measuring the hydrogen gas flow rate.

valve 51 until the pressure gauge at the interstage sampling sytem indicates a pressure rise which means hydrogen gas is flowing into the sampling system. Close valve 51 and depressurize the sampling system.

5. Take the sample out and label.
6. Open valve 50.
7. Open valve 11 (this allows the hydrogen to flow out of sample bomb 1 while valve 12 is already adjusted at a set flow rate).
8. Make sure the pressure in sample bomb 1 is at the operating pressure.
9. Adjust the pressure of nitrogen purge cylinder to 1040 kPa (150 psig). Open valve 6 and then valve 4. This allows the flow of nitrogen into sample bombs 2, 3 and 4.
10. Purge for 5 minutes.
11. Close valve 8. The pressure in sample bombs 2, 3 and 4 will rise to 1040 kPa (150 psig). Close valve 6.
12. Place the sampling jar in the sampling port and gently open valve 5 to allow the liquid sample to flow out.
13. Open valve 7 and let the liquid sample from sample bomb 3 to flow out (if there is any sample).
14. Close valves 5 and 7. Make sure valve 8 is closed.
15. Pressurize the sample bombs to 9.71 MPa (1400 psig).
16. Close valves 4 and 6, and check that valves 5 and 7 are closed.
17. Open valves 3 and 13.
18. Close valve 11.
19. The system is back to normal operation. Check and make sure that each valve is at its correct throttle position.

20. Label the sample and keep for analyses.

Shutdown Procedure

1. Turn off the feed pump switch.
2. Close valve 24.
3. Turn off the temperature programmer/controllers.
4. Depressurize the pump and drain left over liquid from the pump by using valve 20.
5. When the temperatures inside the catalyst beds drop down to 250°C (482°F), cut the hydrogen flow.
6. Depressurize the reactor to 1730 kPa (250 psig) and start nitrogen flow to purge the reactor and help it cool down faster.
7. When the reactor is at room temperature, the sampling procedure is followed to collect the last sample.
8. The reactor system is depressurized and the insulators are removed.
9. The reactors are pulled out from the heating blocks after disconnecting from oil and gas feed lines, three way valve, and sample bomb 1.
10. Each reactor is cut with a saw into five parts and the catalyst is separated into top, middle, and bottom sections and removed from the reactor pieces.
11. The catalyst samples are labeled and kept for analysis.

APPENDIX C

TEMPERATURE PROFILE OF EACH RUN

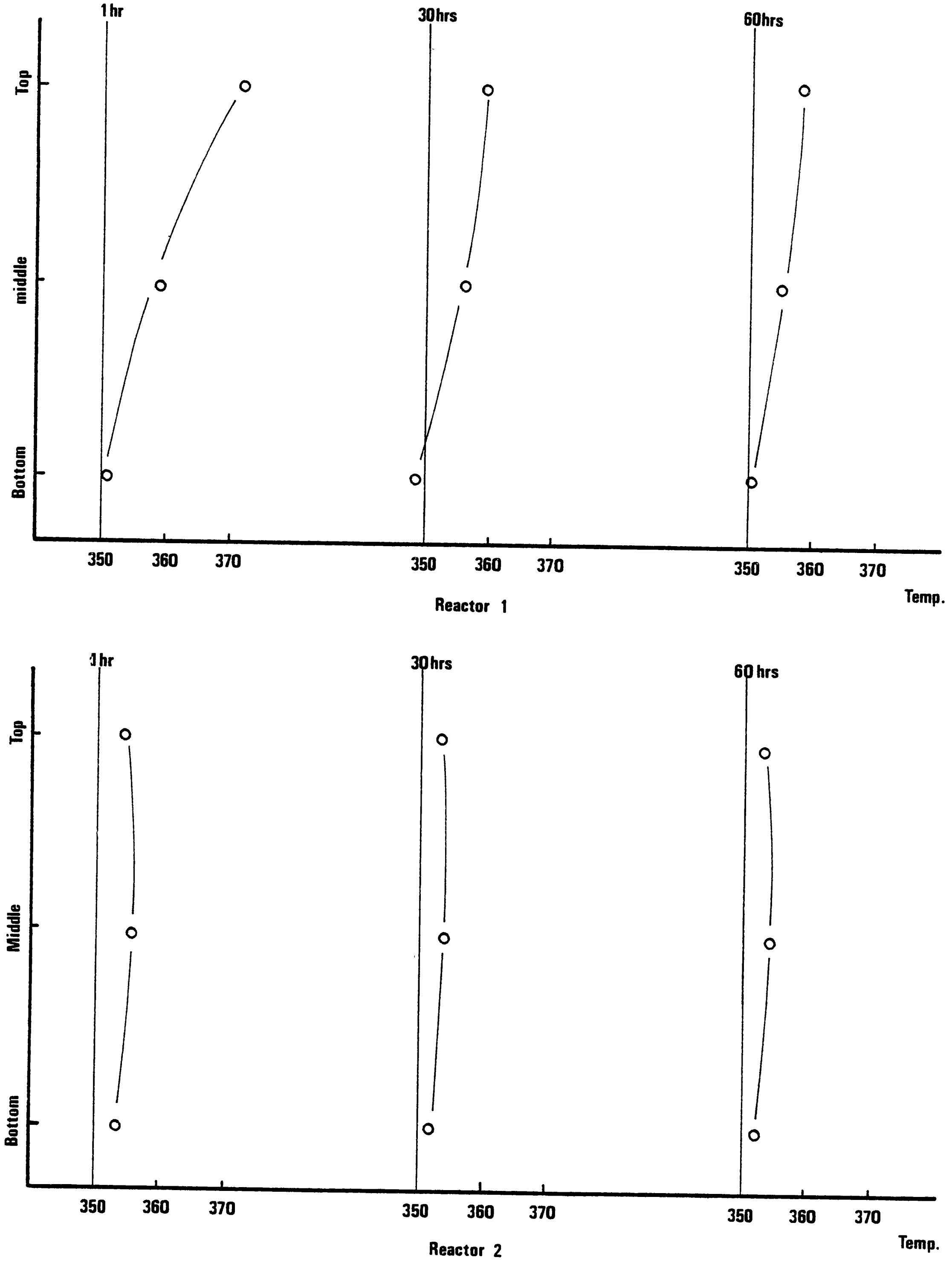
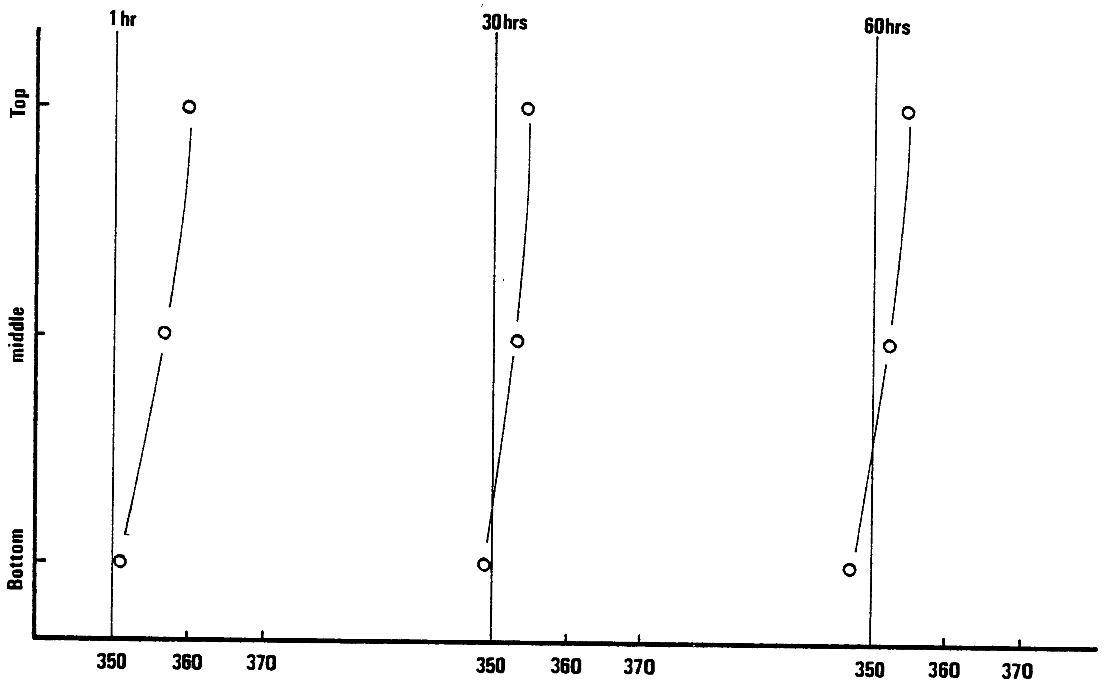
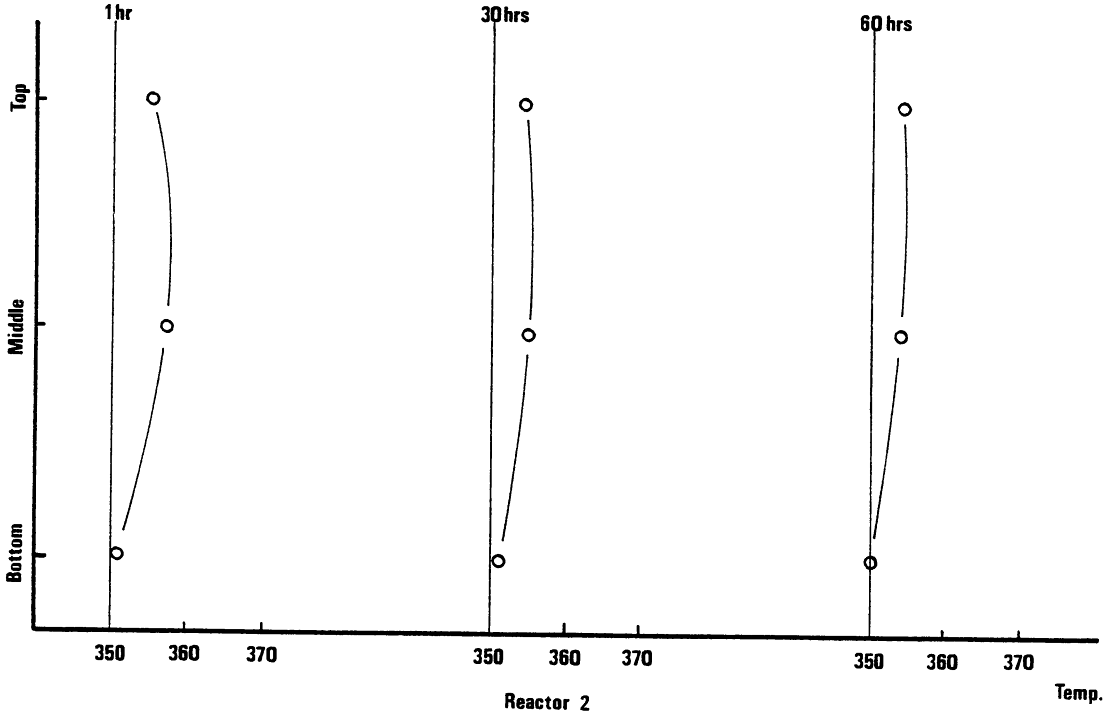


Figure 23. Temperature Profile in Catalyst Bed for Run 1



Reactor 1



Reactor 2

Figure 24. Temperature Profile in Catalyst Bed for Run 2

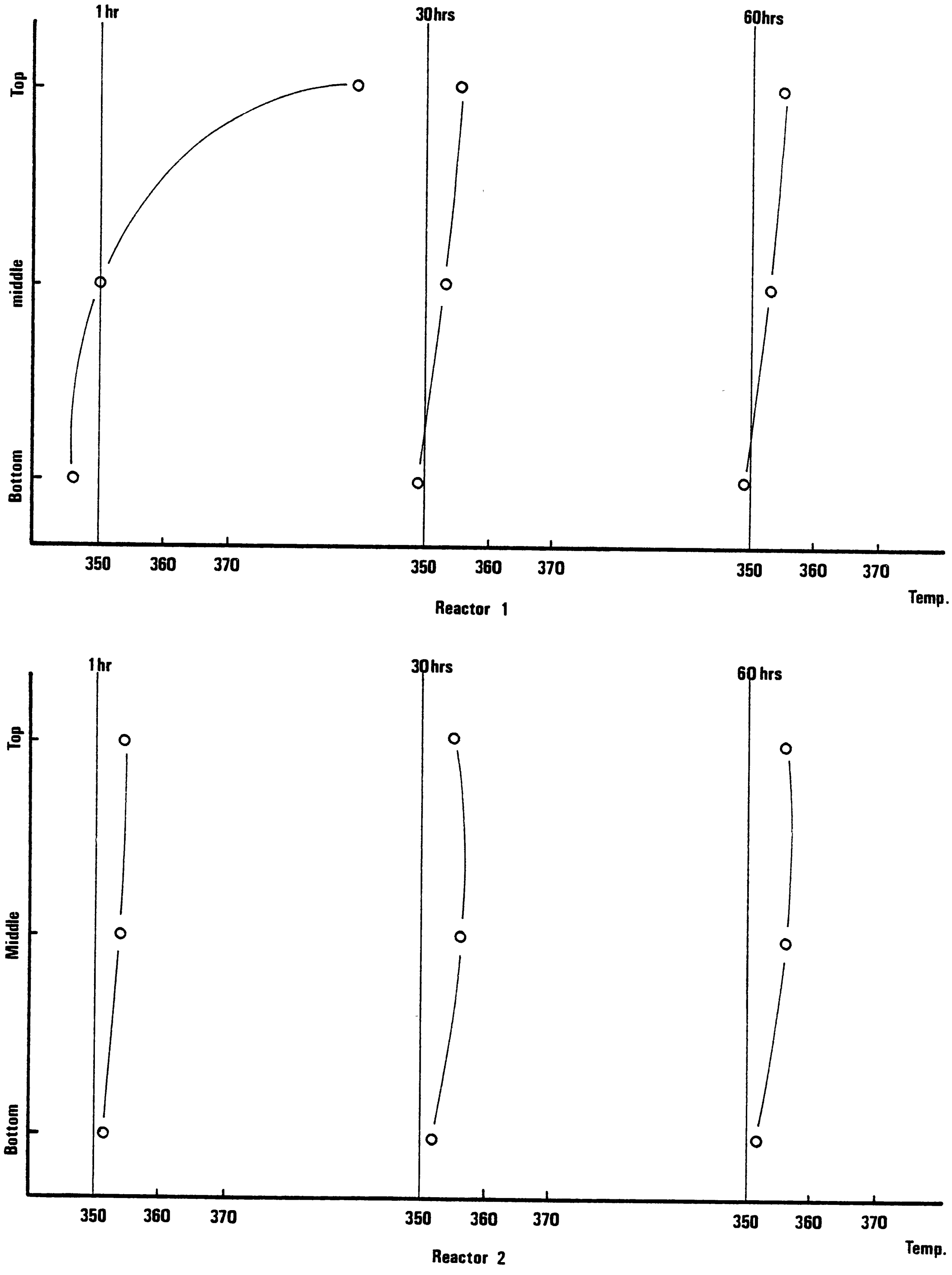


Figure 25. Temperature Profile in Catalyst Bed for Run 3

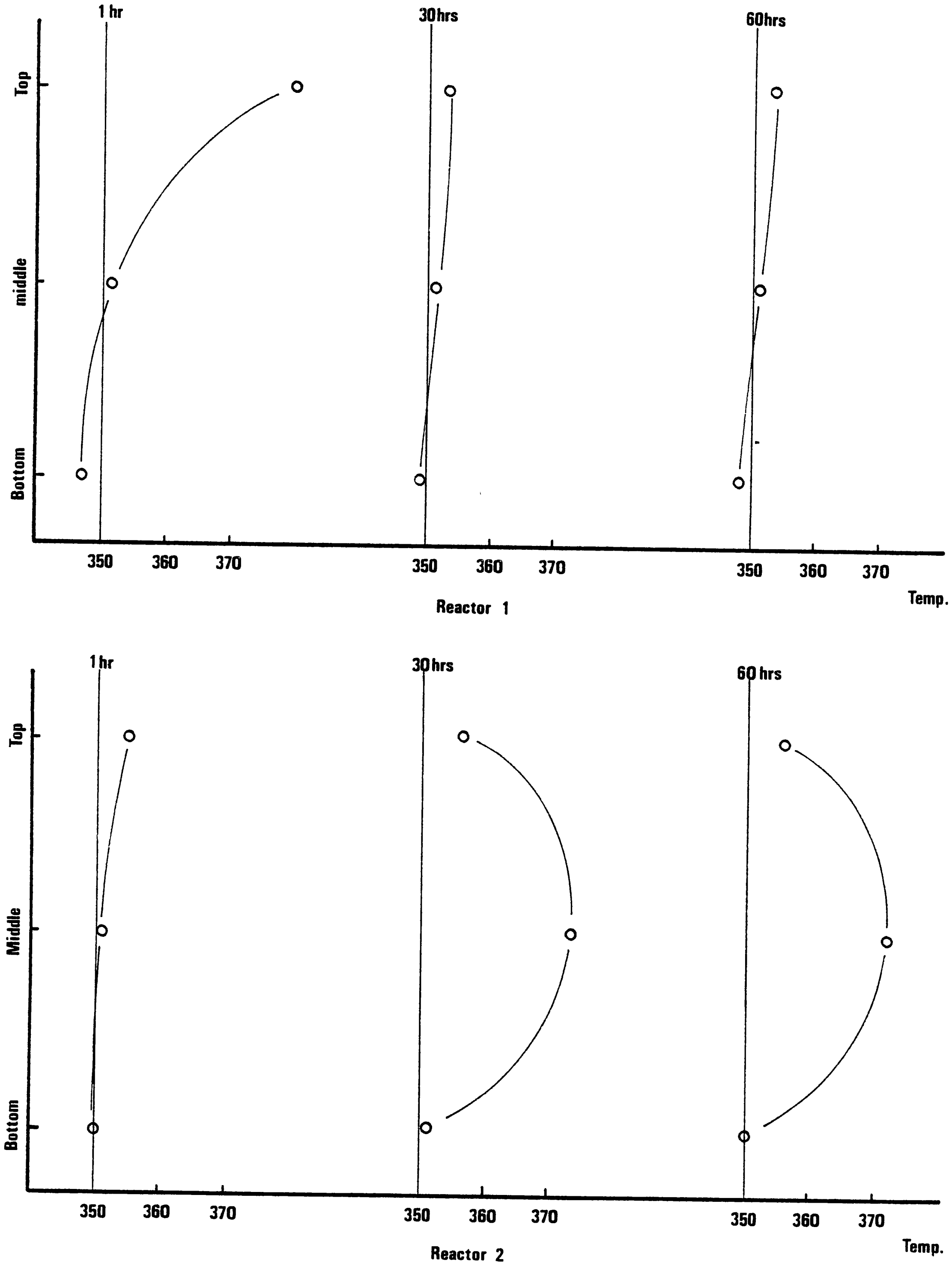
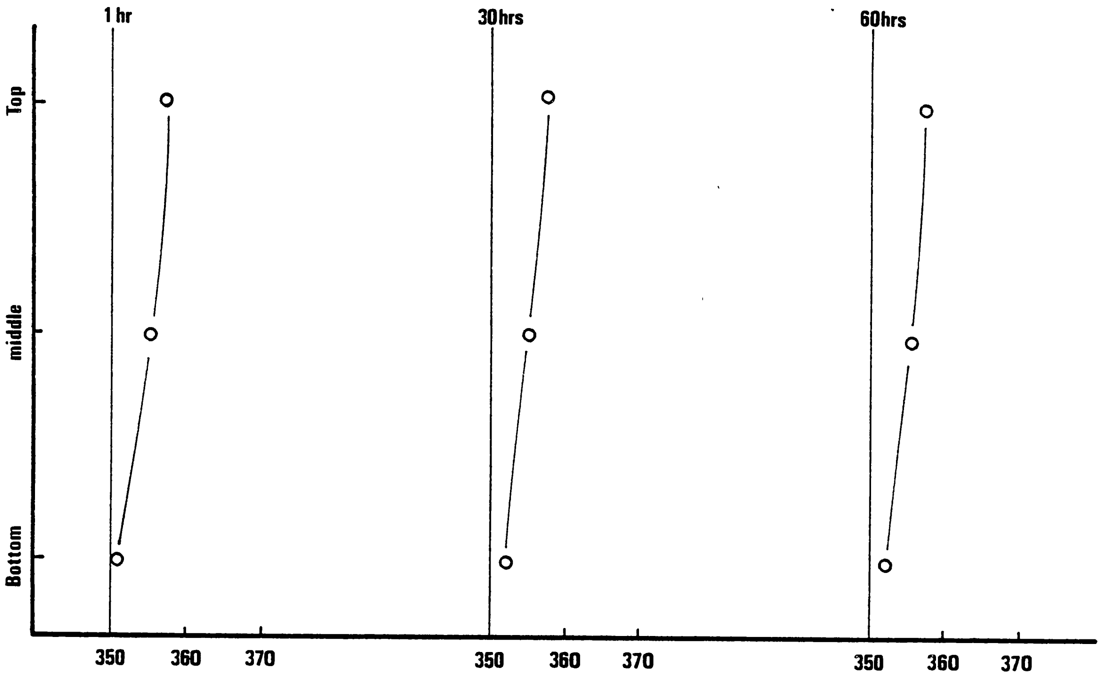
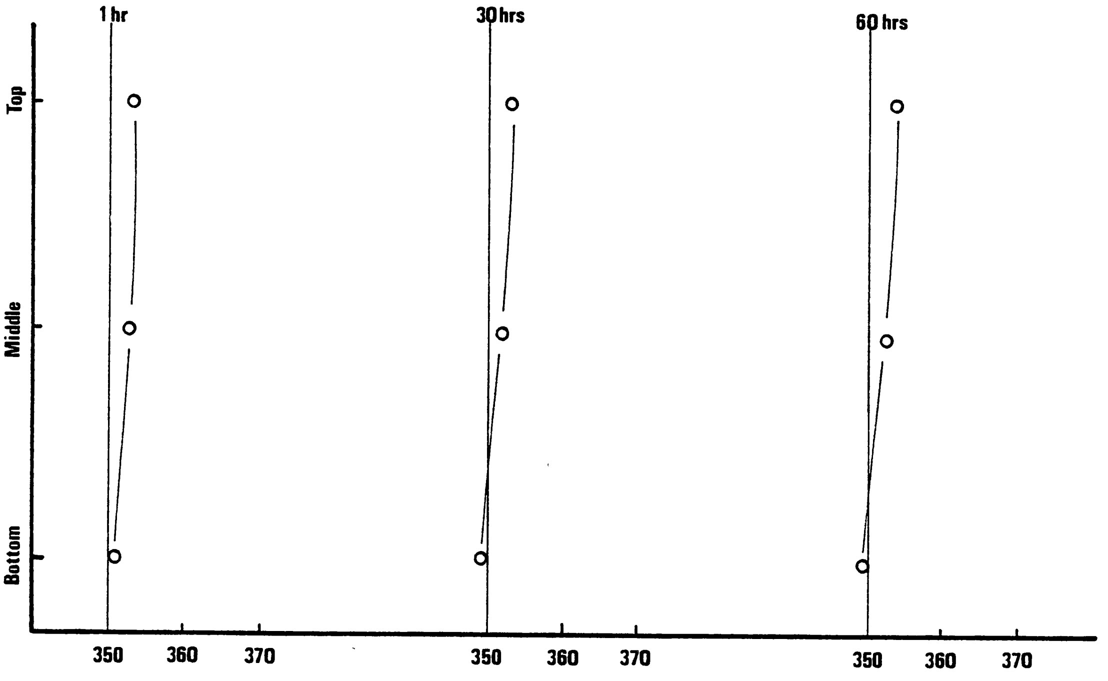


Figure 26. Temperature Profile in Catalyst Bed for Run 4



Reactor 1



Reactor 2

Figure 27. Temperature Profile in Catalyst Bed for Run 5

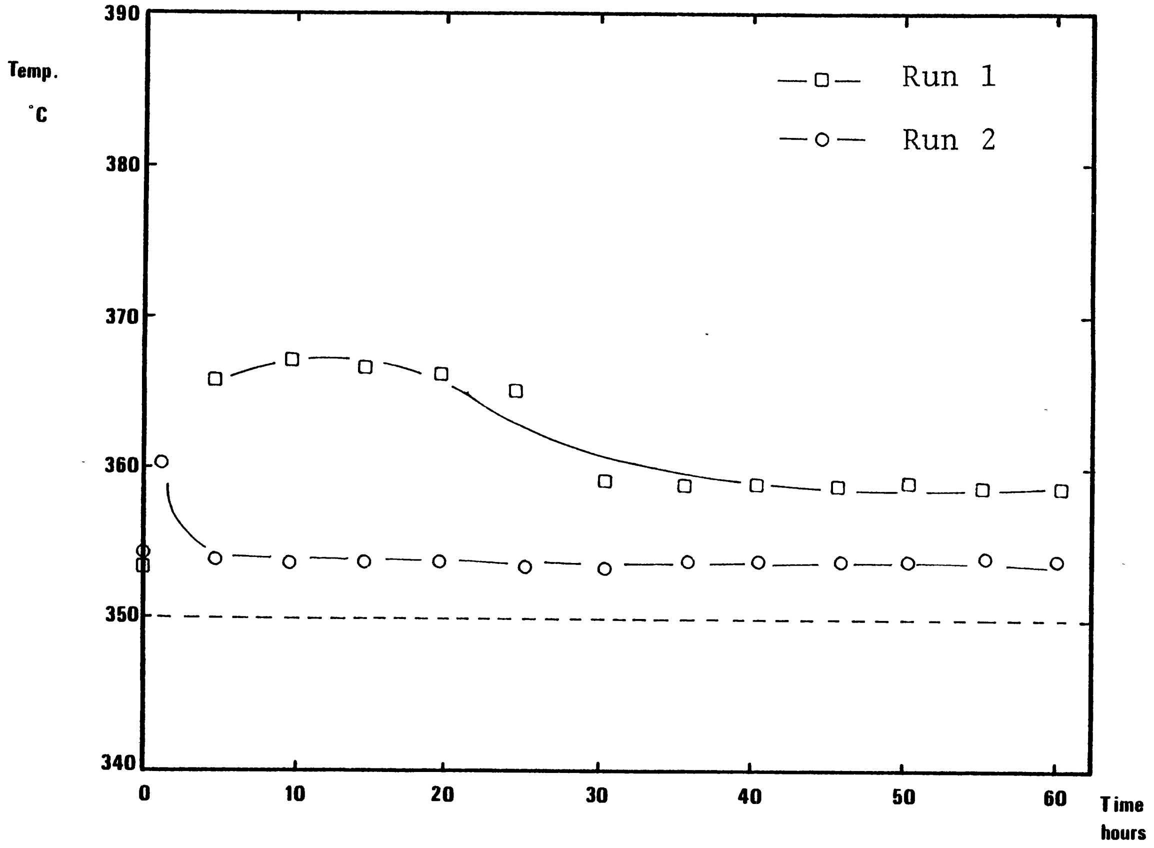


Figure 28. Temperature Profile at the Entrance to the Catalyst Bed of Reactor 1 for Runs 1 and 2

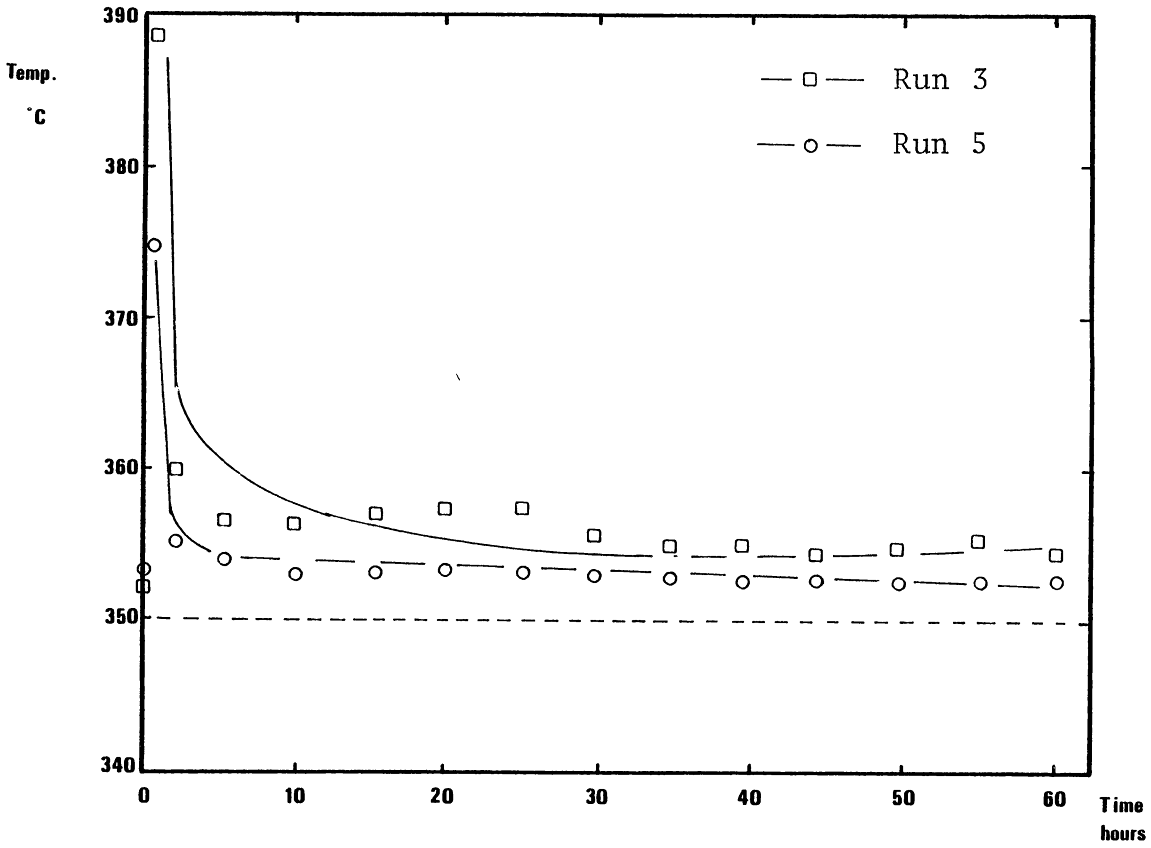


Figure 29. Temperature Profile at the Entrance to the Catalyst Bed of Reactor 1 for Runs 3 and 5

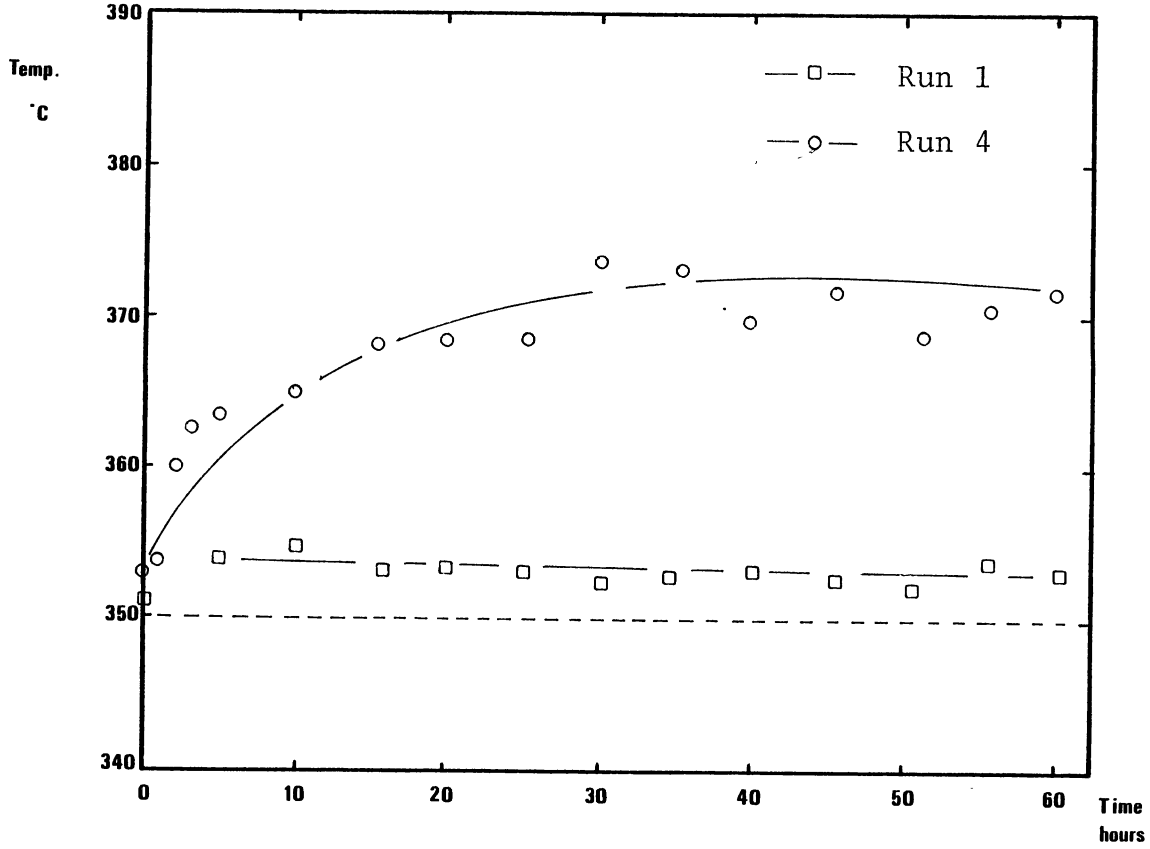


Figure 30. Temperature Profile at the Middle of Reactor 2 for Runs 1 and 4

VITA 2

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